

Develop advanced ceramic electrochemical cells for future sustainable energy solutions

by

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AN ABSTRACT OF A DISSERTATION

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DOCTOR OF PHILOSOPHY

The Tim Taylor Department of Chemical Engineering
Carl R. Ice College of Engineering

KANSAS STATE UNIVERSITY
Manhattan, Kansas

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Abstract

Ceramic electrochemical cells can operate in both fuel cell and steam electrolysis modes for efficient power generation, green hydrogen production and CO₂ conversion. In fuel cell mode, they can efficiently convert the chemical energy contained within hydrogen, hydrocarbons, and ammonia to electricity. In electrolysis mode, they can operate with applied power from a renewable source (e.g., solar) to produce hydrogen or synthesize chemicals. Although some intriguing demonstrations of intermediate-temperature (500-600 °C) protonic ceramic electrochemical cells (IT-PCECs) have been made in the last decade, the operating temperature of PCECs is still too high to revolutionize ceramic electrochemical cell technology. Bringing the operating temperature down to 275-450 °C can entirely transform the architecture and operation of ceramic electrochemical cell systems. For example, inexpensive stainless-steel interconnects, polymeric sealants, and ready-made balance of plants (BOPs) can be used, while the thermal cycling stability, system reliability, and applicability in portable power, transportation markets, and distributed chemical manufacturing industries can be enhanced.

Working in the fuel cells mode, PCECs, which employ proton-conducting oxide as the electrolyte could intensify power generation and chemical manufacturing, such as drying reforming of methane (DRM). DRM occurs at the PCEC anode, where CO₂ reacts with CH₄ to produce H₂ and CO. Air is fed to the PCEC cathode; thus, PCECs function as fuel cells to generate electricity. One unique feature of PCECs is that water is produced at the cathode; therefore, the chemicals produced at the anode are not diluted. As the counterpart of PCECs, solid oxide fuel cells (SOFCs) stand as another highly promising electrochemical energy conversion technology, effectively converting chemical energy into electricity. In contrast to polymer electrolyte membrane fuel cells, which rely on high-purity hydrogen, the exceptional fuel flexibility of

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Working in electrolysis mode, converting CO₂ into valuable chemicals in PCECs has attracted growing attention, which is attributed to their unique advantages over low-temperature (<100 °C) polymer electrolyte membrane electrochemical cells and high-temperature (>700 °C) oxygen-ion solid oxide electrolysis cells. The primary advantage of PCECs is their intermediate operating temperatures (300-600 °C), which thermodynamically and kinetically favor the CO₂ reduction chemistry at the negative electrode, allowing the production of chemicals beyond CO while achieving high energy efficiencies. However, previous PCECs that are equipped with Ni cermet-based negative electrodes, such as BaZr_{0.8-x}Ce_xY_{0.2}O_{3-δ}-Ni or BaZr_{0.8-x}Ce_xY_{0.1}Yb_{0.1}O_{3-δ}-Ni, cannot reduce CO₂ to either CH₄ or CO with a selectivity of >99 %, leading to the production of a CO and CH₄ mixture. Therefore, tailoring the negative electrode, which enables selective production of a specific chemical, is essential for the implementation of CO₂-PCECs.

In order to address above challenges, this PhD thesis focusing on developing highly efficient and durable PCECs/SOFCs for future sustainable energy solutions, both on fuel cell mode and electrolysis mode. Firstly, in order to lowering the operation temperature of PCECs, we present two main approaches to reducing electrolyte ohmic resistance, electrolyte-positive electrode contact resistance, and electrode polarization resistance, which enables PCECs operation at $<450\text{ }^{\circ}\text{C}$, setting several new records for PCECs. First, by using the ultrasonic spray coating system to coat the electrolyte layer on a negative electrode substrate with low Ba-deficiency, a bamboo-structured, ultrathin, and chemically homogeneous electrolyte can be fabricated. The ohmic area specific resistance (ASR_o) is reduced to $0.19\text{ }\Omega\text{ cm}^2$ at $450\text{ }^{\circ}\text{C}$, which is lower and comparable to the PCEC electrolyte fabricated via costly and unscalable pulsed laser deposition (PLD) techniques. Second, a newly self-assembled composite positive electrode, $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}\text{-Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ (SA-BSC+PBSCF), enhances the interfacial bonding between the positive electrode and electrolyte, further reducing ASR_o , while improving both bulk oxygen-ion diffusion coefficient and surface oxygen exchange coefficient at $<450\text{ }^{\circ}\text{C}$, significantly decreasing the ASR_p and allowing an extraordinarily low ASR_p of $0.38\text{ }\Omega\text{ cm}^2$ to be achieved at $450\text{ }^{\circ}\text{C}$ [versus the $0.76\text{ }\Omega\text{ cm}^2$ ASR_p of the state-of-the-art positive electrode]. The newly developed LT-PCECs attain outstanding power densities in fuel cell mode (as high as 0.77 W cm^{-2} in H_2 at $450\text{ }^{\circ}\text{C}$), and exceptional current densities in water electrolysis mode (over -1.28 A cm^{-2} at 1.4 V and $450\text{ }^{\circ}\text{C}$). First, the LT-PCECs attain exceptional fuel cell performance at even $275\text{ }^{\circ}\text{C}$, with a practical power density of 0.1 W cm^{-2} on H_2 . At $400\text{ }^{\circ}\text{C}$, the PCECs that operate in electrolysis mode achieve a high energy efficiency of $>85\%$ at a current density of 0.4 A cm^{-2} . Exceptional durability has been also demonstrated in both fuel cell and electrolysis modes at $<450\text{ }^{\circ}\text{C}$. We tested the PCECs

at 400 °C and a current density of 0.6 A cm⁻² for >250 h, achieving negligible degradation in the applied voltage, Faradaic efficiency, and energy efficiency.

This thesis also demonstrates process-intensified DRM-PCECs for concurrent power generation, chemical production, and greenhouse gas mitigation, with unprecedented performance at intermediate temperatures (<650 °C). To achieve unprecedented performance, Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-δ} (SDC-Ni-Ru) was pioneered to improve DRM activity, which leads to higher fuel cell performance and higher syngas production rates than with Sm_{0.2}Ce_{0.7}Ni_{0.15}O_{2-δ} (SDC-Ni) and Sm_{0.2}Ce_{0.7}Ru_{0.15}O_{2-δ} (SDC-Ru) and yields enhanced coking tolerance. The synergy between Ni and Ru simultaneously facilitates CO₂ activation and CH₄ activation. Moreover, CO₂ can be readily activated over SDC-Ni-Ru, which subsequently accelerates the oxidation of -CH* species formed on the Ni surface, inhibiting the decomposition of -CH* to carbon and hydrogen and consequently enhancing coking tolerance. By coating SDC-Ni-Ru on the PCEC anode as the internal DRM catalytic layer, the operating temperature of DRM-PCECs was lowered to 550-650 °C, achieving a groundbreaking power density of ~0.94 W cm⁻² at 650 °C and 0.30 W cm⁻² at temperatures as low as 550 °C. To underscore the practical implications of SDC-Ni-Ru catalyst, we successfully applied it as CH₄-SOFC internal anode reforming layer. This innovative approach also resulted in remarkable improvements in both peak power densities (PPDs) and operational stability (>2000 hours)

Finally, we have validated the potential of applying PCECs for CO₂ electrochemical conversion. We disclose results on an oxide-supported *in-situ* exsolved Ni-Fe alloyed nanoparticle electrocatalyst, SFM-Ni_{0.175}, which is first employed as the negative electrode of PCECs. The PCECs equipped with this new negative electrode selectively favor the CO₂-to-CO conversion. A selectivity of ~100% toward CO has been demonstrated over a wide range of operating

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Overall, this PhD thesis presents an extensive and thorough investigation into the advanced design and development of ceramic electrochemical cells, addressing their multifaceted applications across various applications such as electricity generation, hydrogen production, CO₂ reduction, and chemical manufacturing. Through systematic research and experimentation, this study endeavors to enhance the performance, efficiency, and versatility of ceramic electrochemical cells to meet the growing demands of sustainable energy solutions. Through a combination of theoretical analysis, experimental validation, and technological advancements, the research presented herein seeks to bridge the gap between fundamental understanding and practical application, paving the way towards a more sustainable and environmentally conscious future.

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Approved by:

Major Professor
Chuancheng Duan

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Chapter 1 – Objectives of my Ph.D. work

My PhD research focuses on the rational design of advanced ceramic electrochemical cells (PCECs) to address the growing need for sustainable energy solutions. This encompasses various applications such as fuel cells, electrolysis, and catalysis for electricity generation, hydrogen production, CO₂ reduction, and chemical manufacturing. The overarching objective is to enhance the efficiency, durability, and sustainability of these energy conversion and storage technologies, thereby contributing to the development of a more sustainable energy future. The more specific objectives are as follows: (1) Rationally design durable and highly active positive electrode for PCECs to lower the operating temperature; (2) Develop and integrate highly efficient, durable and cost-effective catalysts of dry reforming of methane (DRM), CO₂ hydrogenation, and steam methane reforming (SMR) reactions with ceramic electrochemical cells for power generation and chemical synthesizing; (3) Investigate in-situ operando spectroscopy combined with the Density Functional Theory (DFT) calculation to understand the catalytic mechanisms and provide in-depth understanding of materials science and electrochemistry.

The dissertation follows a structured framework, beginning with a general introduction in Chapter 2. Subsequently, Chapters 3 through 8 delve into the specific areas of my PhD research.

Chapter 2 provides an extensive overview of ceramic electrochemical cells and their role in electricity generation, hydrogen (H₂) production, CO₂ reduction reaction and chemical manufacturing. This chapter organizes two papers and one book chapter: (1) Liu, Fan; Duan, Chuancheng, Planar protonic ceramic electrolysis cells for H₂ production and CO₂ conversion. In High-Temperature Electrolysis, IOP Publishing: 2023; pp 14-1-14-24. (2) Liu, Fan; Ding, Dong; Duan, Chuancheng, Protonic Ceramic Electrochemical Cells for Synthesizing Sustainable Chemicals and Fuels. Advanced Science 2023, 10, 2206478,

<https://doi.org/https://doi.org/10.1002/advs.202206478>; (3) Liu, Fan, Duan Chuancheng Direct-Hydrocarbon Proton-Conducting Solid Oxide Fuel Cells. Sustainability 2021, 13(9), 4736, <https://doi.org/10.3390/su13094736>

Chapter 3 focuses on lowering the operation temperature of PCECs. This chapter organizes one papers: (1) Liu, Fan; Deng, Hao; Diercks, David; Kumar, Praveen; Jabbar, Mohammed Hussain Abdul; Gumeci, Cenk; Furuya, Yoshihisa; Dale, Nilesh; Oku, Takanori; Usuda, Masahiro; Kazempoor, Pejman; Fang, Liyang; Chen, Di; Liu, Bin; Duan, Chuancheng, Lowering the operating temperature of protonic ceramic electrochemical cells to <450 °C. Nature Energy 2023, 8, 1145-1157, <https://doi.org/10.1038/s41560-023-01350-4>.

Chapter 4 focuses on process-intensified PCFCs for power generation, chemical production, and greenhouse gas mitigation. This chapter organizes one paper: (1) Liu, Fan; Deng, Hao; Ding, Hanping; Kazempoor, Pejman; Liu, Bin; Duan, Chuancheng, Process-intensified protonic ceramic fuel cells for power generation, chemical production, and greenhouse gas mitigation. Joule 2023, 7, 1308-1332, <https://doi.org/https://doi.org/10.1016/j.joule.2023.05.009>.

Chapter 5 focuses on direct CH₄-fed SOFCs for vehicle applications. This chapter organizes two papers: (1) Liu, Fan; Diercks, David; Hussain, AbdulJabbar Mohammed; Dale, Nilesh; Furuya, Yoshihisa; Miura, Yohei; Fukuyama, Yosuke; Duan, Chuancheng, Nanocomposite Catalyst for High-Performance and Durable Intermediate-Temperature Methane-Fueled Metal-Supported Solid Oxide Fuel Cells. ACS Appl. Mater. Interfaces 2022, 14, 48, 53840–53849, <https://doi.org/10.1021/acsami.2c16233>; (2) Liu, Fan; Deng, Hao, Wang, Zixian; Hussain, AbdulJabbar Mohammed; Dale, Nilesh; Furuya, Yoshihisa; Miura, Yohei; Fukuyama, Yosuke; Ding, Hanping; Duan, Chuancheng, Synergistic Effects of In-Situ Exsolved Ni–Ru

Bimetallic Catalyst on High-Performance and Durable Direct-Methane Solid Oxide Fuel Cells, J. Am. Chem. Soc. 2024, 146, 7, 4704–4715.

Chapter 6 focuses on electrochemical CO₂ hydrogenation in PCECs for syngas production. This chapter organizes two papers: (1) Liu, Fan; Park, Yoo Sei; Diercks, David; Kazempoor, Pejman; Duan, Chuancheng, Enhanced CO₂ Methanation Activity of Sm_{0.25}Ce_{0.75}O_{2-δ}-Ni by Modulating the Chelating Agents-to-Metal Cation Ratio and Tuning Metal–Support Interactions. ACS Applied Materials & Interfaces 2022, 14, 13295-13304, <https://doi.org/10.1021/acsami.1c23881>; (2) Liu, Fan; Fang, Liyang; Diercks, David; Kazempoor, Pejman; Duan, Chuancheng, Rationally designed negative electrode for selective CO₂-to-CO conversion in protonic ceramic electrochemical cells. Nano Energy 2022, 102, 107722, <https://doi.org/10.1016/j.nanoen.2022.107722>.

Chapter 7 presents overall summary and conclusion of this thesis.

Chapter 8 presents suggestions for future directions.

Chapter 2 – General introduction

2.1 Protonic ceramic fuel cells (PCFCs) for electricity generation

2.1.1 Introduction

Fossil energy sources, including coal, oil, and natural gas, are currently accounting for >80% of the global energy consumption. The rapid growth in fossil fuel extraction, transportation, and consumption is leading to significant anthropogenic climate change and global warming accompanied by the principal CO₂ emission¹. Additionally, fossil fuels are not sustainable, and their depletion has been identified as a near-future challenge. Therefore, great efforts have been devoted to ensuring a global economy transition to more efficient utilization of fossil fuels and a low-carbon future².

Solid oxide fuel cells (SOFCs) have stimulated great interest in highly efficient energy conversion³. As electrochemical energy conversion devices, SOFCs can directly and electrochemically convert the chemical energy stored in fuels into clean electric power without the limitation of the Carnot cycle, which, in turn, leading to higher energy conversion efficiency (~60%) than traditional combustion engines. For example, gas turbines are applied to produce electricity from coal or natural gas using the intermediary steam with lower energy efficiency ranging from 30%-40%⁴. Hydrogen is considered as the cleanest fuel, leaving only water as the product, while it is not naturally abundant, and there are many complications in its production, transportation, and storage. Hydrocarbons could offer several attractive advantages over hydrogen, including higher volumetric energy storage density (10.05 kJ/L for hydrogen (LHV) and 36.4 kJ/L for natural gas) and lower transportation cost. For example, in the USA, natural gas or propane is usually distributed through railroad, truck, tanker ship, or pipelines into the urban area. Direct-hydrocarbon SOFCs are therefore one of the most promising power sources, which eliminates the

fuel processor units and could be integrated into the current power grid, drastically enhancing energy conversion efficiency, and reducing emissions.

The SOFC anode, which functions as the catalyst for reforming fuel streams and the electrode for charge transfer, is critical for high-performing direct-hydrocarbon SOFCs. The current SOFC anode is typically a composite of ceramic and metal (i.e., cermet) that exhibits mixed ionic and electronic conduction. For instance, the YSZ-Ni cermet is widely used as the anode for SOFCs because of its excellent catalytic activities and high electronic conductivity⁵. Unfortunately, Ni is vulnerable when exposed to hydrocarbon fuels as it is kinetically favorable for carbon deposition. Additionally, YSZ-Ni anodes are more prone to coking and sulfur poisoning because the relatively acidic surface of YSZ could not contribute to coke mitigation^{6,7}. Furthermore, the YSZ-Ni cermet requires an operating temperature of $>700^{\circ}\text{C}$, which thermodynamically favors the coking ascribed to the pyrolysis of hydrocarbons. Since Ni-based anodes are not perfect for working under hydrocarbons, developing Ni-free or oxide-based anodes are emerging approaches to enhancing the durability of direct-hydrocarbon SOFCs⁸. Despite Ni-free anodes deliver good fuel cell performances under hydrocarbon fuels, Ni-free anodes are still far away from commercialization and the cell configuration is limited to electrolyte-supported SOFCs. Furthermore, Ni-free anodes need a higher operating temperature ($>800^{\circ}\text{C}$) to obtain considerable catalytic activities and thus costly balance of plant (BOP) components are required. Hence, few Ni-free anodes demonstrate electro-catalytic activity and electronic conductivity that can compete with the current Ni-based anode. Therefore, robust SOFC anodes, which are catalytically active at intermediate operating temperatures, coking and sulfur-tolerant, as well as chemically stable, are essential for direct-hydrocarbon SOFCs. Proton-conducting oxides have been developed for numerous electrochemical devices because of high proton conductivity at 300-

650 °C⁹. Due to their relatively basic surface for high water-uptake capability, such oxides are recently applied as anodes for direct-hydrocarbon PCFCs. PCFCs have demonstrated excellent power density and long-term durability (>1000 (h)), opening a new pathway for developing durable direct-hydrocarbon PCFCs^{10,11}.

2.1.2 Proton-conducting oxides

The state-of-the-art proton-conducting oxides are ABO₃ perovskites, including five compositional groups: yttrium-doped barium zirconate (BZY), yttrium-doped barium cerate (BCY), yttrium- and cerium-doped barium zirconates (BZCY/BCZY), and yttrium-, ytterbium, cerium-doped barium zirconates (BCZYYb)¹²⁻¹⁵. Because of the relatively low activation energy of proton conduction (0.4-0.6 eV), the proton-conducting oxides exhibit practically significant proton conductivity (10⁻³-10⁻² S cm⁻¹) at intermediate operating temperatures (400-600 °C)^{14,16}.



The protons are produced via the hydration¹⁴, as shown in equation (1), where the Kröger-Vink notation is used to describe oxygen vacancy (V_O^{••}), lattice oxygen (O_O^X) and proton (OH_O[•]). This defect reaction indicates oxygen vacancies are required for the formation of protons; thus, oxygen vacancy concentration is normally increased by acceptor doping to improve the proton conductivity, i.e., the substitution of Zr⁴⁺ or Ce⁴⁺ host with trivalent dopants (e.g., Y³⁺/Yb³⁺).

In the 1980s, Iwahara et al. firstly recognized that BCY is a proton conductor¹⁷. However, it was noted that BCY is chemically unstable in the presence of water and carbon dioxide^{14,18}. Their poor chemical stability hinders their practical applications and much attention has been shifted to zirconate-based proton conductors, especially BZY, due to their enhanced chemical stability¹⁹. However, with the increased concentration of Zr⁴⁺, its poor sinterability tends to be a

thorny issue. Additionally, BZY displays high grain boundary resistance, resulting in lower proton conductivity than BCY¹⁴. The researchers therefore developed BCZY by synergizing the benefits of both BZY and BCY, improving the conductivity and stability¹⁹. Liu et al. demonstrated that $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_3$ possesses improved chemical stability under 2% CO_2 and 15% H_2O atmosphere and enhanced conductivity ($9 \times 10^{-3} \text{ S cm}^{-1}$) at 500 °C²⁰. The same team then pioneered a novel proton conductor, $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ ¹³, leading to the benchmarking proton conductivity and stability under hydrocarbons with hydrogen sulfide. To tackle the issues associated with sintering, a sintering aid (e.g., ZnO) was added to facilitate the densification and lower the sintering temperatures, increasing the feasibility of using proton-conducting oxides for building fuel cells²¹. A variety of other sintering aids, including NiO and CuO, have also been investigated for fabricating proton-conducting oxides²². In 2015, Duan and O'Hayre et al.²³ applied the solid-state reactive sintering method to PCFCs fabrication and demonstrated PCFCs with remarkable performances and durability with both hydrogen and methane as fuels. PCFCs have demonstrated excellent power density and long-term durability (>1000 hrs.), opening a new pathway for developing durable direct-hydrocarbon PCFCs^{10,11}.

2.1.3 Unique surface properties of proton-conducting oxides

It has been recognized that increasing the basicity of catalyst surface can suppress coking over heterogeneous catalysts⁷. Tatsuya et al.²⁴ investigated the catalytic activity and coking tolerance of Ni-YSZ cermet decorated with four alkaline oxides, including MgO, CaO, SrO, and CeO. CaO was identified as the most effective in improving coking tolerance although it slightly deteriorated the electrochemical activity of the anode. Liu et al.²⁵ later demonstrated that modification of Ni+YSZ anode with nanostructured BaO, which also has relatively basic surface,

could greatly suppress the coke formation. Density functional theory suggests BaO is capable of absorbing and dissociating water and thereby enabling to mitigate the coke. The water-mediated carbon removal mechanism is illustrated in Figure 2.1. (1) The basic surface of BaO promotes the dissociation of water into OH* and H* over the catalyst (* indicates the surface site of catalyst); (2) OH* absorbed on BaO will then react with carbon deposited on the Ni and produce CO* and H*. (3) CO* and H* will subsequently react with the oxygen ions at the triple phase boundary and form CO₂ and H₂O.

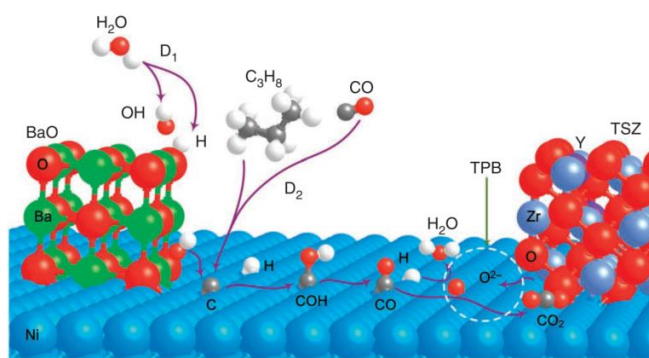


Figure 2.1. Proposed mechanism for water-mediated carbon removal on the anode with BaO/Ni interfaces²⁵.

Surface-enhanced Raman Spectrology (SERS) was employed to better understand the coke mitigation mechanisms of Ni-based anodes coated with BaO, BZY, and BCZYYb respectively²⁶, revealing that abundant -OH is absorbed on all three materials. These absorbed -OH can readily react with carbon and subsequently clean coke. However, BaO can also easily react with CO₂ and form BaCO₃, which is irreversible, leading to exacerbated SOFC performance degradation. Unlike BaO, BZY and BCZYYb are capable of regenerating -OH groups and proton-conducting oxides also possess basic surface, indicating they could be adopted as the materials for direct-hydrocarbons/ethanol SOFCs. Liu et al. integrated BZCY-Ni with SDC as the anode of direct-ethanol SOFCs, aiming to improve its coking tolerance. They demonstrated ethanol-fueled SOFCs

with a power density of 0.75 W cm^{-2} at 750°C and a stable operation of 170 hours. A similar water-mediated carbon removal mechanism was also proposed in this work, suggesting proton-conducting oxides (i.e., BZCY) with high water uptake capacity could accelerate the formation of C-OH intermediates and consequently enhance the carbon removal ability. Furthermore, it has been noted that proton-conducting oxides, such as BCZYYb, can also absorb CO_2 and form $-\text{CO}_3$ groups, which can also clean the carbon, further improving the coking tolerance¹³.

2.1.4 Comparison of PCFCs and solid oxide fuel cells (SOFCs)

Although PCFCs are a nascent technology, they already show significant promise for highly efficient and durable power generation^{9,10,15,23,27-29}. Compared to high-temperature SOFCs and low-temperature polymer electrolyte membrane fuel cells (PEMFCs) or alkaline fuel cells, PCFCs offer several important benefits:

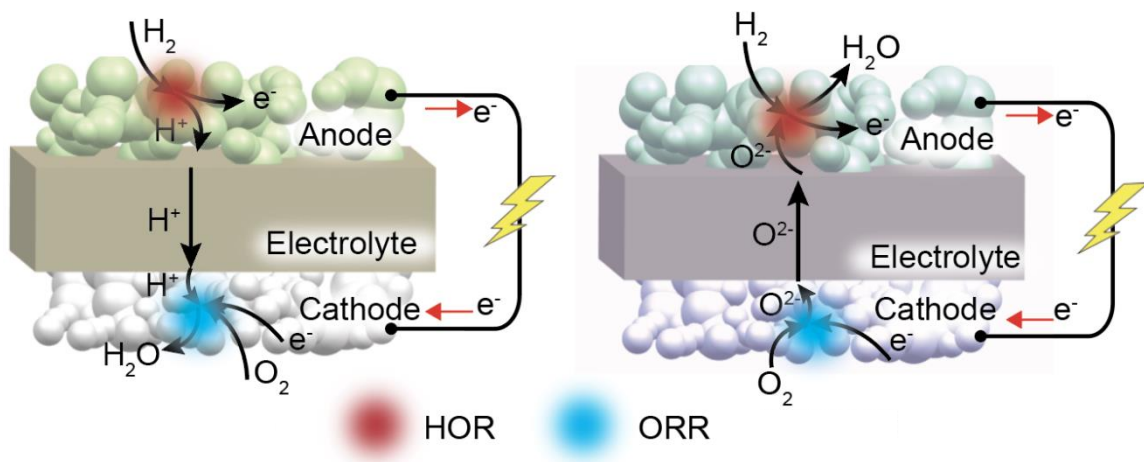


Figure 2.2. Schematic illustration of a (a) PCFC and (b) SOFC.

- (1) Unlike SOFCs, as illustrated in Figure 2.2, PCFCs can produce water in the cathode instead of the anode, which will not dilute the fuel stream, potentially improving the performances, enhancing fuel utilization, and reducing system complexity and cost (that is, no external

condenser required for condensing water and recycling fuel), as well as enhancing overall energy efficiency.

- (2) Intermediate-temperature PCFCs (500–600 °C) enable significantly higher efficiency than low temperature (50–100 °C) PEMFCs and can approach that of HT-SOFCs (700–900 °C)^{30,31}. Reduced operating temperatures (SOFCs) enable relax stack and balance-of-plant constraints, potentially lowering the cost while also improving the reliability, thermal cycling tolerance, and dynamic response.
- (3) High hydrocarbon conversion could be achieved in the PCFCs because of the continuous removal of hydrogen from the anode which shifts the reaction equilibriums of steam reforming and water gas shift reaction²³.
- (4) As shown in Figure 2.3¹⁰, the composition of PCFCs anode gas stream lies in the thermodynamic coking boundary of the whole reaction range or just outside it. On the contrary, with increasing the fuel utilization, the composition of anode gas steam in SOFC moves away from the coking boundary rapidly. However, the experimental studies of PCFCs contradict the thermodynamic predictions, which is due to unique surface properties of proton-conducting oxides. PCFCs are therefore coking and sulfur tolerant, and highly active for internal reforming^{15,23}.

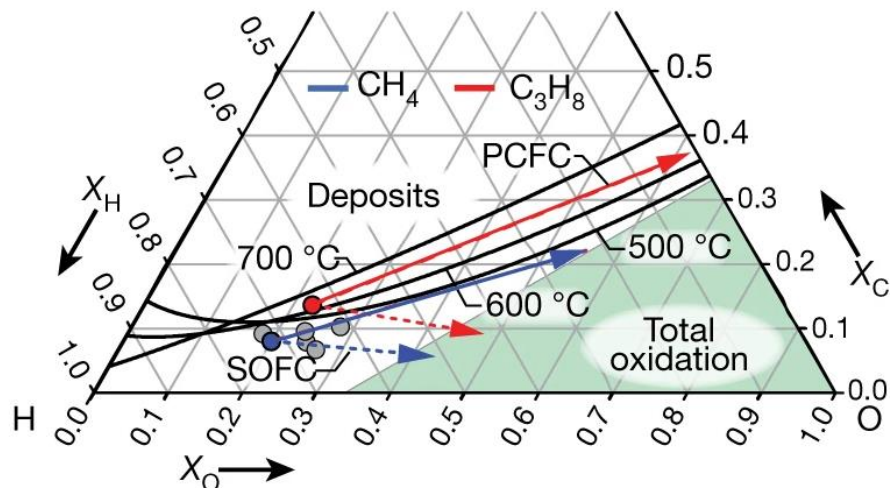


Figure 2.3. The ternary diagram shows the regions of equilibrium carbon formation and full oxidation. The dots indicate experimental fuel compositions. Fuel composition trajectories for propane (red) and methane (blue) are shown as solid lines for PCFCs (increasing current density and removing H) and dashed lines for SOFCs (increasing current density and adding O). The end-point compositions correspond to the complete oxidation of the fuel stream to CO_2 and H_2O . ‘Deposits’ indicates the region where coking is thermodynamically favorable¹⁰.

2.1.5 Notable achievements on coking-tolerant direct-hydrocarbon PCFCs

Both PCFCs and SOFCs are capable of directly converting methane and other hydrocarbon fuels (e.g., C_2H_6 and C_3H_8) into electricity. However, coking on YSZ-Ni anode, which blocks the active sites at the triple phase boundary (TPB), results in severe degradation. This is the main obstacle to the commercialization of SOFCs. For example, Yang et al.²⁵ reported that the terminal voltage of SOFCs, when fed with dry C_3H_8 , quickly dropped to nearly zero at a current density of 500 mA cm^{-2} within the 30 mins operation. There are therefore increasing efforts devoted to developing alternative direct-hydrocarbon fuel cells, such as PCFCs.

Direct-methane PCFCs were firstly validated by Coors in 2003. Although the current densities are too low to be commercially visible at that time, it has been demonstrated that PCFCs shows the unique coking resistance³². Luo et al.³³ proved the feasibility of using propane as the fuel in PCFCs, achieving improved fuel cell performances³⁴. Duan and O’Hayre et al.²³ employed

solid state reactive sintering to fabricate PCFCs, tackling the manufacturing challenges arising from the poor sinterability of proton-conducting oxides. Additionally, they deliberately designed one of the state-of-the-art triple conducting (oxygen ion, proton, and electron hole) cathodes ($\text{BaCe}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_3$), significantly improving performances of PCFCs. Direct-methane PCFCs with remarkable performances and a stable operation of 1400 hours at 500 °C were demonstrated²³. In 2017, Liu et al.³⁵ reported $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_{3-\delta}$ electrolyte-supported cells with a peak power density of 0.35 W cm⁻² and 0.50 W cm⁻² on ethane and hydrogen respectively at 750 °C. More recently, the long-term durability of fuel-flexible PCFCs has been comprehensively investigated. P-SOFCs fuelled with 12 different fuel streams, including hydrogen, methane, natural gas, propane, n-butane, i-butane, iso-octane, and others, exhibit a degradation rate of <1.5% per 1000 h for most fuels at 500-600 °C¹⁰. This entire set of durability measurements have fully validated that direct-hydrocarbon PCFCs are exceptionally stable. In addition to power generation, Luo et al. revealed that PCFCs can simultaneously generate power and produce chemicals³⁶. Both outstanding fuel cell performances and syngas production rate have been achieved.

To improve durability of direct-hydrocarbon SOFCs, proton-conducting oxides have also been used for decorating the anode of SOFCs^{37,38}. Proton-conducting nanoparticles are infiltrated into the anode and distributed over the Ni particles. These proton-conducting nanoparticles with basic surface can absorb and dissociate water, as abovementioned, which subsequently react with deposited carbon or sulfur; thus, this approach alleviates the coking and sulfur poisoning. For example, the peak power density of direct-methane SOFCs at 650 °C was improved from 0.62 W cm⁻² to 1.27 W cm⁻² after decorating the Ni-GDC anode with BCY particles, indicative of the bifunctionality of proton-conducting oxides³⁷.

2.2 Protonic ceramic electrolysis cells (PCECs) for H₂ production

2.2.1 Introduction

The second important application of PCECs is converting CO₂ to carbon-containing compounds, which gives rise to substantial environmental and economic benefits. In the context of growing concern about the high global atmospheric concentration of CO₂, economically viable and efficient technologies for large-scale and reliable CO₂ conversion and utilization must be widely deployed to minimize the environmental risks imposed by human activities with high CO₂ emissions (e.g., coal-fired power plant). Fortunately, PCECs driven by renewable power can provide opportunities to utilize CO₂ for energy storage and synthesizing sustainable chemicals^{39,40}. This modular and electrochemical approach is particularly promising for reducing point-source CO₂ emissions due to its versatility for manufacturing chemical feedstocks onsite⁴¹. PCECs can operate at intermediate temperatures (e.g., 400-500 °C), which favors the production of chemicals beyond carbon monoxide, such as CH₄ that could be used as the sustainable feedstock for various industries. Moreover, reversible methane fuel cells based on PCECs can be used for energy storage, which displays a theoretical round-trip efficiency approaching 100%, creating a closed cycle with minimized carbon footprint. Thus, creating a closed cycle for methane has significant economic and environmental benefits. Therefore, integrating PCECs with deliberately designed CO₂ reduction electrodes can achieve sustainable chemical manufacturing, enhance CO₂ conversion and desired product yield, enable long-term energy storage, and reduce greenhouse gas emissions.

Figure 2.4 shows a typical PCEC configured to convert CO₂ into value-added chemicals. The middle layer of PCEC is the dense proton-conducting ceramic electrolyte membrane which exhibits high proton conductivity at 400-500 °C (10^{-5} - 10^{-3} S cm) and separates the gas streams fed

to the two electrodes⁴². The porous positive electrode releases electrons to the outer circuit, oxidizes water, and produces oxygen and protons. The porous negative electrode, functions as the CO₂ reduction electrode to activate and convert CO₂. The core reaction is that CO₂ molecules are reduced by protons and electrons. According to the chemicals fed to the positive electrode, the electrochemical cell configurations fall into three categories: alkanes, renewable H₂, and water. These feedstocks will not impact the CO₂ reduction mechanisms in the negative electrode; thus, we focus on discussing the recent progress in negative electrode materials.

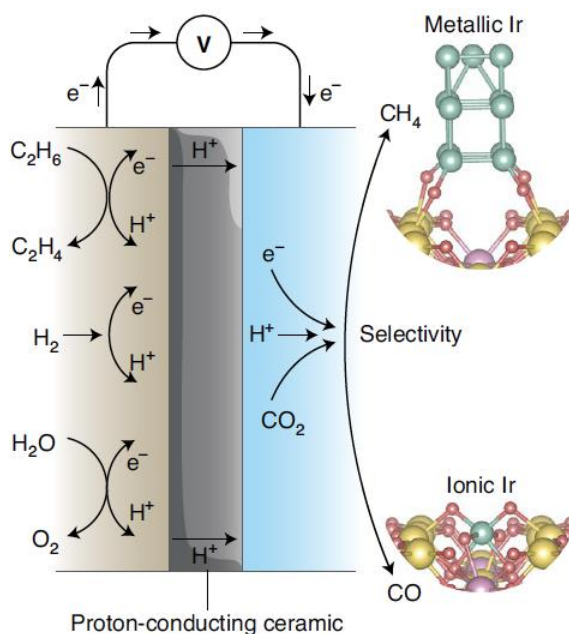


Figure 2.4. Schematic illustration of protonic ceramic electrolysis cells for CO₂ conversion⁴³

2.2.2 Thermodynamics of H₂O electrolysis

Figure 2.5 presents the thermodynamics of CO₂ conversion in PCECs using hydrogen/proton sourced from three different reactants fed to the positive electrode, which include H₂O, alkanes (e.g., C₂H₆), and H₂. The overall electrical energy consumption depends on the feedstock delivered to the positive electrode. The co-conversion of CO₂ and H₂O requires the highest amount of electrical energy (Figures 2.5A and 2.5C). The electrical energy consumption

of CO₂-to-CO conversion is lower than that of CO₂-to-CH₄ conversion as the total energy demand (ΔH) for CO production is lower for CH₄ (Figures 2.5B and 2.5D). Additionally, the heat demand ($T\Delta S$) for producing CO increases with increasing operating temperatures (Figure 2.5B), enabling to utilize heat for CO production. As the total energy demand for CO production is relatively independent of operating temperatures, the electrical energy consumption and reversible voltage for CO production decrease with increasing temperature. However, the heat demand for CH₄ production highly depends on the reactants delivered to the positive electrode (Figure 2.5D).

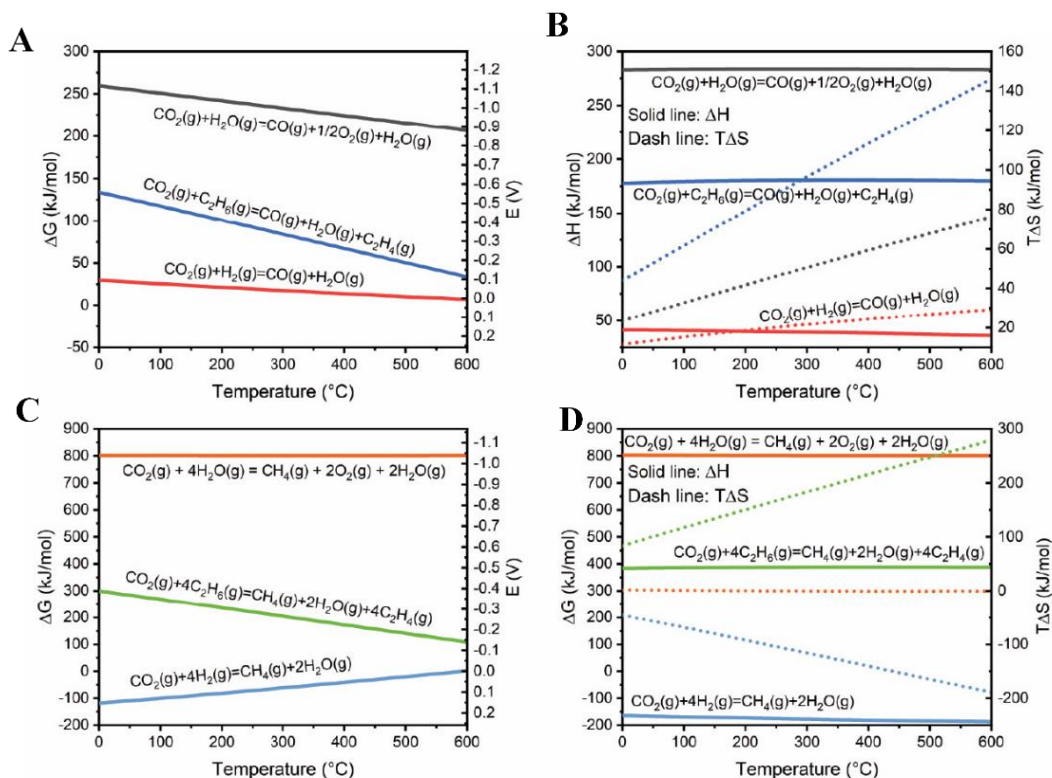


Figure 2.5. Thermodynamics of CO₂ conversion as a function of temperature using hydrogen/proton sourced from three reactants fed to the positive electrode, including H₂O, C₂H₆, and H₂. ΔG is correlated with the reversible voltage (V). ΔG and V share the same plot and different y axes. The results are calculated by using HSC software. (A) ΔG and V of CO₂ reduction to CO as a function of temperature. (B) ΔH and $T\Delta S$ of CO₂ reduction to CO as a function of temperature. (C) ΔG and V of CO₂ reduction to CH₄ as a function of temperature. (D) ΔH and $T\Delta S$ of CO₂ reduction to CH₄ as a function of temperature⁴⁴.

2.2.3 Advantages of employing PCECs for H₂ production

Unlike O-SOECs or polymer membrane-based electrolysis cells, PCECs can produce pure, dry H₂ that is amenable to direct electrochemical compression (without dehumidification) inside the cell^{9,31,45}, potentially reducing system complexity and cost (i.e. no external condenser is required, and the H₂ compressor could be greatly simplified), as well as enhancing overall energy efficiency (electrochemical compression could be more efficient than mechanical compression)⁴⁵.

Operating intermediate-temperature PCECs (600 °C) is more efficient than operating low-temperature (LT, 50 °C–100 °C) polymer membrane-based electrolysis cells; the efficiency of intermediate-temperature PCECs can approach those of high-temperature (HT, 700 °C–900 °C) and intermediate-temperature (IT, 600 °C) SOEC-based cells. Reduced operating temperatures (versus HT-SOEC-based cells) enable hybridization with a broader range of waste heat sources and relax stack and balance-of-plant constraints, potentially lowering costs while improving the reliability, thermal cycling tolerance, and dynamic response. For example, PCECs could be integrated with fossil power plants and nuclear power plants and thus utilize waste heat for H₂ production

2.2.4 Current progress in the field of PCECs for H₂ production

As shown in Figure 2.6³¹, PCECs were pioneered for H₂O electrolysis by Iwahara et al. from the early 1980s to 1990s. However, there is few subsequent works on this topic, which is due to the lack of highly conductive proton-conducting ceramic membranes. Additionally, its poor sinterability and high sintering temperatures hinder its further development. Therefore, the subsequent research centered on developing new compositions, and novel fabrication methods to enhance the conductivity and improve densification

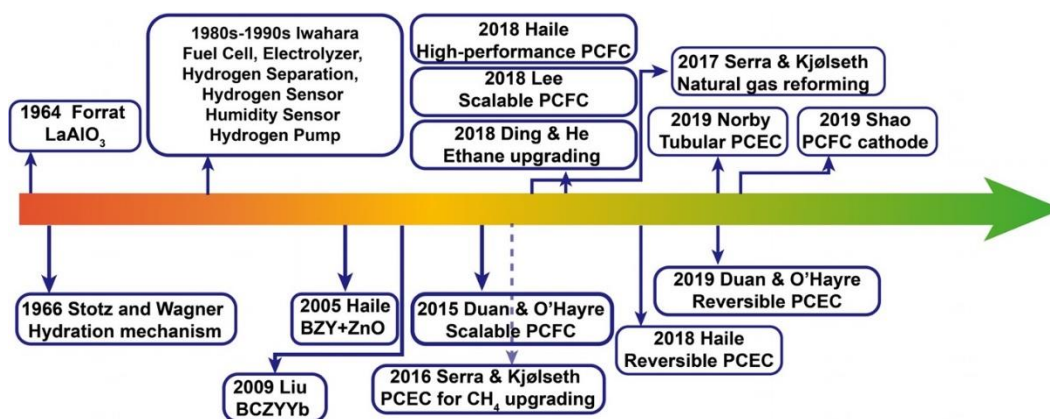


Figure 2.6. Historic overview of proton-conducting oxides, applications, and remarkable breakthroughs.

In 2019, as shown in Figure 2.7A, Haile et al. first demonstrated intermediate-temperature protonic ceramic electrolyzers that deliver comparable performances with SOECs³¹. In 2018²⁷, they developed a new electrolyte composition, $\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ (BCZYYb4411), which reduces its Ohmic loss and enhances long-term stability. A state-of-the-art triple conducting oxide, $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF), was used as the positive electrode. At an operating temperature of 600 °C, an exceptional current density of $>2.0 \text{ A/cm}^2$ was achieved at 1.4 V. Even at an operating temperature of 500 °C, this PCEC can deliver a current density of $>0.5 \text{ A/cm}^2$ at 1.4 V. A concurrent work conducted by Duan and O'Hayre et al. in 2019 also presents similar PCEC performances using $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_3$ (BCZYYb7111) as the electrolyte membrane and $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_3$ (BCFZY4411) as the positive electrode (Figure 2.7B)³¹. To further reduce the overpotential ascribed to the positive electrode, Ding et al.⁴⁶ pioneered a novel positive electrode, $\text{PrNi}_{0.5}\text{Co}_{0.5}\text{O}_3$, which has enhanced proton conduction that could improve the PCEC performances. Furthermore, Ding et al. optimized the morphology of the positive electrode using a template method. As shown in Figure 2.7C, the PCEC performance has been significantly enhanced and reasonable current density can be achieved at 400 °C.

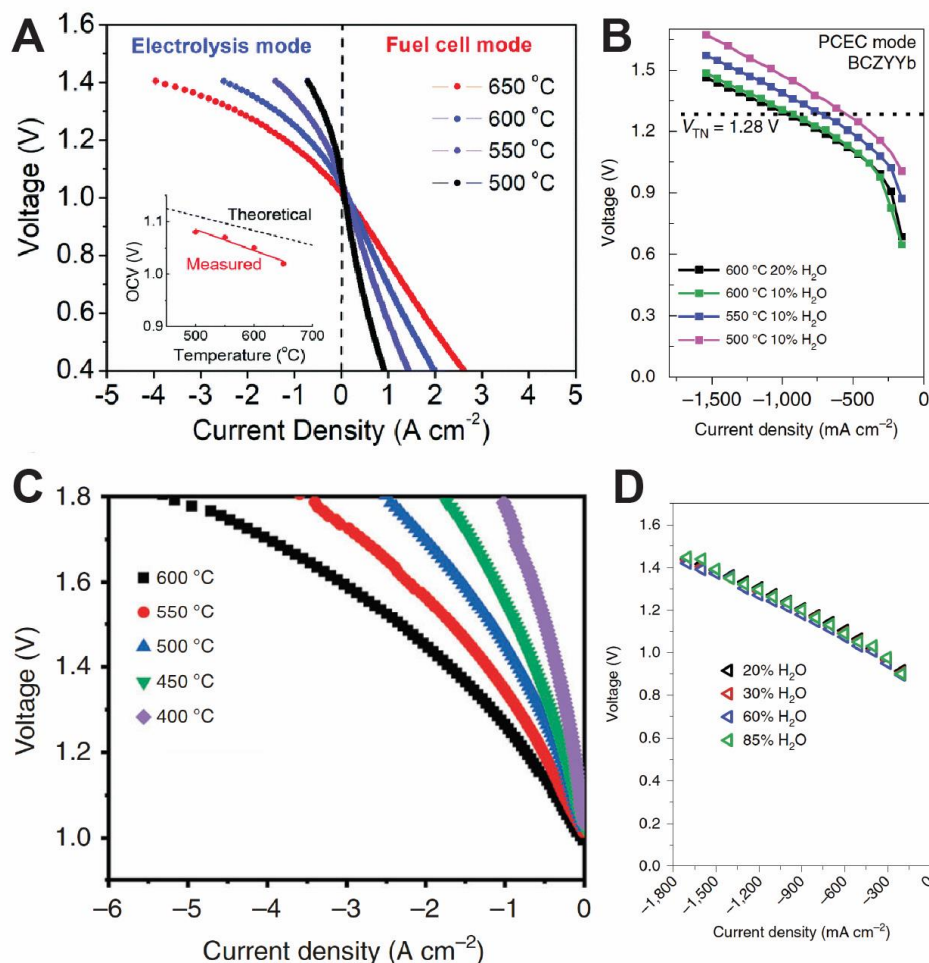


Figure 2.7. Performances of protonic ceramic electrolysis cells for H₂ production. (A) BCZYYb4411-based PCECs with PBSCF as the positive electrode.⁴⁷. (B) BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹. (C) BCZYYb4411-based PCECs with PBN as the positive electrode⁴⁶. (D) Impact of steam concentration on performances of BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹.

Significant progress has been made in optimizing PCECs and developing positive electrode materials to improve PCEC performance^{9,31,47-50}. Although compelling current densities have been obtained, which are comparable or even higher than SOECs, electronic leakage and low Faradaic efficiency of PCECs are being noted. Figure 2.7D shows the voltage of PCECs as a function of current density under various steam concentrations at 600 °C, which does not change with adjusting the steam concentration. However, the steam concentration significantly affects the

Faradaic efficiency, especially at a relatively low current density (Figure 2.8A). The Faradaic efficiency tends to decrease with reducing the steam concentration at the positive electrode. This impact of steam concentration on Faradaic efficiency has been widely recognized⁴⁶. Haile et al. also noted that reducing air flow rate from 150 mL/min to 100 mL/min can slightly increase the Faradaic efficiency (Figure 2.8B)⁴⁷. As the steam concentration is controlled by using a gas bubbler and air as the carrier gas, a high carrier gas flow rate could slightly reduce the steam concentration; thus, reducing the carrier gas flow rate can slightly enhance the Faradaic efficiency, which is consistent with what was observed by Duan and O'Hayre et al.³¹.

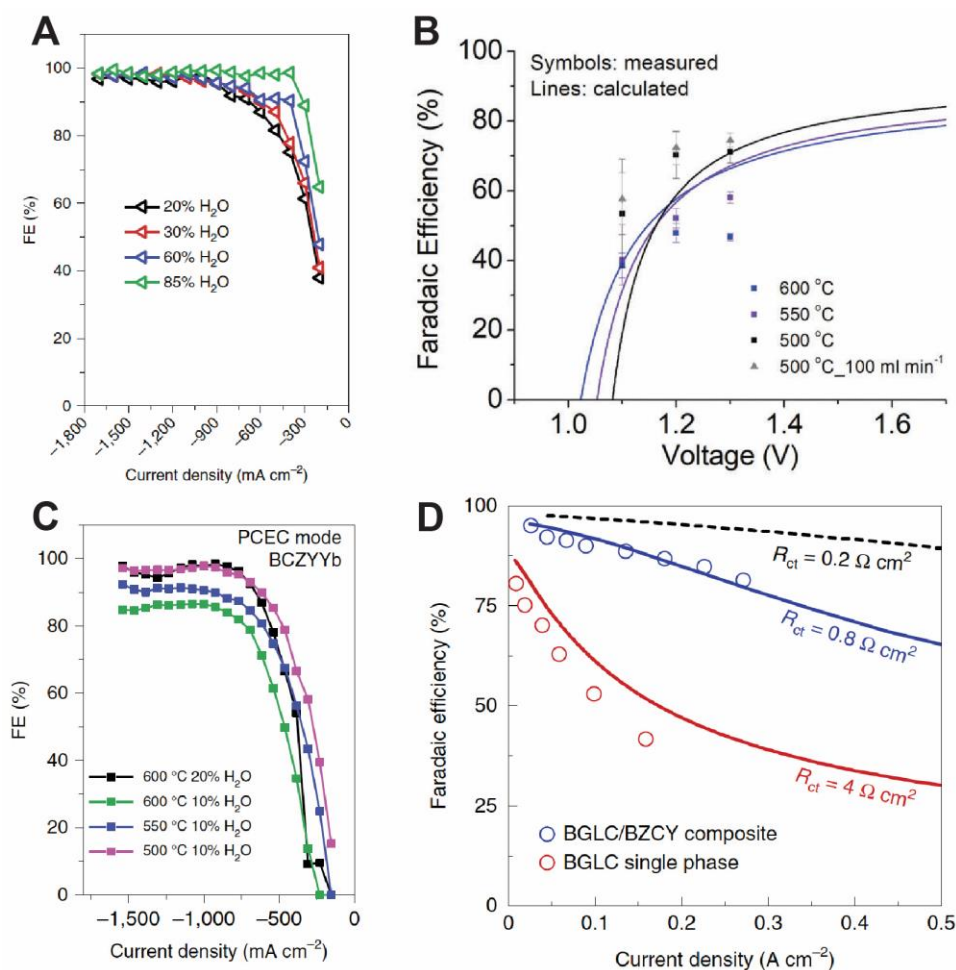


Figure 2.8. Faradaic efficiency of protonic ceramic electrolysis cells as a function of current density or applied voltage. (A) Impacts of steam concentration on performances of BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹. (B) Impacts of operating temperature

on faradaic efficiency of BCZYYb4411-based PCECs with PBSCF as the positive electrode⁴⁷. (C) Impacts of operating temperature on faradaic efficiency of BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹. (D) Faradaic efficiency of BZCY-based PCECs with Ba_{1-x}Gd_{0.8}La_{0.2+x}Co₂O_{6-δ} (BGLC) as the positive electrode⁴⁸.

It should be noted that the operating temperatures can significantly affect the faradaic efficiency. As shown in Figures 2.8B and 2.8C, increasing the operating temperatures tends to decrease the faradaic efficiency. While high operating temperatures can improve the current density, due to more severe electronic leakage, the overall H₂ production rate might not increase, leading to reduced energy efficiency.

Moreover, it is important to recognize that the faradaic efficiency of PCECs shows a high dependency on the current density or applied voltage. Figures 2.8B and 2.8C show that the Faradic efficiency is extremely low at a relatively low current density or voltage while increasing the current density can quickly increase the faradaic efficiency until it shows the propensity of being constant. A current density approaching zero, the faradaic efficiency is undetectable, and reaches zero at a low current density (e.g., <100 mA/cm²).

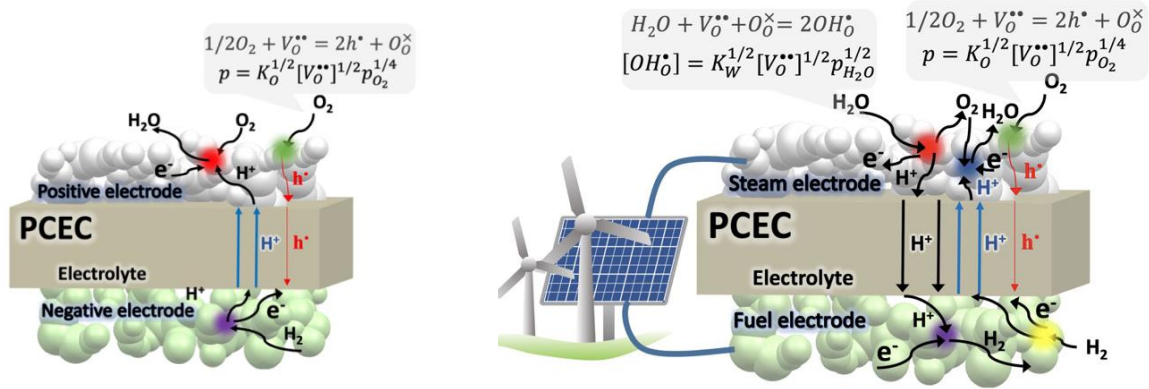


Figure 2.9. Schematic illustration of why the faradaic efficiency drops sharply when the current densities are close to zero. (A). Under OCV condition. (B) Under charging condition at relatively low current density.³¹

It has been recognized that the proton-conducting ceramic shows a mixed electronic and ionic conduction, especially in an oxidizing atmosphere. As shown in Figure 2.9A, the p-type electronic conduction can lead to a net flux of protons from the negative electrode to the positive electrode. Thus, the protonic ceramic membrane functions as a hydrogen permeation membrane, suggesting the faradaic efficiency is negative at a current density that is close to zero. Increasing the applied current density in electrolysis mode produces additional hydrogen via H_2O electrolysis (Figure 2.9B). However, the direction of proton flux ascribed to H_2O electrolysis is opposite to direction of the proton flux due to the permeation. Thus, these two proton fluxes act to offset each other. If the permeation flux is higher than H_2O electrolysis proton flux, this leads to a negative faradaic efficiency. The faradaic efficiency tends to sharply increase once the H_2O electrolysis proton flux dominates the proton flux.

Therefore, the transference number of electron holes is essential for the faradaic efficiency of PCECs. The electron holes are attributed to the oxidation of the electrolyte membrane, indicating the electrolyte material and operating conditions could be modulated to reduce the electronic leakage and enhance the faradaic efficiency. The strategies include (1) developing proton-conducting ceramic that favor hydration and suppress oxidation; (2) supplying a gas stream to the positive electrode that has a low oxygen partial pressure and high steam concentration to further enhance hydration and suppress oxidation; and (3) operating the PCECs at appropriately low operating temperatures and high current densities to achieve an enhanced faradaic efficiency.

The durability of PCECs is key to their implementation for H_2 production. Figure 2.10 presents the most recent work on long-term stability testing of PCECs, which shows that PCECs are stable under a high current density at intermediate operating temperatures. For example, Haile et al. have tested BCZYYb4411-based PCECs under a constant voltage of 1.3V at 550 °C for >500

hours. The corresponding current density is stable over 500 hours⁴⁷. Duan and O’Hayre et al. also tested the stability on BCZYYb7111-based PCECs under a constant current density of $\sim 1.4 \text{ A/cm}^2$ at 600 °C and 550 °C. The recorded terminal voltage does not significantly degrade over >1000 hours¹⁰. A similar stability testing was conducted by Ding et al. using the constant voltage approach⁴⁶.

The approach that is used to evaluate the PCEC stability is operating the PCEC in either constant current or constant voltage mode while recording the cell voltage or current as a function of time. As PCECs are a relatively nascent technology, it is suggested to simultaneously conduct additional measurements to better analyze the stability of PCECs and probe its potential degradation mechanisms. These measurements include time-resolved electrochemical impedance spectroscopy that could identify the degradation mechanism, and measuring the H_2 production rate and Faradaic efficiency as a function of time. As abovementioned, unlike SOECs that typically have negligible electronic leakage, PCEC could potentially have severe electronic leakage. Therefore, the stability measurement under a constant current or voltage might not be able to comprehensively represent the PCEC stability.

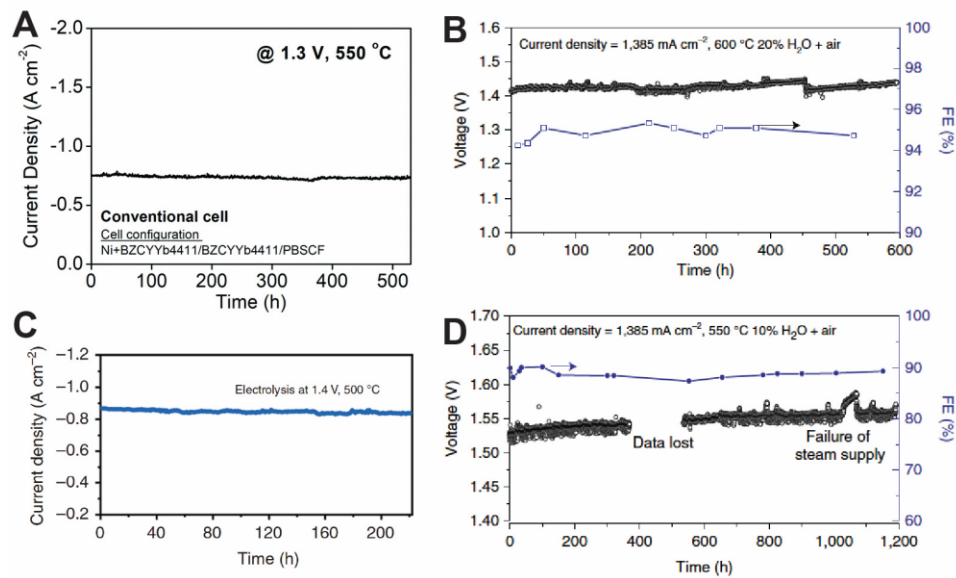


Figure 2.10. Stability of protonic ceramic electrolysis cells for H₂ production. (A) BCZYYb4411-based PCECs with PBSCF as the positive electrode⁴⁷. (B) BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹. (C) BCZYYb4411-based PCECs with PBN as the positive electrode⁴⁶. (D) Impacts of steam concentration on performances of BCZYYb7111-based PCECs with BCFZY4411 as the positive electrode³¹.

As electronic leakage is widely recognized as the primary issue regarding PCECs, Duan and O'Hayre et al. have concurrently measured the faradaic efficiency as a function of operation time. Although the terminal voltage slightly increases at a constant current, the faradaic efficiency is relatively constant, suggesting the transport properties of proton-conducting electrolyte membrane are stable. The long-term operation did not give rise to increased electronic leakage. However, there is only a handful of published work on measuring the faradaic efficiency as a function of operating time. Furthermore, operating the PCECs under constant voltage mode complicates the measurement of faradaic efficiency, suggesting the stability of PCECs should be conducted under a constant current mode to better determine the faradaic efficiency as a function of time.

2.2.5 Challenges and opportunities of H₂ production in PCECs

Faradaic efficiency of PCECs for H₂ production. Despite the outstanding performance which PCECs have demonstrated for H₂ production, challenges related to efficient H₂ production remain. The primary challenge is their relatively low faradaic efficiency, which is attributed to electronic leakage. The electronic leakage is due to the oxidation of the proton-conducting electrolyte membrane. However, the electrolyte is always exposed to an oxidizing atmosphere on the positive electrode side. Therefore, the oxidation of the electrolyte membrane is inevitable, but it can be suppressed. The oxidation of the electrolyte membrane is thermodynamically controlled, which in turn is intrinsically determined by its composition. Additionally, the operating

temperature and oxygen partial pressure also affect oxidation. To minimize oxidation and electronic leakage, the electrolyte membrane's composition should be deliberately designed to hinder oxidation and favor hydration, reducing the transference number of p-type electronic charge carriers and enhancing faradaic efficiency. Extensive efforts have been devoted to studying and modulating the defect chemistry and transport properties of proton-conducting electrolyte membranes. For example, it has been noted that Sc-doped BCZY leads to lower electronic leakage than Yb-doped BCZY, implying that BCZYSc-based PCECs could potentially give rise to higher faradaic efficiencies than BCZYYb-based PCECs⁵¹. Furthermore, the dehydration temperature of BCY is much higher than that of BZY, indicating that BZY is more prone to being oxidized at 500 °C–600 °C⁵². Therefore, it is expected that PCECs with BCY electrolytes can achieve higher faradaic efficiencies than those of BZY-based PCECs. However, it has been noted that high Ce contents could be detrimental to their long-term durability. Moreover, it should be recognized that a high sintering temperature could result in Ba vaporization and create an A-site deficiency, which could alter the defect chemistry of the electrolyte and its transport properties. The sintering aid (e.g. NiO) that is typically used to densify the electrolyte membrane could also modify the transport properties and affect the electronic leakage. Therefore, the electronic leakage of the electrolyte membrane is a complicated issue, which cannot be straightforwardly addressed by developing a new electrolyte. Both the electrolyte composition and the corresponding fabrication procedures can impact the faradaic efficiency of PCECs. As the oxidation of protonic ceramics is endothermic, appropriately reducing the operating temperature can help to enhance efficiency. However, the reduced operating temperature increases the overpotential and decreases the energy efficiency. Therefore, it is suggested that the operating temperature should be carefully adjusted to achieve the highest energy efficiency. Additionally, the atmosphere at the positive electrode

also impacts electrolyte oxidation. A high $p(\text{O}_2)$ and a low $p(\text{H}_2\text{O})$ facilitate oxidation and decrease faradaic efficiency. It should be noted that the current density can also change the atmosphere and affect the faradaic efficiency. For example, operating the PCEC at a high current density can increase H_2O utilization, which reduces the $p(\text{H}_2\text{O})$ and simultaneously produces O_2 , which can exacerbate electronic leakage and reduce faradaic efficiency. Therefore, the operating current density should also be rigorously selected to obtain high energy efficiency. In summary, the challenges related to low faradaic efficiency could be addressed by considering both the materials and operating conditions required to achieve high energy efficiencies.

Long-term durability. As mentioned above, the degradation of PCECs for H_2 production is primarily ascribed to the positive electrode. Therefore, enhancing the chemical stability of the positive electrode should be at the heart of optimizing PCECs. Since PCECs for H_2 production have been revigorated for less than ten years, only a handful of papers have been published on this topic. Other potential degradation mechanisms have not been identified, suggesting that additional work could be conducted to probe the degradation. Although some studies have performed long term durability testing, there has been a lack of comprehensive postmortem characterization to better understand PCECs after long-term operation, which could assist in probing the degradation mechanisms. It is therefore suggested that it would be beneficial to conduct additional characterizations such as transmission electron microscopy, energy-dispersive x-ray spectroscopy, and x-ray photoelectron spectroscopy to study the electrodes, electrolyte, and interfaces.

2.3 CO₂ reduction reaction in PCECs for chemical production

2.3.1 Introductions

The second important application of PCECs is converting CO₂ to carbon-containing compounds, which gives rise to substantial environmental and economic benefits. In the context of growing concern about the high global atmospheric concentration of CO₂, economically viable and efficient technologies for large-scale and reliable CO₂ conversion and utilization must be widely deployed to minimize the environmental risks imposed by human activities with high CO₂ emissions (e.g., coal-fired power plant). Fortunately, PCECs driven by renewable power can provide opportunities to utilize CO₂ for energy storage and synthesizing sustainable chemicals^{39,40}. This modular and electrochemical approach is particularly promising for reducing point-source CO₂ emissions due to its versatility for manufacturing chemical feedstocks onsite⁴¹. PCECs can operate at intermediate temperatures (e.g., 400-500 °C), which favors the production of chemicals beyond carbon monoxide, such as CH₄ that could be used as the sustainable feedstock for various industries. Moreover, reversible methane fuel cells based on PCECs can be used for energy storage, which displays a theoretical round-trip efficiency approaching 100%, creating a closed cycle with minimized carbon footprint. Thus, creating a closed cycle for methane has significant economic and environmental benefits. Therefore, integrating PCECs with deliberately designed CO₂ reduction electrodes can achieve sustainable chemical manufacturing, enhance CO₂ conversion and desired product yield, enable long-term energy storage, and reduce greenhouse gas emissions.

Figure 2.11 shows a typical PCEC configured to convert CO₂ into value-added chemicals. The middle layer of PCEC is the dense proton-conducting ceramic electrolyte membrane which exhibits high proton conductivity at 400-500 °C (10^{-5} - 10^{-3} S cm) and separates

the gas streams fed to the two electrodes⁴². The porous positive electrode releases electrons to the outer circuit, oxidizes water, and produces oxygen and protons. The porous negative electrode, functions as the CO₂ reduction electrode to activate and convert CO₂. The core reaction is that CO₂ molecules are reduced by protons and electrons. According to the chemicals fed to the positive electrode, the electrochemical cell configurations fall into three categories: alkanes, renewable H₂, and water. These feedstocks will not impact the CO₂ reduction mechanisms in the negative electrode; thus, we focus on discussing the recent progress in negative electrode materials.

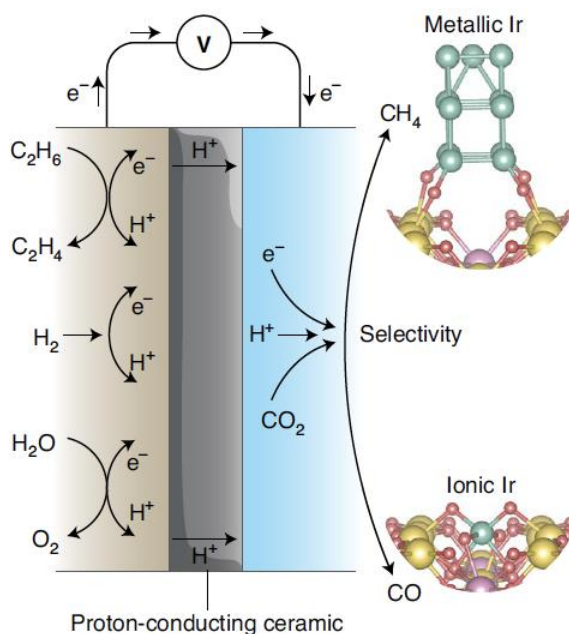


Figure 2.11. Schematic illustration of protonic ceramic electrolysis cells for CO₂ conversion⁴³

2.3.3 Thermodynamics of CO₂ electrolysis in PCECs

Figure 2.12 presents the thermodynamics of CO₂ conversion in PCECs using hydrogen/proton sourced from three different reactants fed to the positive electrode, which include H₂O, alkanes (e.g., C₂H₆), and H₂. The overall electrical energy consumption depends on the feedstock delivered to the positive electrode. The co-conversion of CO₂ and H₂O requires the

highest amount of electrical energy (Figures 2.12A and 2.12C). The electrical energy consumption of CO₂-to-CO conversion is lower than that of CO₂-to-CH₄ conversion as the total energy demand (ΔH) for CO production is lower for CH₄ (Figures 2.12B and 2.12D). Additionally, the heat demand ($T\Delta S$) for producing CO increases with increasing operating temperatures (Figure 2.12B), enabling to utilize heat for CO production. As the total energy demand for CO production is relatively independent of operating temperatures, the electrical energy consumption and reversible voltage for CO production decrease with increasing temperature. However, the heat demand for CH₄ production highly depends on the reactants delivered to the positive electrode (Figure 2.12D).

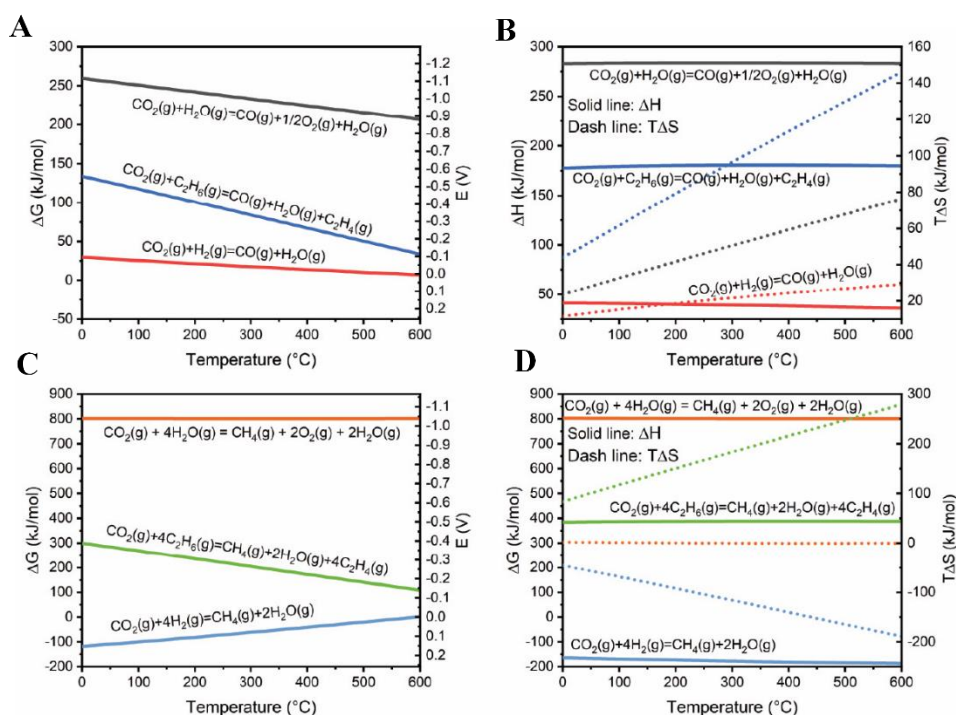


Figure 2.12. Thermodynamics of CO₂ conversion as a function of temperature using hydrogen/proton sourced from three reactants fed to the positive electrode, including H₂O, C₂H₆, and H₂. ΔG is correlated with the reversible voltage (V). ΔG and V share the same plot and different y axes. The results are calculated by using HSC software. (A) ΔG and V of CO₂ reduction to CO as a function of temperature. (B) ΔH and $T\Delta S$ of CO₂ reduction to CO as a function of temperature. (C) ΔG and V of CO₂ reduction to CH₄ as a function of temperature. (D) ΔH and $T\Delta S$ of CO₂ reduction to CH₄ as a function of temperature⁴⁴.

2.3.4 Advantages of employing PCECs for CO₂ production

Under an external potential, PCECs reduce CO₂ at the negative electrode using renewable electrons and protons generated by converting various feedstocks at the positive electrode. PCECs uniquely achieve a high proton flux at moderate operating temperatures (400 °C–500 °C), placing them in a thermodynamic and kinetic ‘sweet spot’ for CO₂ reduction that overlaps with temperatures relevant to CO₂ hydrogenation. Thus, the co-conversion of CO₂ and H₂O into CH₄ or other hydrocarbons is feasible.

The electrochemical conversion of CO₂ in ceramic electrochemical reactors can lead to coking (ascribed to the Boudouard reaction ($2\text{CO} = \text{C} + \text{CO}_2$)) and the pyrolysis of hydrocarbons, while the unique characteristics of protonic ceramics (e.g. relatively basic surfaces) can mitigate carbon formation; this, in turn, enables excellent coking tolerance and may even eliminate the coking entirely^{53,54}.

2.3.5 Current progress in PCECs for CO₂ conversion

With the advancements of PCECs for H₂ production, reducing CO₂ in PCECs for high-value chemicals production tends to gain more attention as converting CO₂ in PCECs does show various benefits. Duan and O’Hayre et al. have directly used PCECs that were developed for H₂O electrolysis for CO₂ conversion³¹. As shown in Figure 2.13A, CO₂ could be reduced to both CO and CH₄ with a high CO₂ conversion at an intermediate operating temperature. The intermediate operating temperature allows the production of CH₄, which is one of the main benefits of converting CO₂ in PCECs. However, it also leads to poor selectivity, producing a mixture of CO and CH₄. Furthermore, Duan and O’Hayre et al. recognized that the negative electrode favors hydrogen evolution reaction (HER), leading to high Faradaic selectivity toward H₂. As shown in Figure 2.13A, the current density does not proportionally enhance CO₂ conversion, implying the

HER is more severe at a higher current density or potential. This study suggests that PCECs designed for H₂O electrolysis might not lead to the most favorable CO₂ conversion, as they could give rise to substantial HER and poor selectivity. Thus, the negative electrode should be rationally designed to suppress HER and selectively reduce CO₂. For example, Ding et al. have pioneered an approach to modulating the CO₂ reduction pathway to selectively produce either CO or CH₄⁵⁵. By using a metallic Ir-based negative electrode, CO₂ can be selectively reduced to CH₄ with an outstanding faradaic selectivity of >95%. The negative electrode can favor CO production if it is integrated with Ir-O-based catalysts. Furthermore, both catalysts drastically inhibited HER and improved CO₂ conversion. The work conducted by Ding et al. validates the concept that modulating the negative electrode could tune the CO₂ reduction pathway and selectively produce the desired product.

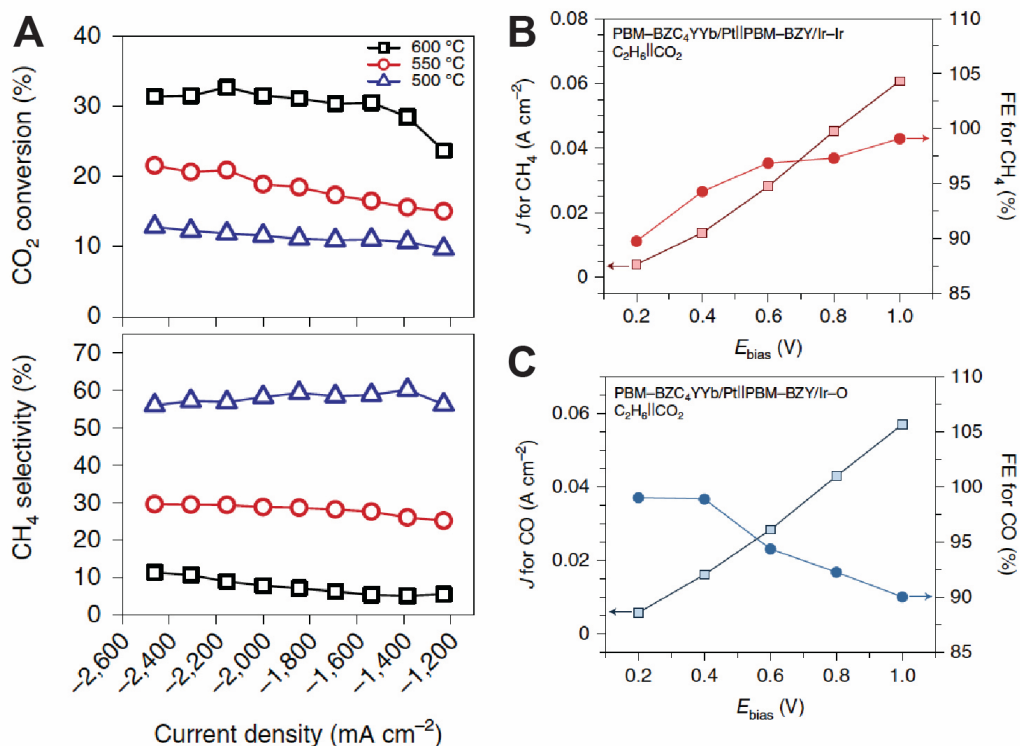


Figure 2.13. Performances of CO₂ conversion in PCECs. (A) BCZYYb7111-based PCEC with Ni-based negative electrode³¹. (B) BCZYYb4411-based PCEC with metallic Ir-based negative electrode⁵⁵. (C) BCZYYb4411-based PCEC with Ir-O-based negative electrode⁵⁵.

According to the thermodynamics of CO₂ conversion and H₂O electrolysis, reducing CO₂ to CO enables to utilize more heat than H₂O electrolysis, leading to lower potential applied on PCEC and lower electrical energy consumption. Therefore, conversion of CO₂ in PCECs allows the use of additional waste heat for chemical manufacturing, which has been demonstrated by Medvedev et al.⁵⁶. However, CO₂ reduction with hydrogen to CH₄ is highly exothermic; thus, it cannot utilize heat. Integrating CO₂ reduction to CH₄ with endothermic reaction, for instance, H₂O electrolysis in endothermic mode, can directly use the heat produced from CO₂ reduction for H₂O electrolysis, potentially creating a thermo-neutral zone, maximizing the overall energy efficiency. Integrating CO₂ conversion with H₂O electrolysis, which can reduce the applied overpotential, has been experimentally demonstrated.

CO₂ conversion in PCECs could also be realized by integrating it with dry reforming. Luo et al. have intimately integrated CO₂ dry reforming with PCECs, which generates power while concurrently producing syngas³⁶. Oxygen-ion solid oxide fuel cells (SOFCs) could fully oxidize the fuel delivered to the anode in fuel cell mode; thus, dry reforming of methane in O-SOFC cannot convert and utilize CO₂ as the CO could be ultimately oxidized to CO₂. As the electrolyte membrane of PCECs exhibits relatively low oxygen- ion conduction at <600 °C, PCECs cannot further oxidize CO and could only utilize H₂ for power generation. Therefore, PCECs enable co-generation of power and syngas via dry reforming. Luo et al. have rationally designed a Ni_{0.8}Co_{0.2}–La_{0.2}Ce_{0.8}O_{1.9} (NiCo–LDC) composite as the anode, which significantly improved the drying reforming activity and achieved a CO₂ conversion of 91.5% at 700 °C. Moreover, long-term durability has also been tested and no degradation has been observed, indicating the PCEC exhibits excellent coking tolerance under a high CO/CO₂ ratio.

2.3.6 Mechanisms of CO₂ reduction in PCECs

A detailed understanding of the CO₂ reduction mechanisms will open the “black box” of CO₂RR in PCECs. Due to the lack of appropriate tools to conduct *in situ* operando experiments and probe the active intermediates involved in CO₂ reduction, the CO₂ reduction mechanisms in PCECs are not illuminated. Establishing this understanding, especially by leveraging the thermochemical knowledge^{57,58}, will therefore assist in rationally designing CO₂ reduction catalysts that could be applied on PCECs.

Figure 2.14 displays the proposed CO₂ reduction pathways, including the associative CO₂ reduction pathways and dissociative pathways. The associative pathways denote the pathways where the C-O bond cleavage occurs after its hydrogenation while the dissociative pathways represent the C-O bond will first break and then be hydrogenated. The CO₂ reduction pathway could also be divided into two categories depending on the product, which is CO or CH₄. Despite other hydrocarbons, such as ethylene and light olefins, could be produced in PCECs that operate at an intermediate temperature at which the C-C bond coupling is thermodynamic favorable, this concept has not been experimentally validated. Thus, the CO₂-to-light olefins mechanisms are not discussed in this review. As shown in Figure 2.14, the protons from the positive electrode could first pair with electrons to form hydrogen adsorbed on the negative electrode (*H). The negative electrode is typically a composite of oxide support and a metallic phase. The proton is therefore reduced at the oxide-metal interface and the hydrogen will then adsorb on the surface of the metallic phase. It will subsequently reduce the intermediate species adsorbed on the oxide.

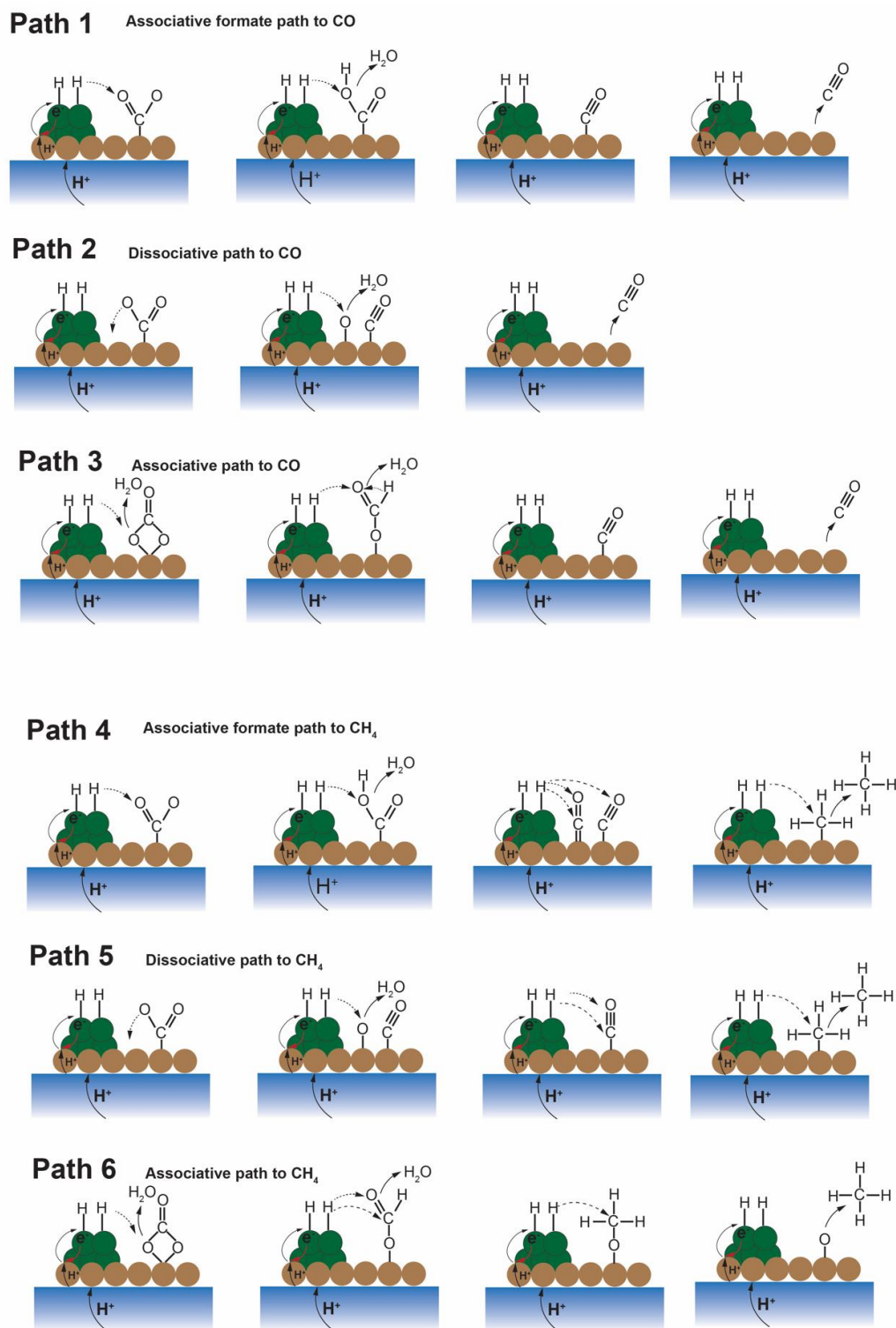


Figure 2.14. Schematic illustration of the proposed CO₂RR mechanisms in PCECs. The blue rectangle is the proton-conducting electrolyte membrane. The brown dots are the oxide supports. The green dots are metallic particles.

The potential CO₂ reduction pathways are outlined as follows:

- (1) Path 1: CO₂ is associatively adsorbed on the oxide surface and forms carbonate that will be then reduced to formate. The formate species will be further reduced to CO.
- (2) Path 2: Oxygen vacancies are available on the oxide support. One oxygen atom in a CO₂ molecule occupies the oxygen vacancy. CO₂ will then be dissociatively adsorbed on the oxide surface. The resultant CO will desorb and produce CO.
- (3) Path 3: CO₂ molecules associatively adsorb on the negative electrode followed by the formation of bidentate carbonate. The bidentate carbonate will be subsequently hydrogenated to bicarbonate that can be further reduced to CO.
- (4) Path 4: This path displays the associative formate path for CH₄ production. CO₂ molecules associatively adsorb on the negative electrode and form formate species that can be subsequently reduced to CH₄.
- (5) Path 5: CO₂ molecules dissociatively adsorb on the negative electrode and produce *CO that will be consecutively reduced to CH₄.
- (6) Path 6: CO₂ molecules associatively adsorb on the negative electrode and produce formate that will be further reduced to CH₄.

2.3.7 Challenges associated with CO₂RR in PCECs

The challenges of converting CO₂ in PCECs include: high H₂ selectivity; poor Faradaic selectivity to either CO or CH₄; poor chemical stability; and the lack of established CO₂ reduction mechanisms. These challenges are detailed as follows:

- (1) As PCECs for CO₂ conversion is a truly nascent technology, most previous studies were performed directly using the negative electrode of protonic ceramic fuel cell (PCFC),

which is a composite of proton-conducting oxide and Ni^{31,56}, as the CO₂ reduction electrode. Ni-based cermet also favors HER. Therefore, the Faradaic selectivity toward carbon-containing molecules is poor. Additionally, oxide-supported Ni is not prone to selectively produce either CO or CH₄. Thus, the product is commonly a mixture of H₂, CO, and CH₄. Furthermore, the negative electrode that favors HER leads to poor CO₂ conversion.

- (2) Oxygen-ion solid oxide electrochemical cells (O-SOECs) have been widely used for efficiently producing syngas via co-electrolysis of CO₂ and H₂O or producing pure CO via CO₂ electrolysis⁵⁹. However, the products are limited to either syngas or CO. As the operating temperature of PCECs is lower than that of O-SOECs, it is feasible to produce CH₄^{31,43,55}. However, this competitive advantage also poses challenges on selectively producing high-purity chemicals. The selection of negative electrode materials will determine the Faradaic selectivity. There is a lack of rationally designed negative electrode materials that can lead to the production of pure CO, syngas, or CH₄. To selectively produce pure CO or CH₄, the negative electrode should also significantly suppress the HER.
- (3) One of the innovations of CO₂ reduction in PCECs is that PCECs can operate at a lower temperature than O-SOECs. However, as the CO₂ molecules are thermodynamic stable, the CO₂ reduction kinetics is slower than that at high operating temperatures, especially for CO production. Therefore, the CO₂ conversion to CO in PCECs is lower than that in O-SOECs. The intermediate operating temperatures thermodynamically favor CO₂ reduction to hydrocarbons. Therefore, it is suggested future research should be geared toward enhancing the electrocatalytic activity of negative electrodes at intermediate operating temperatures (e.g., 300-500 °C) to improve CO₂ conversion to hydrocarbons.

- (4) One of the impediments to the development of commercially relevant PCECs is the long-term durability of PCECs, especially the negative electrode under an atmosphere with CO₂. Reduced operating temperatures thermodynamically favor the CO₂ reduction to hydrocarbons. However, lowering the operating temperature may compromise the chemical stability of negative electrodes that are more prone to react with CO₂ and form BaCO₃ at low temperatures. The BaCO₃ phase is an insulator and catalytically inert, leading to the degradation of PCECs^{11,60}.
- (5) Despite coking (or carbon deposition) has not been observed in PCECs, it does not indicate coking is not possible as the current CO₂ conversion in PCECs is poor. The future PCECs developed for CO₂ reduction to CO could achieve a high CO/CO₂ ratio. The intermediate operating temperature further favors the exothermic Boudouard reaction, posing potential risks of coking⁶¹.
- (6) The CO₂ reduction mechanism in PCECs is the “black box”. It is widely accepted that CO₂ is reduced by either the proton or the gaseous H₂. However, there is no direct evidence of how electrocatalysis occurs and what intermediate species are involved in the reactions. The lack of this fundamental understanding hinders the rational design of negative electrodes for PCECs. Therefore, without understanding the CO₂ reduction pathway over negative electrodes, it is impossible to deliberately modulate the negative electrode composition and structures to tune the CO₂ reduction pathways.

2.3.8 Strategies to address the challenges of CO₂ conversion and utilization

Figure 2.15 displays the challenges of synthesizing chemicals in PCECs via CO₂ reduction and corresponding strategies. There is a variety of strategies that can tackle these problems, which

include (1) designing CO₂ reduction electrodes for PCECs to inhibit HER, enhance CO₂RR activity, and tune the CO₂ reduction pathways for enhancing the propensity to produce desired products; (2) enhancing chemical stability of CO₂ reduction electrode by improving the CO₂ tolerance of proton-conducting oxide support; (3) alternating the operating conditions to modulate selectivity while achieving high CO₂ conversion and product yield; and (4) conducting *in situ* operando experiments to probe the CO₂RR mechanisms in PCECs,. These strategies can also be intertwined to better control the selectivity and further enhance CO₂ conversion.

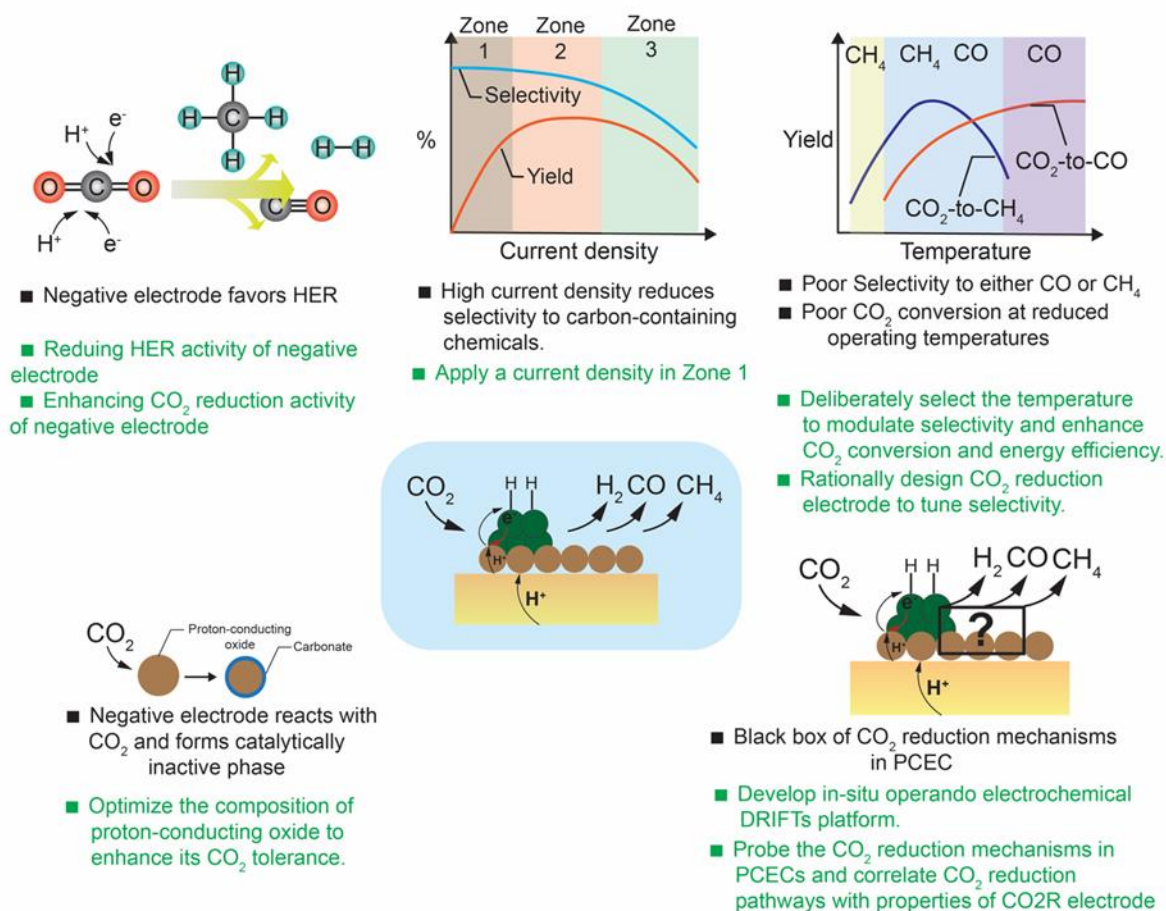


Figure 2.15. Summary of challenges and future perspectives to improve the chemical synthesis in PCECs via CO₂RR.

2.4 Other applications in PCECs energy conversion and storage

2.4.1 Nitrogen reduction reaction for ammonia synthesis

There is significant commercial and economic incentive to produce ammonia more efficiently and sustainably, as ammonia is widely used as fertilizer, refrigerant gas, the building block for other chemicals, and fuel for power generation⁶²⁻⁶⁴. The ammonia production industry based on the conventional Haber-Bosch (HB) process is responsible for >1.0% global greenhouse gas (GHG) emissions, striking the development of alternative ammonia synthesis technologies and the optimization of conventional HB ammonia synthesis processes. The main challenges of the HB process arise from (1) harsh operating conditions, especially high pressure (e.g., 300 bar), which is required to activate the $\text{N}\equiv\text{N}$ bond and thermodynamically favor the ammonia production^{65,66}, and (2) hydrogen is produced primarily from natural gas via steam reforming⁶⁷⁻⁶⁹, which is of high emissions and energy-intensive. PCECs with different configurations have been employed to address these challenges by integrating electrochemical ammonia synthesis with other thermochemical and electrochemical processes, aiming to increase ammonia yield while simultaneously enhancing overall energy efficiency and reducing GHG emissions.

Four major PCEC reactor configurations have been designed and validated for ammonia synthesis, which are schematically illustrated in Figure 2.16. Some of these reactors integrate electrochemical/thermochemical processes and separation processes with ammonia synthesis, aiming to circumvent the thermodynamic limitations of ammonia synthesis that are typically encountered in a classical HB reactor. This integration also allows using renewable power for ammonia synthesis, which enhances the sustainability of ammonia production and reduces the carbon footprint of ammonia manufacturing industries. Ammonia produced via this sustainable approach can also serve as energy storage media or hydrogen carrier, which is attributed to its high

energy density, high compressibility, carbon-neutral nature, and lower transportation costs than hydrogen. When additional electricity is needed to supplement the intermittent renewable power sources, PCECs can function as fuel cells to directly convert ammonia to electrical energy without any changes to the configuration of PCECs^{31,70}.

Figure 2.16 shows that PCECs for synthesizing ammonia can be classified according to the configurations and feedstocks. Reactors 1 and 2 have been developed to electrochemically reduce nitrogen to ammonia to enhance the ammonia production rate under mild conditions, such as ambient pressure. Reactor 3 intensifies steam methane reforming with ammonia synthesis, eliminating the external reformer and separating the H₂ stream from the CO₂ stream, which consequently simplifies CO₂ capture and reduces carbon footprint. Reactor 4 can convert H₂O and N₂ to ammonia via nitrogen reduction reaction and water electrolysis that provides alternative hydrogen.

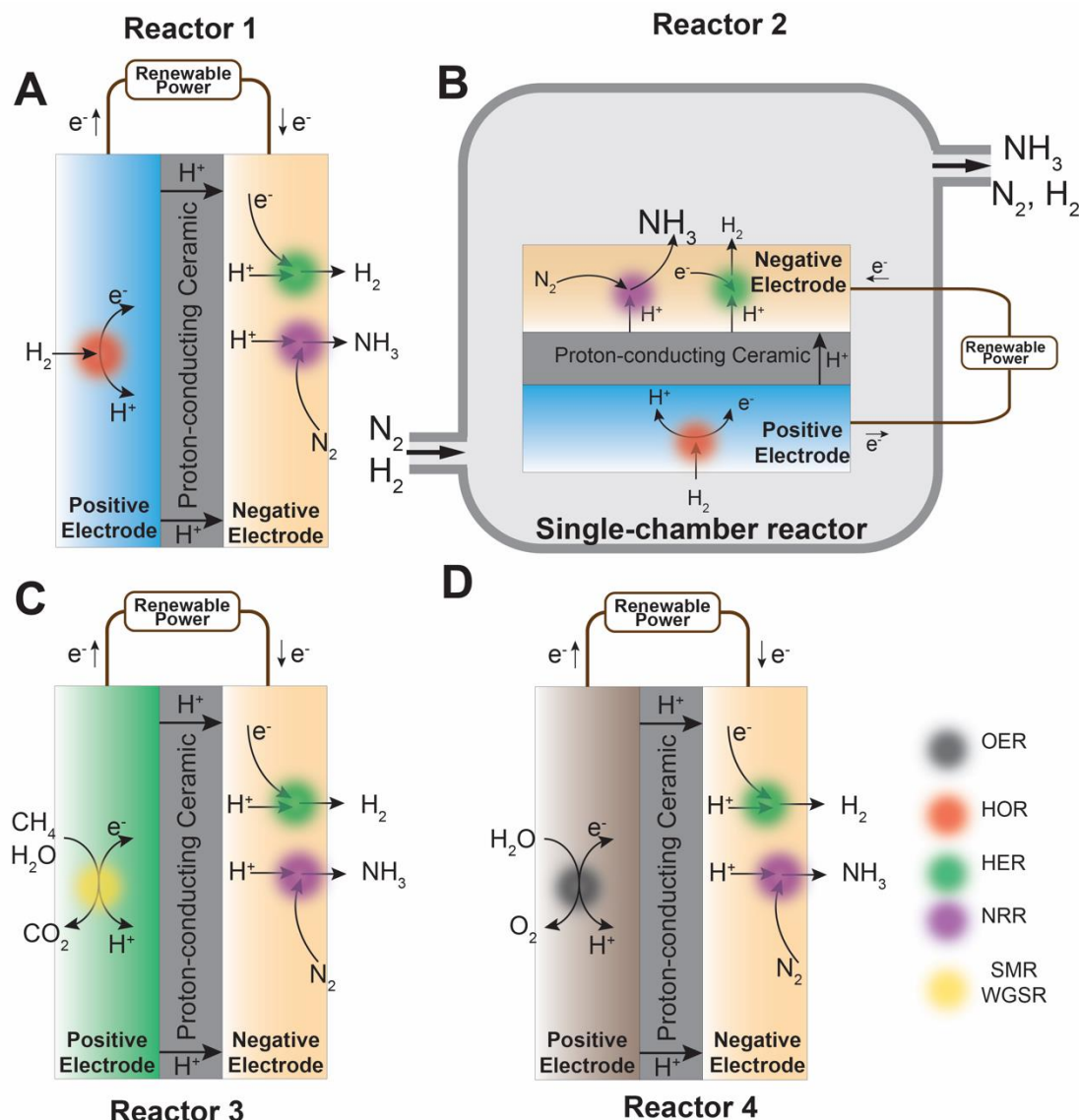


Figure 2.16. Schematic illustration of four primary PCEC configurations developed for ammonia synthesis. (A) Reactor 1 that converts H_2 and N_2 to ammonia in a two-chamber configuration, (B) single-chamber reactor 2 that electrochemically promotes ammonia synthesis, (C) Reactor 3 that intensifies steam methane reforming with ammonia synthesis, and (D) Reactor 4 that converts H_2O and N_2 to ammonia. OER: oxygen evolution reaction. HOR: hydrogen oxidation reaction. HER: hydrogen evolution reaction. NRR: nitrogen reduction reaction. SMR: steam methane reforming. WGSR: water gas shift reaction.

2.4.2 Upgrading natural gas in PCECs

PCECs offer several intriguing advantages for upgrading natural gas to value-added chemicals and provide potential opportunities for distributed chemical production. First, we

provide a brief overview of the industrial context that stimulates the research of employing PCECs for upgrading natural gas.

The depletion of conventional oil reserves has shifted much oil production to remote and offshore reservoirs, which imposes severe restrictions on the utilization of co-produced natural gas. Facilities for natural gas conversion rarely exist onsite, while transporting gas to centralized facilities is cost-prohibitive and/or infeasible. Consequently, flaring and venting are commonly used to dispose co-produced natural gas. Nonetheless, both practices flagrantly waste precious resources with deleterious environmental impacts.

Efficient and economical utilization of flared and vented natural gas motivates the development of distributed and modular technologies for producing liquid or solid chemicals to enable economical transportation and utilization of the resulting value-added products^{71,72}. Figure 2.17 summarizes the pathways of synthesizing chemicals from methane (the primary component of natural gas). Currently, the syngas and Fischer-Tropsch synthesis route is the most mature technology for converting natural gas to commodity chemicals (Figure 2.17, top panel). However, this centralized technology is not suitable for onsite chemical production because it is a complicated process that is difficult to downsize and requires costly infrastructure to transport natural gas⁷³. Additionally, Fischer-Tropsch synthesis consumes either extra CO or H₂ to remove the oxygen from CO, leading to lower carbon utilization or consumption of valuable H₂⁷². Alternatively, syngas can be converted to methanol followed by methanol-to-olefins conversion⁷⁴ or methanol-to-aromatics conversion⁷⁵. However, this technology also relies on energy-intensive and centralized syngas production.

There is an urgent need for modular and distributed chemical production systems (Figure 2.17, bottom panel) that can directly, efficiently, and economically convert natural gas to high-

value and transportable chemicals. It should be noted that the global demand for benzene has reached about 43 million tonnes in 2020⁷⁶. Moreover, the U.S. imports 20% of all the benzene it uses because of a shortage of benzene supply⁷⁶. These facts are driving the industry toward producing aromatic compounds directly from methane via nonoxidative methane dehydroaromatization (MDA), oxidative methane aromatization, or oxidative coupling of methane to ethylene followed by further oligomerization to aromatics⁷⁷⁻⁸¹.

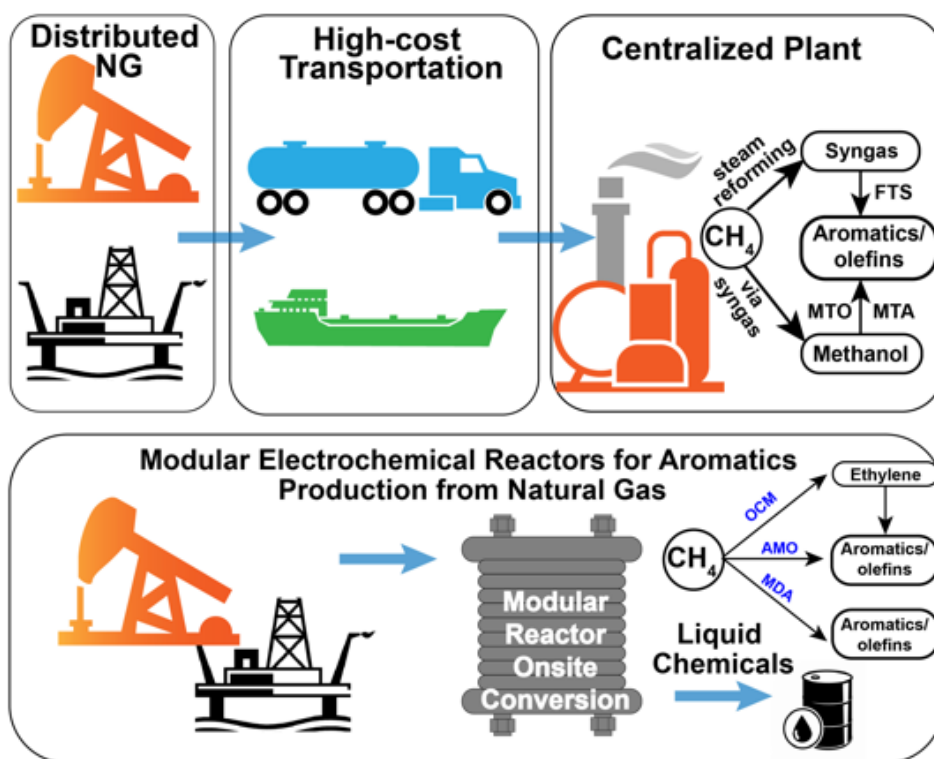


Figure 2.17. Pathways of synthesizing chemicals from natural gas/methane.

Direct, nonoxidative conversion of methane to aromatics has attracted widespread attention because it enables high-value liquid chemicals production, eliminates complex reactors and processes, and avoids methane overoxidation, as well as significantly reduces CO₂ emissions⁸¹. However, the nonoxidative MDA over heterogeneous catalysts in conventional packed bed reactors is challenging because of its low methane conversion (typically ~10% at 750 °C), coking,

and the high operating temperatures ($>800\text{ }^{\circ}\text{C}$) for C-H bond activation⁸¹⁻⁸⁵. Although a high methane conversion of 48.1% and a stable operation exceeding 60 hours have been demonstrated over single-atom iron sites embedded in a silica matrix, its operating temperature is impractically high ($>1000\text{ }^{\circ}\text{C}$), and the selectivity of the aromatic compounds is low ($<50\%$)⁸¹. In the last decades, a host of technologies have been proposed for addressing these challenges. These include injecting oxygen to mitigate coke and improve durability, and extracting hydrogen to circumvent the severe thermodynamic limitations and thereby enhancing methane conversion and product yield⁸⁶⁻⁸⁹. Unfortunately, it is infeasible to achieve simultaneous hydrogen extraction and oxygen injection in packed bed reactors to tackle all the above challenges.

As an alternative strategy, protonic ceramic electrochemical cells (Figure 2.18), which can operate in power-driven (electrolytic reactor, Figure 2.18A) mode and hydrogen permeation mode (Figure 2.18B), enable continuous and high-flux hydrogen extraction, and minor oxygen injection. The hydrogen extraction aims to enhance methane conversion and aromatics yield while minor oxygen injection can improve its coking tolerance. Figure 2.18A displays the PCECs with a mixed proton and oxygen-ion conductor as the membrane, which extracts H_2 and injects minor O_2 under an external potential. Figure 2.18B shows the PCECs that employ a mixed proton, oxygen-ion, and electronic conductor as the membrane. The chemical potential drives H_2 permeation and oxygen injection.

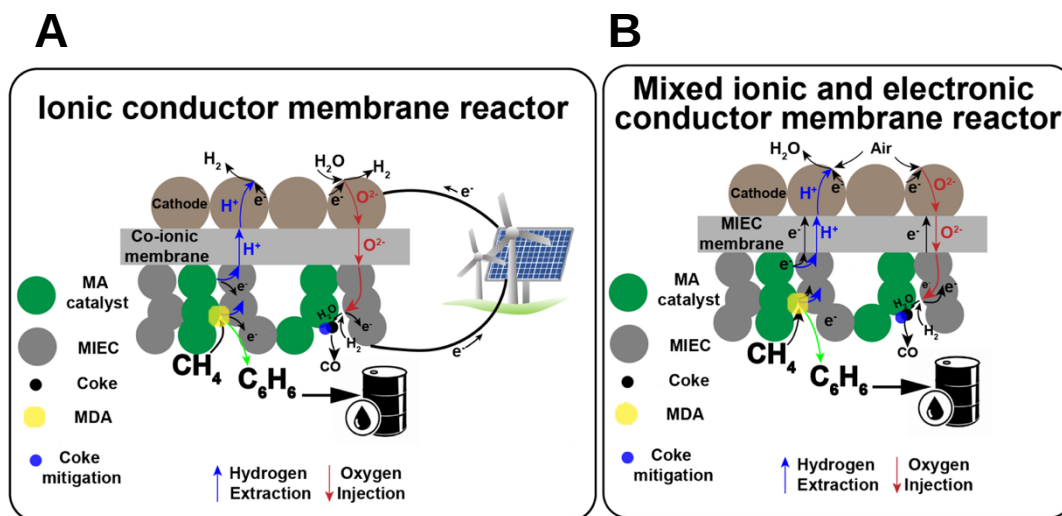


Figure 2.18. Schematic illustration of PCECs for producing aromatics from natural gas. (A) PCECs with a mixed proton and oxygen-ion conductor as the membrane. (B) PCECs with a mixed proton, oxygen-ion, and electronic conductor as the membrane.

The oxygen-ion conduction of the membrane is key to durability. Additionally, the transference number of oxygen ions can affect the selectivity of products. A relatively low oxygen-ion transference number can mitigate coking while selectively producing aromatics. However, an excessively high oxygen-ion conduction can oxidize the hydrocarbons and reduce the selectivity to aromatics. Therefore, the transference number of oxygen ions should be controlled at lower than 10% to simultaneously achieve durable operation and high aromatics yield. It has been widely recognized that the operating temperature and atmosphere can alter the transference number of oxygen ions^{31,90,91}. In general, increasing the operating temperature and oxygen partial pressure can increase the transference number of oxygen ions. Duan and O'Hayre et al. also noted $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ exhibits a higher transference number of oxygen ions than $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, indicating the electrolyte composition also affects the oxygen-ion injection. As one of the benefits of employing PCECs for producing aromatics is the reduced operating temperature, increasing the temperature to achieve a relatively high transference number of oxygen ions is not

favorable. However, the oxygen partial pressure of the cathode side or electrolyte composition can be adjusted to control the oxygen-ion injection.

Incorporating deliberately designed methane aromatization catalysts into PCECs and synergizing the mixed proton and oxygen-ion conduction address the two main issues of methane aromatization in conventional thermochemical catalytic processes: (1) low methane conversion due to thermodynamic limitations and (2) rapid catalyst deactivation due to coking. By continually removing hydrogen (blue arrows in Figure 2.18) from the methane aromatization electrode side, this hybrid process pushes the reaction equilibrium toward aromatics, thereby increasing methane conversion (Figure 2.18, yellow dot) at reduced temperatures (e.g., 600 °C). Second, the electrolyte membrane exhibits minor oxygen-ion conductivity, which enables the concomitant injection of oxygen (red arrows in Figure 2.18) to the methane aromatization electrode which can act to burn off coke or selectively react with H₂ and hydrocarbons to produce H₂O and CO₂ which can then mitigate coking (blue dot in Figure 2.18).

A computational study⁷⁹ found that the addition of an appropriate amount of oxygen facilitates methane aromatization by the formation of ethylene via oxidative coupling of methane followed by the aromatization of ethylene. Cao et al.⁸⁰ have experimentally demonstrated oxidative methane aromatization in mixed oxygen-ion and electronic membrane reactors. Although enhanced stability and inhibited coke formation were achieved in the reactor, the aromatics yield, in particular the initial aromatics yield, was not significantly enhanced⁸⁰. In conventional fixed bed reactors, there have been attempts to regenerate the methane aromatization catalyst by burning out the carbon using oxygen at 700 °C⁹²⁻⁹⁴. However, due to relatively high oxidation temperature, Mo₂C, the active site on methane aromatization catalysts, tends to be reoxidized into mobile Mo-oxides (i.e., overoxidation). Therefore, the regeneration of catalysts at lower temperatures (500-

600 °C) has been employed to reactivate the catalysts^{86,95}. However, temperature cycling in a fixed bed reactor is inefficient and complex.

Extracting a considerable amount of hydrogen to shift reaction equilibrium has been achieved in PCECs to enhance methane conversion and aromatics yield^{88,89}. The potential of PCECs for improving methane aromatization has been validated⁹⁶. If MDA can run at lower temperatures, coke formation will be suppressed since the formation of polyaromatic type carbon, the main reason for catalyst deactivation, is more prone to occur at high temperatures^{85,97}. Liu et al. also recognized that reduced operating temperatures will inhibit coke formation⁹⁸. However, further dehydrogenation favors undesired naphthalene and thus will lead to its oligomerization to polyaromatic hydrocarbons, which are the deleterious coking species^{82,88}. Rival et al. noted that dehydrogenation via the Pd-alloy membrane reactor results in more severe graphitic coke⁸⁸. Therefore, although enhanced methane conversion was achieved in hydrogen-permeation membrane reactors (e.g., Pd and Pd-alloy membrane reactor), the exacerbated coking makes it impractical for economically viable methane conversion.

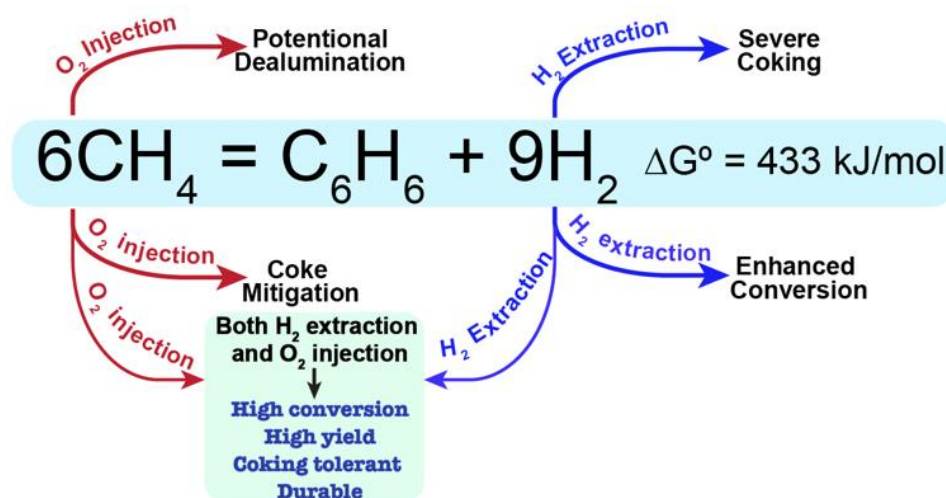


Figure 2.19. Impacts of H₂ extraction and O₂ injection on methane aromatization.

In summary, either hydrogen extraction or oxygen injection exhibits both beneficial and detrimental impacts, which are summarized in Figure 2.19, implying the challenges of methane aromatization cannot be solely addressed via hydrogen extraction or oxygen injection. As depicted in Figure 2.19, it is expected that the integration of hydrogen extraction with oxygen injection could potentially address all issues of low conversion, low yield, and poor durability. Thanks to the unique defect chemistry and transport properties of the protonic ceramic electrolyte (e.g., $\text{BaCe}_x\text{Zr}_y\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$, $x+y=0.8$), simultaneous hydrogen extraction and oxygen injection can be easily achieved in PCECs.

Chapter 3 – Lowering the operating temperature of PCECs to <450

°C

3.1 Abstract

Protonic ceramic electrochemical cells (PCECs) can be employed for power generation and sustainable hydrogen production. Lowering the PCEC operating temperature can facilitate its scaleup and commercialization. However, achieving high energy efficiency and long-term durability at low operating temperatures is a long-standing challenge. Herein, we report a simple and scalable approach for fabricating ultrathin, chemically homogeneous, and robust proton-conducting electrolytes and demonstrate an in-situ formed composite positive electrode, $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}\text{-Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$, which significantly reduces ohmic resistance, positive electrode-electrolyte contact resistance, and electrode polarization resistance. The PCECs attain high power densities in fuel cell mode ($\sim 0.75 \text{ W cm}^{-2}$ at 450 °C and $\sim 0.10 \text{ W cm}^{-2}$ at 275 °C) and exceptional current densities in steam electrolysis mode (-1.28 A cm^{-2} at 1.4 V and 450 °C). At 600 °C, the PCECs achieve a power density of $\sim 2 \text{ W cm}^{-2}$. Additionally, we demonstrate the direct utilization of methane and ammonia for power generation at <450 °C. Our PCECs are also stable for power generation and hydrogen production at 400 °C.

3.2 Introduction

Ceramic electrochemical cells based on both oxygen-ion conductors and proton-conducting oxides have been demonstrated for efficient power generation and green hydrogen production^{31,99-101}. Ceramic electrochemical cells have key merits, including fuel flexibility in fuel cell mode and higher energy efficiency in steam electrolysis mode compared to low-temperature polymer electrolyte membrane electrochemical cells^{55,102-104}. However, the scaleup and commercialization of ceramic electrochemical cells have lagged behind those of polymer electrolyte membrane electrochemical cells, which is mainly ascribed to the high operating temperature of ceramic electrochemical cells ($>500\text{ }^{\circ}\text{C}$)¹⁰⁵. Therefore, creating low-temperature ceramic electrochemical cells has been one of the primary challenges and opportunities in this research field (Supplementary Figure 1).

The operating temperature of solid oxide electrochemical cells based on oxygen-ion conductors (O-SOECs) has been successfully reduced to $\sim 500\text{ }^{\circ}\text{C}$ ^{3,106-109}. However, due to the relatively high activation energy of oxygen-ion conduction, reducing the operating temperature of O-SOECs to $<450\text{ }^{\circ}\text{C}$ is challenging^{3,110,111}. Due to proton conduction having a lower activation energy than oxygen-ion conduction, protonic ceramic electrochemical cells (PCECs) have been recurrently researched and proposed to operate at $<450\text{ }^{\circ}\text{C}$ ^{11,112}.

Only a handful of studies have reported that PCECs can operate at $<450\text{ }^{\circ}\text{C}$ ^{11,27,112,113}. Depositing a dense interfacial layer between the electrolyte and positive electrode can reduce the ohmic resistance and increase the peak power density (PPD) to 0.36 W cm^{-2} on H_2 -air at $450\text{ }^{\circ}\text{C}$ ²⁷. To reduce the electrode polarization resistance, a highly porous $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$ (PBSCF-1) positive electrode using a template-assisted method, which improved the mass transport kinetics, leading to a PPD of 0.41 W cm^{-2} on H_2 - O_2 at $400\text{ }^{\circ}\text{C}$ ¹¹³. A recent study reported

that employing an acid-etched electrolyte and a positive electrode fabricated via this template method further increased the PPD to 0.65 W cm^{-2} on $\text{H}_2\text{-O}_2$ at 450°C ¹¹². Furthermore, most of these approaches that have been validated are either complicated or unscalable. Therefore, it is urgent to demonstrate straightforward and scalable methods to fabricate PCECs with low-resistance electrolytes and active positive electrodes to achieve good PCEC performance at $<450^\circ\text{C}$.

Supplementary Figure 2 shows a PCEC ohmic conductivity analysis, estimated by dividing the electrolyte thickness by the ohmic area specific resistance (ASR_O). There is a discrepancy between intrinsic electrolyte conductivity and PCEC ohmic conductivity, implying that PCEC devices contribute additional ohmic resistance, mainly high electrolyte-grain boundary resistance and positive electrode-electrolyte contact resistance. Therefore, PCECs should be better fabricated to optimize their microstructure, aiming to minimize grain boundary resistance while enhancing the bonding between the electrode and electrolyte, particularly the weakly bonded positive electrode-electrolyte interface created in a separated high-temperature step. Supplementary Figure 3 indicates that the electrode polarization area specific resistance (ASR_P) accounts for 70-90% of the total resistance at 450°C . Furthermore, it has been widely recognized that the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), which occur at the positive electrode, tend to be more sluggish with decreasing operating temperatures. These results suggest that both the electrolyte and positive electrode should be optimized to enhance PCEC performance at $<450^\circ\text{C}$.

Herein, we report approaches for overcoming these challenges and fabricating high-performance low-temperature ($<450^\circ\text{C}$) PCECs (LT-PCECs). We demonstrate PCECs that achieve a high fuel cell power density of $\sim 0.75 \text{ W cm}^{-2}$ at 450°C . At an operating temperature of

as low as 275 °C, a practical power density of $\sim 0.10 \text{ W cm}^{-2}$ is achieved. Moreover, at 1.4 V and 450 °C, our PCECs attain a promising current density of -1.28 A cm^{-2} in steam electrolysis mode. Furthermore, durable operation at 400 °C in both fuel cell and electrolysis modes are demonstrated.

3.3 Materials and Methods

3.3.1 PCECs powder synthesis

Negative electrode powder with low Ba deficiency. The negative electrode powder was composed of $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb7111), NiO, and corn starch in a weight ratio of 2:3:1. The solid-state sintering (SSS) with a fast heating rate of 10 °C/min was employed to prepare the BCZYYb7111 powder¹⁰⁰. 1 wt% NiO was added to BCZYYb7111 as the sintering aid. In brief, a stoichiometric amount of BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 , Yb_2O_3 , and NiO was first ethanol ball-milled together for 48 h. The mixture was dried at 120 °C for 24 h and then calcined at 1350 °C for 5 h in air, which was then crushed into fine powder. Upon another round of ball milling, the as-synthesized BCZYYb7111 was then mixed and ball milled with NiO and corn starch for 48 h. After drying at 120 °C, the negative electrode powder with a low Ba deficiency was synthesized.

Negative electrode functional layer powder. The negative electrode functional layer powder was composed of 40 wt.% BCZYYb7111 and 60 wt.% NiO. The powder synthesis procedure was the same as that of the abovementioned negative electrode powder synthesis process. The only difference was that no corn starch was added.

$\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb4411) electrolyte powder. BCZYYb4411 was synthesized via a wet-chemistry method¹⁰ using Y_2O_3 , Yb_2O_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and zirconyl nitrate solution as the precursors. Briefly, the calculated amounts of Y_2O_3 and Yb_2O_3 were first dissolved in diluted nitric acid solution at 100 °C to synthesize yttrium and ytterbium nitrate solution. The $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, and zirconyl nitrate solution were mixed with the yttrium and ytterbium nitrate solution. After stirring for half of an hour, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were added to the above mixture. The mixture was stirred for 1 h to ensure complete complexation. Subsequently, the *pH* of the mixture was adjusted to ~9

with using an aqueous NH_4OH solution. The viscosity of the mixture gradually increased with heating it at $250\text{ }^\circ\text{C}$. Once a gel is formed, it was then dried at $175\text{ }^\circ\text{C}$ for 24 h in a drying oven, followed by calcining the powder at $1250\text{ }^\circ\text{C}$ for 5 h to obtain the BCZYYb4411 electrolyte powder.

In-situ formed positive electrode $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}+\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$ (BSC+PBSCF). The in-situ formed BSC+PBSCF positive electrode powder was synthesized via a wet-chemistry method¹⁰ with using Pr_6O_{11} , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ as the precursors. The dried gel was calcined at $600\text{ }^\circ\text{C}$ for 5 h in air, followed by ball-milling in ethanol for 1 day and then drying at $100\text{ }^\circ\text{C}$ for the following positive electrode ink preparation. Upon sintering at $765\text{ }^\circ\text{C}$, the calcined powder will be crystallized to BSC+PBSCF powder.

$\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{6-\delta}$ (PBSCF-1) positive electrode powder. The PBSCF-1 powder was synthesized via the same method as BSC+PBSCF. After obtaining the powder calcined at $600\text{ }^\circ\text{C}$, the powder will be subsequently sintered at $950\text{ }^\circ\text{C}$ and crystallized to PBSCF-1.

3.3.2 PCECs ink and device fabrication

BCZYYb4411 electrolyte ink. BCZYYb4411 electrolyte powder was mixed and ball milled with 1 wt. %NiO (sintering aid), di-n-butyl phthalate, fish oil, b-98 polyvinyl butyral, and ethanol to prepare the electrolyte ink. The ball milling process took four days. The particle size distribution of the electrolyte powder in ink was evaluated using a Malvern Zetasizer Nano S. The obtained data were analyzed utilizing the Mie theory¹¹⁴.

PBSCF-1 and BSC+PBSCF slurry preparation. To prepare positive electrode slurry, a mixture of 5 g PBSCF-1 or BSC+PBSCF powder, 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved

in α -terpinol), and 1 g dispersant (20 wt.% solspers 28000 (Lubrizol) dissolved in α -terpinol) were manually ground using a mortar and pestle. The same recipe and process were also used to prepare the SDC-Ni-Ru catalyst slurry and BSC slurry, which were used for MSR and ECR testing, respectively.

Negative electrode tape casting ink preparation. The negative electrode powder was mixed with and ball milled with cyclohexanone, menhaden fish oil, polyethylene glycol 400, b-98 polyvinyl butyral, di-n-butyl phthalate, xylenes, and ethanol. The ball milling process took two days.

Negative electrode functional layer tape casting ink preparation. Similarly, the negative electrode functional layer ink was also prepared by mixing and ball-milling BCZYYb7111 + NiO and the above organic materials and ethanol. Supplementary Table 6 provides detailed information about the chemicals and materials used in this work.

3.3.3 PCECs manufacturing and testing

PCEC half-cell fabrication. PCEC half-cells were fabricated with a combination of tape casting and spray coating. The negative electrodes substrates, which are composed of negative electrode functional layer and negative electrode support layer, were prepared via two-layers tape casting. The obtained two layers were dried at room temperature and pre-sintered at 800 °C for debinding.

A lab-scale ultrasonic coating system (Siansonic, model: UC330) was used to fabricate the ultrathin (quasi two dimensional), chemically homogeneous, and robust proton-conducting electrolyte. The coating time, spray spot size, coating speed, ultrasonic power, and substrate

temperature were optimized to achieve the desired electrolyte thickness and density. The obtained PCECs were co-sintered at 1450 °C for 5 h to fabricate the PCEC half-cells.

Current collection and single-cell testing. MO·SCI glass sealant (OL-GL1709P/-45) was used to seal PCECs. Gold paste was first applied to both electrodes. To enhance current collection, a silver grid was then affixed on the gold paste. The thermocouple was inserted into the reactor near the PCECs, to ensure accurate temperature readings. Upon sealing the PCECs on an alumina tube, the negative electrodes (anode in the fuel cell mode; cathode in the electrolysis mode) of all PCECs were first reduced under H₂ (20 sccm) at 600 °C for 20 min. In this work, the heating/cooling rate was set as 4 °C/min. At each testing temperature, before collecting the results, the cells were held for 15 min to ensure that the PCECs achieved a steady state. The effective electrode area of all PCECs was 0.5 cm². A Princeton Applied Research potentiostat with multiple channels was used to conduct all electrochemical measurements. All the cells tested in this work were numbered; detailed information can be found in Supplementary Table 7.

PCECs with PBSCF-1 positive electrodes. The PBSCF-1 ink was first brush-painted on the electrolyte side and then fired at 950 °C for 5 h to obtain the PBSCF-1 positive electrode. After sealing the cell according to the abovementioned process, the PCEC temperature was increased to 765 °C to melt the sealing glass (OL-GL1709P/-45). The PCEC temperature was then reduced to 600 °C for performing electrochemical measurements. Hydrogen was used as the fuel, and air was used as the oxidant, with flow rates of 80 sccm and 200 sccm, respectively.

PCECs with in-situ formed BSC+PBSCF positive electrodes. After brush-painting the BSC+PBSCF ink on the electrolyte, the PCEC single-cell was then directly sealed on the alumina tube without presintering the positive electrode. The PCEC temperature was first increased to 765 °C to melt the sealing glass (OL-GL1709P/-45), whereby BSC+PBSCF was simultaneously

obtained. The PCEC performance was evaluated at temperatures ranging from 600 °C to 300 °C. Air or O₂ with a flow rate of 200 sccm was fed to the positive electrode as the gas stream. To evaluate the PCEC fuel-cell performance on hydrogen, a hydrogen stream with a flow rate of 80 sccm was fed to the negative electrode. To determine the PCEC fuel-cell performance using ammonia as the fuel, the ammonia flow rate, which was set as 40 sccm at 600 °C, 35 sccm at 550 °C, 30 sccm at 500 °C, 25 sccm at 450 °C, 20 sccm at 400 °C, and 10 sccm at 400 °C. To test the PCEC fuel-cell performance on methane, the SDC-Ni-Ru ink was brush-painted on the negative electrode as a catalytic reforming layer. A mixture of methane with steam at a methane-to-steam ratio of 1:1 was fed to the negative electrode. Herein, the CH₄ flow rate was set as 16 sccm at 500 °C, 12 sccm at 450 °C, and 8 sccm at 400 °C.

The SMR catalytic activities of Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-δ}, Sm_{0.2}Ce_{0.7}Ni_{0.15}O_{2-δ}, and Sm_{0.2}Ce_{0.7}Ru_{0.15}O_{2-δ} were first evaluated in packed bed reactors. A total of 120 mg of each catalyst was loaded into a quartz tubular reactor with an inner diameter of 0.28 inches at 1 atm. The catalyst was reduced under 20% H₂ at 600 °C for 30 mins. The reactor temperature was then lowered to 500 °C, and a mixture of CH₄ and steam was fed to the reactor. The CH₄ flow rate is 15 sccm and the steam-to-carbon (S/C) ratio is 1:1. An INFICON 3000 Micro GC was used to measure the outlet gas compositions at each steady-state operating temperature. The CH₄ conversion (X_{CH_4}) was calculated as equation (1):

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (1)$$

where F_{in} and F_{out} represent the flow rate of inlet gas or outlet gas, respectively.

To evaluate the PCEC electrolysis performance for hydrogen production, a mixture of steam and nitrogen was supplied to the positive electrode with a steam concentration of 40%. Pure hydrogen gas (15 sccm) was fed to the negative electrode as the sweep gas. To evaluate the FE

(%), the negative electrode outlet gas was mixed with a nitrogen gas stream, which was then injected into an online gas chromatograph (INFICON 3000 Micro GC) to quantify the hydrogen production rate (Supplementary Note 4). The *FE* (%) was calculated using equation (2):

$$FE (\%) = \frac{n_{H_2, measured}}{n_{H_2, theoretical}} = \frac{n_{H_2, measured} \times (n \times F)}{I} \times 100\% \quad (2)$$

where *FE* (%) is the Faradaic efficiency at different current densities, $n_{H_2, measured}$ is the measured hydrogen production rate (mol/s), n is 2, F is the Faradaic constant (96485 C mol⁻¹), and I is the applied current (A).

The electrolysis energy efficiency, *EEE* (%), was calculated based on the lower heating value of H₂ (LHV), according to the equation (3):

$$EEE (\%) = \frac{\Delta H_{H_2, LHV} \times n_{H_2, measured}}{I \times V} = \frac{n_{H_2, measured} \times (n \times F)}{I \times V} \times 100\% \quad (3)$$

where *EEE* (%) is the LHV *EEE* of PCECs, $\Delta H_{H_2, LHV}$ is the LHV reaction enthalpy for steam electrolysis with a value of 241.8 kJ mol⁻¹, $n_{H_2, measured}$ is the molar production rate of hydrogen (mol s⁻¹), I is the applied current (A), V is the corresponding voltage (V), and F is the Faradaic constant (96485 A s mol⁻¹)

Peeling strength testing. The peeling strength of the positive electrodes (BSC+PBSCF and PBSCF-1) was measured according to the ASTM D903 180-degree peeling strength testing standard. PCEC full cells with different positive electrodes were tested under the same testing conditions. Briefly, the specimen was placed in the peeling strength test machine by fixing the negative electrode using heavy-duty double-sided tape. One end of a piece of rectangular tape was stuck on the positive electrode, while the other end was fixed to the peeling strength testing machine. The tape was then pulled back according to the ASTM D903 180-degree peeling strength testing standard, and the real-time applied force was measured.

Dilatometry testing. The dilatometry experiments were carried out using the Netzsch DIL 402 Expedit instrument to determine the linear thermal expansion profiles of the positive electrode samples. Cylindrical samples were used in this experiment. Briefly, 0.6 g of each sample powder was first dry pressed by using a carbonized stainless-steel die set under a pressure of 50 bar for 1 min, producing a green cylinder. The cylinders were then sintered in air to get the desired sample composition (BSC+PBSCF cylinder was calcined at 765 °C for 5 min; PBSCF-1 cylinder was calcined at 950 °C for 5 h). The linear thermal expansion profiles of the samples were measured using a heating and cooling rate of 10 °C/min. The dilatometer was calibrated and corrected for each measurement.

BCZYYb4411 electrolyte pellet conductivity testing. The conductivity of PCEC electrolytes was measured by using the EIS and a comprehensive analysis of the EIS spectra was performed to determine the grain bulk and grain boundary conductivity. BCZYYb4411 powder was subjected to uniaxial dry pressing to form a 20 mm diameter pellet at a pressure of 150 bar, which was then sintered for 5 hours at 1450 °C. The resulting pellet was polished with sandpaper to attain a flat surface with a thickness of ~1 mm. Platinum (Pt) paste was applied on both sides of the pellet (with an effective area of 0.5 cm²) as the current collector via brush painting, which was then calcined at 350 °C for 30 minutes. The ohmic resistance of this BCZYYb4411 electrolyte pellets was measured by performing EIS under a humidified argon atmosphere (3% steam) from 500 to 250 °C. Before each measurement, the pellet was held at each temperature for approximately 1 hour to achieve a steady state.

The EIS spectra were collected using a Gamry 1010 interface. The obtained impedance spectra were then analyzed using Zview software to separate and analyze the bulk and grain

boundary resistances. The “brick layer model”^{115,116} was used to calculate the bulk and grain boundary conductivities.

Electrical conductivity relaxation (ECR) testing. Two samples were prepared for the ECR testing, which include PBSCF-1 and PBSCF-2 coated with BSC. The PBSCF-1 powder was first axially pressed at 100 bar for 2 min using a 2 cm (diameter) die, followed by sintering at 1250 °C for 3 h to densify the pellets. A bar was prepared using a high-precision diamond saw. For comparison, PBSCF-2 was also prepared with the same procedure. BSC was then uniformly coated on PBSCF-2 bar, followed by sintering at 1000 °C for 2 h. ECR measurement was conducted at 700 °C, 650 °C, 600 °C, 550 °C, and 500 °C. At each temperature, the oxygen concentration was initially set as 2 vol.% (10 sccm O₂ + 490 sccm Ar). ECR was measured via a four-probe method with a current of 40 mA. Once the voltage reached equilibrium, the oxygen concentration was immediately changed from 2 vol.% to 20 vol.%. The voltage response was recorded. The relative conductivity change data was calculated using the NETL ECR analysis tool ¹¹⁷, which determines the surface exchange coefficient (k_{chem}) and bulk diffusion coefficient (D_{chem}).

3.3.4 Structural characterizations

The crystal structure of all prepared materials was analyzed using a Rigaku MiniFlex X-ray diffractor (XRD) with a scan rate of 1°/min. The morphology, microstructure, and chemical composition of BSC+PBSCF were examined using transmission electron microscopy (TEM, FEI Tecnai Osiris 200 Kv S/TEM system and Talos F200X S/TEM system operated at 200 kV, equipped with an FEG (field emission gun) cathode and four in-column Super-X energy dispersive X-ray spectrometer (EDS) detectors. The microstructure of the PCECs was examined by using scanning electron microscopy (Hitachi/S-3400 N). Nitrogen Brunauer–Emmett–Teller (BET)

surface area analysis and O₂-temperature-programmed desorption (O₂-TPD) were conducted using a ChemBET Pulsar chemisorption analyser.

3.4 Results and discussion

3.4.1 Strategies to validate PCECs running at <450 °C

To validate PCECs that can run at <450 °C, LT-PCECs with ultrathin, bamboo-structured (single-grain thick), and chemically homogeneous electrolytes were first fabricated via a scalable and cost-effective ultrasonic spray-coating process, which minimizes the resistance of proton conduction across the grain boundary (Supplementary Figure 4), reducing the ASR_O attributed to the electrolyte (Figure 3.1a). Second, we demonstrate an *in-situ* formed positive electrode composed of $Ba_{0.62}Sr_{0.38}CoO_{3-\delta}$ - $Pr_{1.44}Ba_{0.11}Sr_{0.45}Co_{1.32}Fe_{0.68}O_{6-\delta}$ (BSC+PBSCF). This positive electrode reduces the coefficient of thermal expansion (CTE), improves the positive electrode-electrolyte bonding, and reduces the contact resistance, further reducing the ASR_O . Additionally, this positive electrode simultaneously facilitates the surface oxygen exchange and bulk oxygen-ion diffusion, particularly at low operating temperatures, which significantly decreases the ASR_P (Figure 3.1b), allowing a low ASR_P of $0.38 \Omega \text{ cm}^2$ to be achieved at 450 °C [versus the $0.76 \Omega \text{ cm}^2$ ASR_P of the state-of-the-art positive electrode]. The LT-PCECs with low-resistance electrolytes and the positive electrodes developed in this work exhibit remarkable performance at <450 °C (Figure 3.1c). For example, at 400 °C, a fuel cell PPD of $\sim 0.34 \text{ W cm}^{-2}$ is achieved using H_2 , which doubles the PPD of the current state-of-the-art PCECs. Figure 3.1d and Supplementary Table 1 show that LT-PCECs can produce hydrogen with a comparable or higher rate and electrolysis energy efficiency at 400 °C compared to previously reported PCECs that operate at >500 °C (Supplementary Video 1).

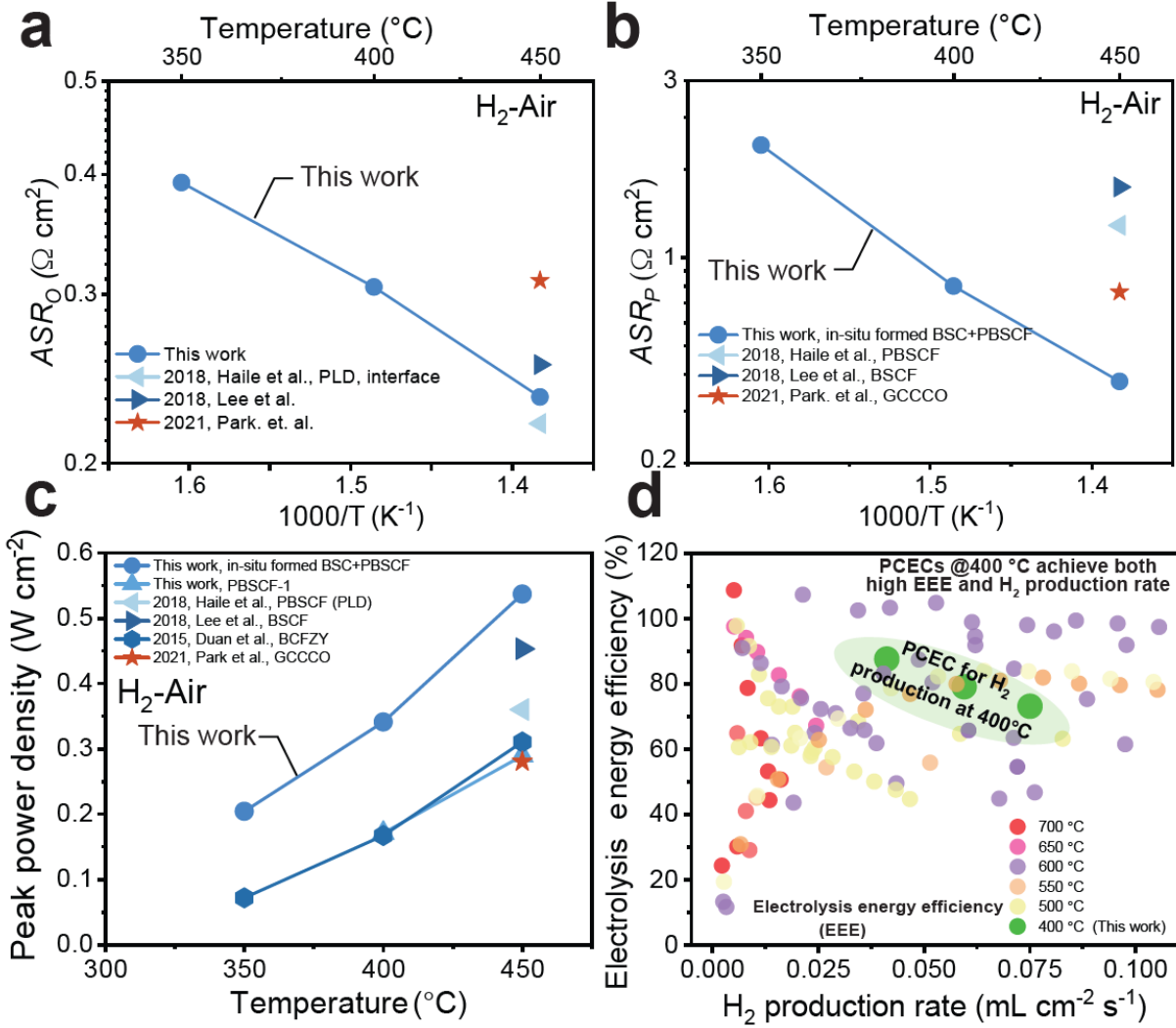


Figure 3.1. Lowering the operating temperature of PCECs to <450 $^{\circ}\text{C}$. (a) Comparison of ASR_O (This work, cell 1) of PCECs with the literature results. PCECs readily fabricated in this work achieve ASR_O that are comparable to the PCECs fabricated using the costly and complicated pulsed laser deposition (PLD) method. (b) Comparison of ASR_P of PCECs (This work, Cell 1) with the literature results. The developed positive electrode in this work leads to the lowest ASR_P . (c) Comparison of PCEC fuel cell peak power densities (Cell 1 and Cell 6) with literature results. (d) Comparison of PCEC energy efficiency in electrolysis mode (as a function of H_2 production rate) with the literature results at 400-700 $^{\circ}\text{C}$ (Cell 2). This work has demonstrated PCECs for hydrogen production at 400 $^{\circ}\text{C}$, which achieve comparable or higher electrolysis energy efficiency and hydrogen production rate than previous PCECs operated at >500 $^{\circ}\text{C}$. 2018 Haile et. al., PBSCF (PLD)²⁷; 2018, Lee et. al., BSCF¹¹⁸; 2015 Duan et. al., BCFZY¹¹; 2021 Park et. al., GCCCO¹¹⁹.

3.4.2 Readily fabricated ultrathin proton-conducting electrolyte

Poor sinterability and Ba evaporation are two main challenges associated with proton-conducting electrolyte fabrications¹²⁰. It is also well known that the grain boundary is less conductive than the grain bulk (Supplementary Figure 5)^{115,116}. Therefore, fabricating PCECs with ultrathin, large-grain, and chemically homogeneous electrolytes is one of the most essential steps for realizing high performance. Herein, we employed an ultrasonic spray coating system to coat electrolyte on the negative electrode (Figure 3.2a and Supplementary Note 1, which is scalable and reproducible (Supplementary Video 2). Additionally, high-quality PCECs with relatively large areas have been fabricated using the ultrasonic spray coating system, which yields dense and defect-free PCEC electrolytes with a uniform thickness of $\sim 3.5\ \mu\text{m}$, further validating the feasibility of employing this process for large-scale PCEC manufacturing (Supplementary Figures 6-11, Supplementary Video 3). Furthermore, the ultrasonic spray coating improves the PCEC electrolyte microstructure and conductivity compared to the traditional compressed air spray coater (Supplementary Figures 12-13).

The SEM images of the electrolyte cross-section show that the electrolyte layer is dense, with a uniform thickness of $\sim 3\ \mu\text{m}$ (Figure 3.2b). Figure 3.2b and Supplementary Figure 4a show that the electrolyte exhibits a bamboo structure, leading to a low ASR_o . PCECs manufactured via this simple coating and co-sintering process are reproducible (Supplementary Figure 14). Figure 3.2c shows the electrolyte surface has an average grain size of $\sim 8\ \mu\text{m}$, much larger than the electrolyte thickness ($\sim 3\ \mu\text{m}$). Therefore, the PCEC obtained via this process has a quasi-2D electrolyte, which exhibits a low grain boundary area and reduces ASR_o (Figure 3.2d).

The high-angle annular dark field (HAADF) image (Figure 3.2e) also displays that the ultrathin electrolyte layer exhibits a bamboo structure where the grain boundaries appear

perpendicular to the negative electrode. Moreover, the energy dispersive X-ray spectroscopy (EDS) line scanning profile (Figure 3.2f) and mapping images (Figures 3.2g and 3.2h) at both the microscale and nanoscale indicate that this thin electrolyte layer is chemically homogeneous. No element segregation or depletion was observed across the electrolyte or at the grain boundary. The EDS line scanning profile (Supplementary Figure 15) across the electrolyte also shows a homogeneous elemental distribution, implying that the chemical composition is consistent throughout the electrolyte. Element segregation at the grain boundary can lead to a positive potential, which decreases proton conduction^{121,122}. Figures 3.2h and 3.2i show that the chemical composition of the grain boundary appears to be homogenous within the bulk at the nanoscale, which is beneficial for high proton conductivity. The PCECs fabricated in this work achieved an ASR_O that is comparable to that of PCECs fabricated via costly and complicated PLD (Figure 3.1a).

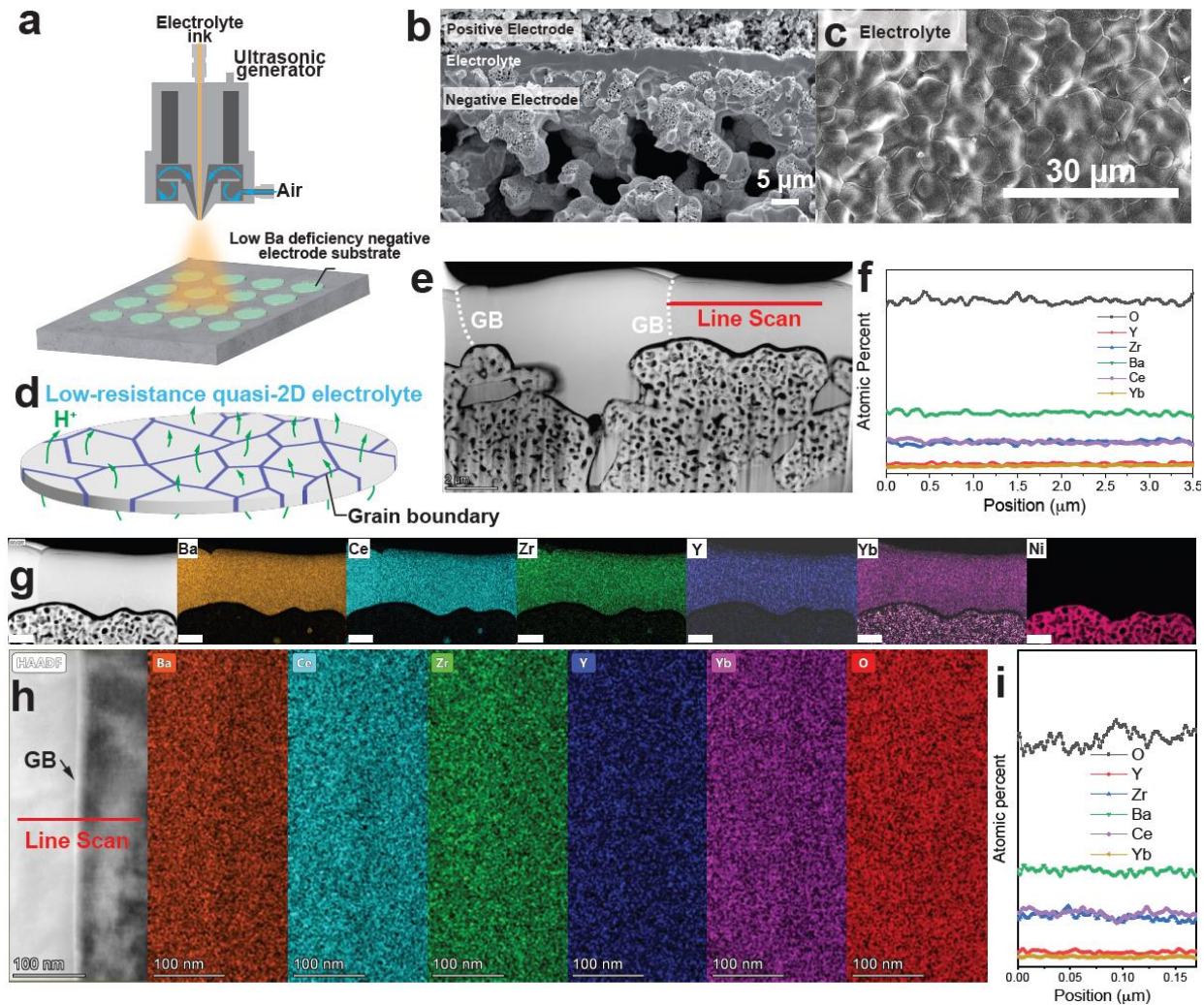


Figure 3.2. Readily fabricated ultrathin proton-conducting electrolyte using ultrasonic spray coating and negative electrode with low Ba deficiency. (a) Schematic illustration of the ultrasonic spray coating process for applying electrolyte. (b) The cross-section SEM image of PCEC full cell, which shows an ultrathin ($\sim 3 \mu\text{m}$), dense, and bamboo-structured electrolyte layer can be fabricated via ultrasonic spray coating (Cell 2). (c) The SEM image of PCEC electrolyte surface, which displays an average grain size of $8 \mu\text{m}$ (Cell 3). (d) An illustration of the ultrathin ($\sim 3 \mu\text{m}$), dense, and bamboo-structured electrolyte layer, which shows the quasi-2D feature. The grain size is much bigger than the thickness, which could be considered as a quasi-2D electrolyte. The proton flux (green arrows) does not cross grain boundaries, reducing the ASR_O . (e) High-angle annular dark field (HAADF) image of the electrolyte and anode. GB: grain boundary. (f) Energy-dispersive X-ray spectroscopy (EDS) line scan profile along the red line shown in (e). (g) HAADF image and EDS mapping for constituent cations at the microscale, which include Ba, Ce, Zr, Y, Yb, and Ni. The scale bar is $1 \mu\text{m}$. (h) HAADF image of an electrolyte grain boundary at the nanoscale and the corresponding EDS mapping for constituent elements, including Ba, Ce, Zr, Y, Yb, and O. (i) EDS line scan profile along the red line shown in (h). The results from (e)-(i) are based on Cell 4.

3.4.3 Reduced ASR_p with in-situ formed positive electrode

Many positive electrode materials and advanced electrode processing techniques have been demonstrated to enhance the electrocatalytic activity of positive electrodes and reduce ASR_p ^{11,31,46-48,119,123-125}. However, one of the state-of-the-art positive electrodes, $Gd_{0.3}Ca_{2.7}Co_{3.82}Cu_{0.18}O_{9-\delta}$, exhibited an ASR_p of $>0.7 \Omega \text{ cm}^2$ on H_2 -air at 450°C ¹¹⁹. The target of this study was to reduce the ASR_p to $<0.4 \Omega \text{ cm}^2$ at 450°C , which would further improve the PCEC performance at $<450^\circ\text{C}$. Herein, we aimed to develop an in-situ formed composite positive electrode (BSC+PBSCF) composed of a perovskite phase ($Pr_{1.44}Ba_{0.11}Sr_{0.45}Co_{1.32}Fe_{0.68}O_{6-\delta}$, PBSCF-2) and $Ba_{0.62}Sr_{0.38}CoO_{3-\delta}$ (BSC) nanoparticles dispersed on (or mixed with) the perovskite phase to reduce the ASR_p . This composite positive electrode is denoted as in-situ formed BSC+PBSCF (or BSC+PBSCF). The XRD Rietveld refinement results (Figure 3.3a and Supplementary Table 2) confirm that BSC+PBSCF consists of a PBSCF-2 phase (space group: P4/mmm, 69.4 wt. %, $a=b=3.83 \text{ \AA}$; $c=7.72 \text{ \AA}$) and a BSC phase (space group: P63/mmc, 30.6 wt. %, $a=b=5.56 \text{ \AA}$; $c=4.75 \text{ \AA}$).

analysis of EDS results also confirms the weight percent of BSC phase is ~30.0 wt. % and PBSCF-2 is ~70.0 wt. %, which is consistent with the XRD refinement results.

Transmission electron microscopy (TEM) and EDS were performed to further determine the microstructure, crystal structure, and composition of BSC+PBSCF. As displayed in Figure 3.3b, BSC+PBSCF exhibits a particle size of ~20-40 nm. The high-resolution TEM (HR-TEM) images shown in Figure 3.3c confirm that BSC+PBSCF is composed of two fully crystallized phases, PBSCF-2 and BSC. Four main lattice planes with interplanar distances of 0.199 nm, 0.270 nm, 0.340 nm, and 0.283 nm were observed, which corresponded to PBSCF-2 (200), PBSCF-2 (102), BSC (101), and BSC (110), respectively. The d-spacings determined by TEM are consistent with those calculated using the XRD refinement results (Supplementary Table 2), affirming that the chemical compositions used for XRD refinement are reliable. Additionally, the EDS mapping images show that the BSC phase is Ba-rich and contains a negligible amount of Pr and Fe (Figure 3.3d). Both PBSCF-2 and BSC contain high amounts of Sr and Co. Therefore, the region where Ba is sparse, whereas Pr and Fe are abundant, is assumed to be the PBSCF-2 phase (Figure 3.3d). Moreover, the areas that contain Ba, Sr, and Co but not Pr and Fe are assumed to be the BSC phase. The EDS spectra shown in Figure 3.3e indicate the composition of PBSCF-2 is close to $\text{Pr}_{1.44}\text{Ba}_{0.11}\text{Sr}_{0.45}\text{Co}_{1.32}\text{Fe}_{0.68}\text{O}_{6-\delta}$, while that of BSC is identified as $\text{Ba}_{0.62}\text{Sr}_{0.38}\text{CoO}_{3-\delta}$ (Supplementary Table 3). The stoichiometries of these two phases were then used for the XRD refinement shown in Figure 3.3a. Additionally, according to the mole balance of Pr and the EDS results (Figures 3.3c-3.3e and Supplementary Table 3), it was determined that BSC+PBSCF contains ~30.0 wt. % BSC and ~70.0 wt.% PBSCF-2, consistent with the results obtained from the XRD refinement (~30.6 wt. % BSC and ~69.4 wt.% PBSCF-2), affirming that the stoichiometries

and chemical compositions are valid. Additional TEM and EDS mapping images shown in Supplementary Figures 16-17 further affirm the composition of BSC+PBSCF.

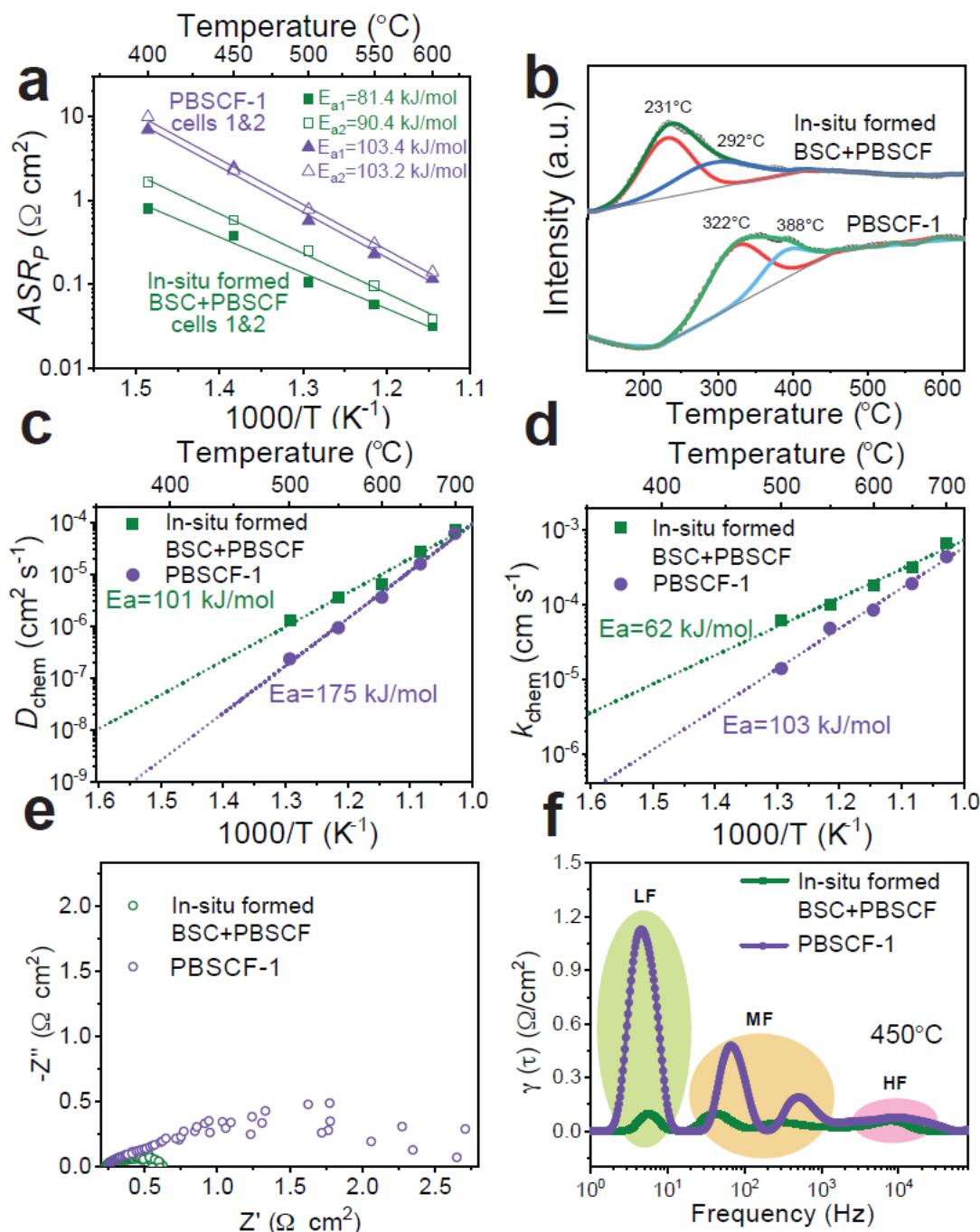


Figure 3.4. In-situ formed BSC+PBSCF positive electrode reduces ASR_P . (a) The area-specific electrode polarization resistance (ASR_P) of PCECs equipped with BSC+PBSCF and PBSCF-1 positive electrodes under OCV conditions (Cell 1, Cell 5, Cell 6, and Cell 7). (b) O₂-TPD profiles of BSC+PBSCF and PBSCF-1. (c) Bulk oxygen-ion diffusion coefficient (D_{chem}) of BSC+PBSCF

and PBSCF-1 as a function of operating temperature. (d) Surface oxygen exchange coefficient (k_{chem}) of BSC+PBSCF and PBSCF-1 as a function of operating temperature. (e) EIS spectra of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes, which were measured under OCV conditions at 450 °C (Cell 1 and Cell 6). H₂ was fed to the negative electrode and air was fed to the positive electrode. (f) Corresponding distribution of relaxation times (DRT) analysis of the EIS spectra shown in (e).

As presented in Figure 3.4a and Supplementary Figure 18, we determined the ASR_p , which clearly shows that BSC+PBSCF has an improved electrocatalytic activity. At 400 °C, the ASR_p of BSC+PBSCF is 1.1 $\Omega\text{ cm}^2$ (The 1st BSC+PBSCF cell), which is 15.9% of the ASR_p achieved with PBSCF-1 (6.9 $\Omega\text{ cm}^2$, the 1st PBSCF-1 cell). Additionally, the Arrhenius plots shown in Figure 3.4a indicate that BSC+PBSCF exhibits a smaller activation energy than PBSCF-1, suggesting that BSC+PBSCF can function as a promising positive electrode at lower operating temperatures. Oxygen temperature-programmed desorption (O₂-TPD) experiments were conducted to investigate the oxygen mobility and diffusion of BSC+PBSCF and PBSCF-1 (Figure 3.4b). Two main peaks were observed for both positive electrode materials, possibly due to the oxygen molecules adsorbed on the surfaces exhibiting different binding energies. The corresponding peak temperatures of BSC+PBSCF (231 °C and 292 °C) are lower than those of PBSCF-1 (322 °C and 388 °C), indicating that the surface oxygen on BSC+PBSCF is more easily released from the surface than that on PBSCF-1, which leads to enhanced oxygen surface oxygen exchange kinetics¹²⁶. Both surface oxygen exchange and bulk oxygen-ion diffusion kinetics are essential for high OER and ORR activities, which were determined by electrochemical conductivity relaxation (ECR) experiments (Figures 3.4c-3.4d and Supplementary Figures 19-20). Figure 3.4c shows that BSC+PBSCF has higher bulk oxygen-ion diffusion coefficients (D_{chem}) than PBSCF-1, suggesting that BSC+PBSCF has enhanced oxygen-ion diffusion in the bulk. Furthermore, the surface oxygen exchange coefficient (k_{chem}) of BSC-coated PBSCF-2 (BSC+PBSCF) is much higher than that of

PBSCF-1 (Figure 3.4d). At 550 °C, the k_{chem} of BSC+PBSCF is more than twice that of PBSCF-1, implying that the BSC phase is beneficial for accelerating the surface oxygen exchange kinetics. This is also consistent with the O₂-TPD profiles. Figures 3.4c and 3.4d show that the activation energies of BSC+PBSCF associated with D_{chem} and k_{chem} are both lower than those of PBSCF-1, further highlighting its promising activity at lowered operating temperatures. Therefore, the synergy between PBSCF-2 and BSC results in improved electrocatalytic activity, especially at <450 °C.

Figure 3.4e displays the electrochemical impedance spectroscopy (EIS) of PCECs with different positive electrodes collected at 450 °C under OCV conditions. With BSC+PBSCF applied as the positive electrode, the ASR_p is reduced by a factor of five. The corresponding distribution of relaxation time (DRT) analysis was then performed. As shown in Figure 3.4f, the DRT plots present distinct characteristics in three primary frequency regions, the low-frequency (LF, <100 Hz), intermediate-frequency (MF, 100-10000 Hz), and high-frequency (HF, >10000 Hz) regions, which correspond to oxygen mass transport, oxygen exchange on the positive electrode, and the charge transfer process, respectively^{50,127}. First, BSC+PBSCF exhibits smaller LF peaks, implying enhanced oxygen gas diffusion over BSC+PBSCF, which is attributed to the porous structure of the BSC+PBSCF electrode. The BET-measured surface area of BSC+PBSCF is 9.2 m²/g (Supplementary Figure 21 and Supplementary Table 4), which is ~2 times as high as that of PBSCF-1 (4.8 m²/g), agreeing well with the LF peak results. Second, the MF peaks, which are associated with the surface exchange processes, of BSC+PBSCF are also much smaller than those of PBSCF-1, further affirming that BSC+PBSCF has enhanced surface oxygen exchange kinetics, which is consistent with the ECR results (Figure 3.4d). Additionally, both BSC+PBSCF

and PBSCF-1 show similar HF peaks, which are smaller than the LF and MF peaks, indicating that the charge transfer processes on both electrodes are not rate-limiting steps.

Spin-polarized DFT calculations were performed to investigate bulk oxygen vacancy formation (ΔE_{Ov}) and oxygen diffusion in PBSCF-1, PBSCF-2, and BSC to understand the observed experimental behaviors (Figure 3.5, Supplementary Note 2, Supplementary Table 5 and Supplementary Data 1). ΔE_{Ov} associated with Ov1 and Ov2 follow a decreasing order of PBSCF-1 > PBSCF-2 > BSC, indicating a gradual increase in the likelihood of oxygen vacancy formation. As shown in Figure 3.5a-3.5b, the oxygen atom located at the Ov2 site of PBSCF-1 is bonded with four Sr and two Co atoms, while the Ov1 site in PBSCF-1 and the Ov1 and Ov2 sites in PBSCF-2 are surrounded by four Sr, one Co, and one Fe atoms. Hence, based on DFT calculations, we can conclude that a higher concentration of Sr and a proper mixing of Fe help stabilize Ov and lower the oxygen vacancy formation energies. The chemical environment for Ov1 and Ov2 in the hexagonal BSC cell is different, in which they are surrounded by two Ba, two Sr, and two Co atoms (Figure 3.5c).

BSC+PBSCF displays a superior ORR performance owing to the higher oxygen diffusivity. As shown in Figure 3.5d, the energy barriers ($E_{a,bulk}$) exhibit a decreasing order of BSC (1.05 eV) > PBSCF-1 (0.88 eV) > PBSCF-2 (0.51 eV). The $E_{a,bulk}$ in PBSCF-2 is 0.37 eV lower than in PBSCF-1. The energy differences will have a meaningful impact on atomic oxygen diffusion and correlate very well with the measured diffusivities (Figure 3.4c).

Using the DFT results, we also attempted to understand the observed surface exchange rates (Figure 3.4d). It has been reported that¹²⁸ the oxygen surface exchange coefficient (k_{chem}) varies linearly against the bulk oxygen vacancy formation energy (ΔE_{Ov}). Furthermore, a lower

ΔE_{Ov} would indicate a higher k_{chem} . As such, the high k_{chem} observed in BSC can also be successfully explained based on the trends in the calculated oxygen vacancy formation energies.

Combining the trends in oxygen diffusivity and the surface exchange coefficients, a synergistic effect may be supported in the BSC+PBSCF system, in which the BSC top layer facilitates surface oxygen exchange. Then, PBSCF-2 enhances the bulk diffusions with low $E_{a,bulk}$, both owing to the promoted oxygen vacancy formations.

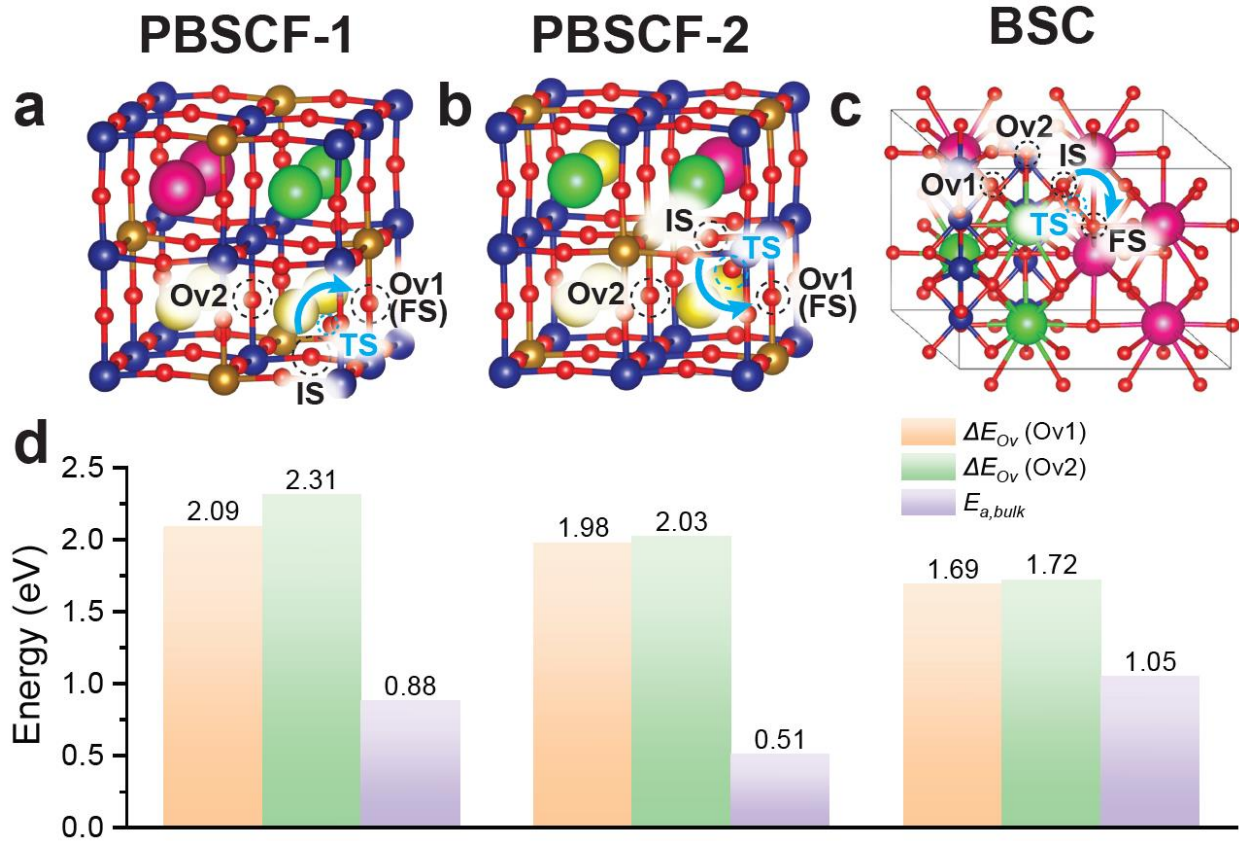


Figure 3.5. DFT calculations to study the bulk oxygen vacancy formation and oxygen diffusion of PBSCF-1, PBSCF-2 and BSC. Lattice structures of (a) PBSCF-1, (b) PBSCF-2 and (c) BSC. The Pr, Ba, Sr, Co, Fe, and O atoms are yellow, scarlet, green, blue, brown, and red, respectively. The most stable oxygen vacancy (Ov1) and the second stable vacancy (Ov2) sites are marked with black circles. The oxygen diffusions pathways are indicated by the arrows. The initial state (IS, black), final state (FS, black), and transition state (TS, blue) are also marked. The ΔE_{Ov} corresponding to Ov1 and Ov2 and $E_{a,bulk}$ are labeled and shown in (d).

3.4.4 Enhanced positive electrode-electrolyte interfacial bonding

Figure 3.6a presents the ASR_O of PCECs equipped with the developed BSC+PBSCF and PBSCF-1 positive electrodes, which indicates that BSC+PBSCF reduces the ohmic resistance. For example, the ASR_O of PCECs with BSC+PBSCF is reduced from $0.27 \Omega \text{ cm}^2$ to $0.17 \Omega \text{ cm}^2$ at 500°C (The 2nd BSC+PBSCF cell and the 2nd PBSCF-1 cell). The dilatometry results (Figure 3.6b) indicate that BSC+PBSCF positive electrode has a lower CTE ($18.0 \times 10^{-6} \text{ K}^{-1}$) than that of PBSCF-1 positive electrode ($23.4 \times 10^{-6} \text{ K}^{-1}$), which can improve the positive electrode-electrolyte compatibility and interfacial bonding. Additionally, the *in-situ* formed BSC+PBSCF achieves a much lower CTE than other Co-based positive electrodes reported in the literature (Supplementary Figure 22). Peeling strength testing was then conducted to quantify the positive electrode-electrolyte bonding strength and determine the coherence of the positive electrode-electrolyte interface (Figure 3.6c, Supplementary Figures 23 and 24). A more uniform and stronger peeling strength was obtained by using the BSC+PBSCF positive electrode, indicating that BSC+PBSCF leads to a positive electrode-electrolyte interface with improved chemical bonding and coherence, which reduces the positive electrode-electrolyte contact resistance and consequently decreases the ASR_O . As summarized in Figure 3.6d, the BSC+PBSCF positive electrode exhibits an average peeling strength of 6.8 N, 42% higher than that of the PBSCF-1 positive electrode (4.8 N). Therefore, the BSC+PBSCF positive electrode simultaneously improves the electrochemical performance and reduces the ohmic resistance at lower operating temperatures. Figure 3.6e displays the HAADF and EDS images of the positive electrode-electrolyte interface. At the interface, both BSC and PBSCF-2 were observed, which might enhance the chemical bonding of the positive electrode with the electrolyte, thus, reducing ASR_O .

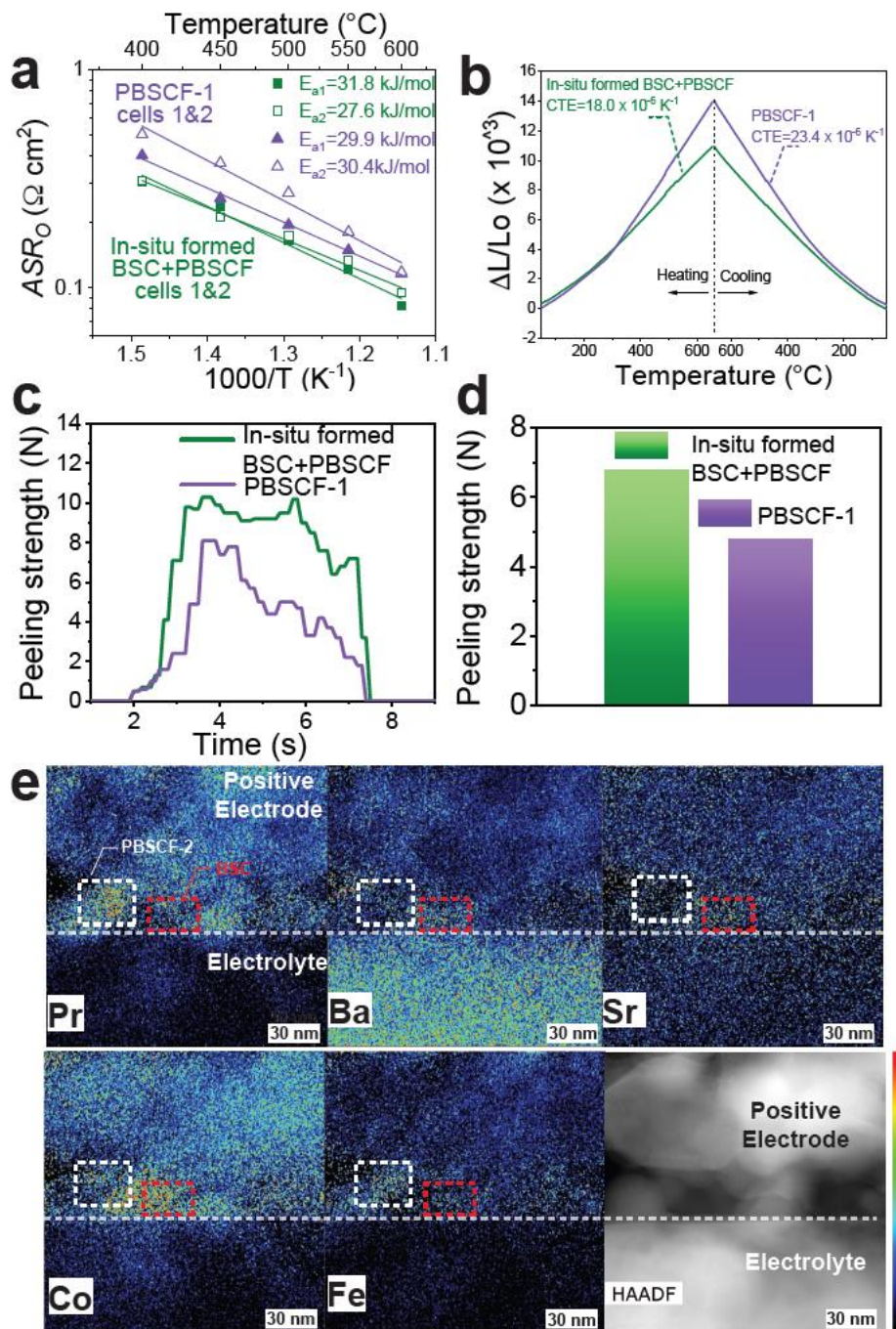


Figure 3.6. In-situ formed BSC+PBSCF reduces the positive electrode-electrolyte contact resistance. (a) The area-specific ohmic resistance (ASR_O) of PCECs equipped with BSC+PBSCF and PBSCF-1 positive electrodes (Cell 1, Cell 5, Cell 6, and Cell 7). (b) Linear thermal expansion profiles of positive electrodes as a function of temperature during heating and cooling, and the corresponding CTEs. (c) Representative peeling strength measurement profiles for BSC+PBSCF and PBSCF-1 positive electrodes (Cell 8 and Cell 9). (d) The average peeling strength of positive electrodes. The BSC+PBSCF positive electrode leads to a more coherent and stronger bonding with the electrolyte than PBSCF-1 (Cell 8 and Cell 9). (e) High-angle annular dark field (HAADF) image of the BSC+PBSCF positive electrode-electrolyte interface and the corresponding energy

dispersive X-ray spectroscopy (EDS) mapping images of Pr, Ba, Sr, Co, Fe, and O. The horizontal dashed line shows the positive electrode-electrolyte interface. The white dashed box shows the PBSCF-2 phase formed at the interface. The red dashed box shows the BSC phase formed at the interface. The scale bar in Figure 3.6e quantitatively shows the concentration of elements, where black indicates the lowest concentration while red displays the highest concentration. The results from (e) are based on Cell 10.

3.4.5 LT-PCEC electrochemical performance and long-term durability

Fabricating PCECs via tape-casting followed by an ultrasonic spray-coating process and employing the in-situ formed BSC+PBSCF as the positive electrode allowed the creation of high-performance PCECs operated at $<450\text{ }^{\circ}\text{C}$ (Supplementary Figure 25). The open-circuit voltages (OCVs) for all PCECs under fuel cell operation are higher than 1.05 V (Figures 3.7a-3.7b), indicating that the PCECs with an ultrathin and bamboo-structured electrolyte do not exhibit obvious electronic leakage or gas leakage. The created LT-PCECs achieve a much higher fuel cell performance than the PCECs with the PBSCF-1 positive electrode and literature results (Figure 3.1e, Figure 3.7c). With air fed to the positive electrode, a PPD of 1.64 W cm^{-2} is attained at $600\text{ }^{\circ}\text{C}$ (Figure 3.7a), greater than that of previously reported PCEC fuel cells in the literature^{11,27,118-120,125,129,130}. To compare these PCECs with the most recently developed PCECs¹¹², oxygen is fed to the positive electrode, achieving a PPD of $\sim 2.0\text{ W cm}^{-2}$ at $600\text{ }^{\circ}\text{C}$ (Supplementary Figures 26-27), which is higher than that of PCECs with acid-etched electrolytes and 3D positive electrodes¹¹² (Supplementary Figure 28). The PCECs also achieve remarkable performance at $<450\text{ }^{\circ}\text{C}$. For example, a PPD of $\sim 0.77\text{ W cm}^{-2}$ is reached at $450\text{ }^{\circ}\text{C}$ (Figure 3.7b). Additionally, at $450\text{ }^{\circ}\text{C}$, the BSC+PBSCF positive electrode facilitates an ~ 2.7 -fold increase in PPD compared to the PBSCF-1 positive electrode (0.77 W/cm^2 versus 0.29 W/cm^2 ; Figure 3.7c). This work also demonstrated that PCEC operated at $275\text{ }^{\circ}\text{C}$ delivers a practical fuel cell PPD of $\sim 0.1\text{ W cm}^{-2}$ on $\text{H}_2\text{-O}_2$ (Figure

3.7b). Several LT-PCECs were tested to validate the reproducibility (Figures 3.7a-3.7d and Supplementary Figures 29-36).

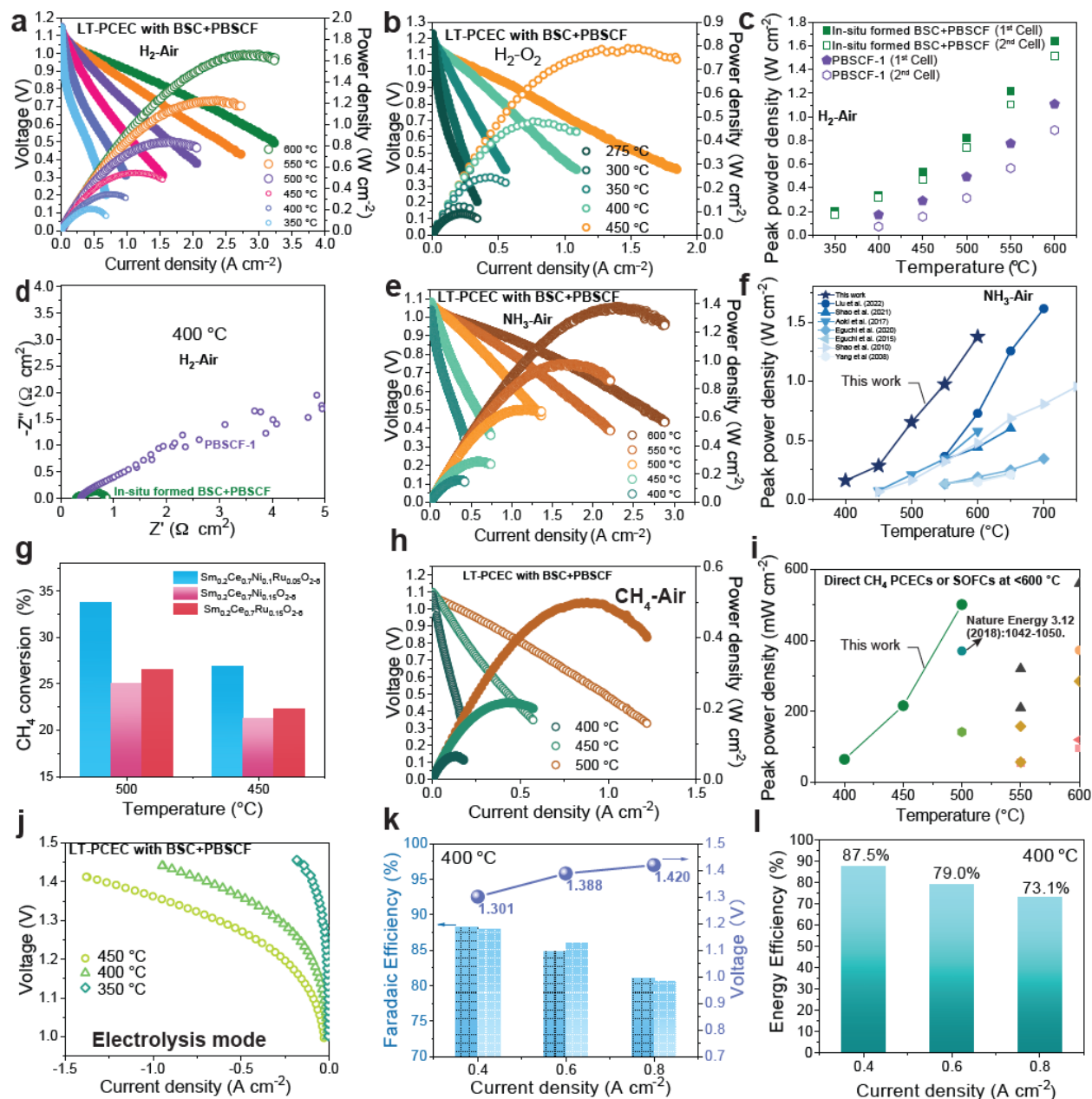


Figure 3.7. LT-PCECs attain exceptional fuel-cell and electrolysis performance. (a) I - V and I - P curves of a representative LT-PCEC at 350–600 °C. H_2 was fed to the negative electrode and air was fed to the positive electrode (Cell 1). (b) I - V and I - P curves of a representative LT-PCEC at 275–450 °C (Cell 11). H_2 was fed to the negative electrode and O_2 was fed to the positive electrode. (c) Comparison of fuel cell peak power densities (PPDs) of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes (Cell 1, Cell 5, Cell 6, and Cell 7). (d) EIS spectra of PCECs with BSC+PBSCF and PBSCF-1 as the positive electrodes, which were measured under OCV

conditions at 400 °C (Cell 5 and Cell 6). H₂ was fed to the negative electrode and air was fed to the positive electrode. (e) *I-V* and *I-P* curves of a representative LT-PCEC using ammonia as the fuel. (Our work: Cell 12) The LT-PCEC is equipped with BSC+PBSCF as the positive electrode. NH₃ was fed to the negative electrode and air was fed to the positive electrode. (f) Comparison of PCEC fuel-cell performance on ammonia with literature results¹³¹⁻¹³⁷ (Our work: Cell 12). (g) CH₄ conversion over three SMR catalysts, including Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-δ}, Sm_{0.2}Ce_{0.7}Ni_{0.15}O_{2-δ}, and Sm_{0.2}Ce_{0.7}Ru_{0.15}O_{2-δ}, which were tested in packed bed reactors. The steam-to-carbon ratio is 1:1. (h) *I-V* and *I-P* curves of a representative LT-PCEC on methane. (Our work: Cell 13). The LT-PCEC is equipped with BSC+PBSCF as the positive electrode. A mixture of methane and steam was fed to the negative electrode and air was fed to the positive electrode. The steam-to-carbon ratio is 1:1. (i) Comparison of PCEC fuel cell performance on methane with literature results^{11,15,138,139} (Our work: Cell 13). (j) Polarization curves of the LT-PCEC in electrolysis mode for hydrogen production at 350-450 °C (Cell 14). 40 vol.% H₂O + 60 vol.% N₂ was fed to the positive electrode. (k) Faradaic efficiency of LT-PCEC in electrolysis mode at 400 °C (Cell 2). At each current density, the FE% was measure twice. (l) Energy efficiency of LT-PCEC in electrolysis mode at 400 °C (Cell 2).

The PCECs operating at <450 °C also present good fuel flexibility. With ammonia fed to the anode, without using any additional ammonia cracking catalysts, the PCECs achieve PPDs of 0.65 W cm⁻² at 500 °C, 0.28 W cm⁻² at 450 °C, and 0.16 W cm⁻² at temperatures as low as 400°C (Figure 3.7e, Supplementary Figure 37). The direct-ammonia PCECs also attain outstanding performance at 600-500 °C, achieving a PPD of 1.38 W cm⁻² at 600 °C, which well exceeds the results reported in the literature (Figure 3.7f)¹³¹⁻¹³⁷. After conducting the performance evaluation under ammonia, there is no evidence of grain boundary fractures, indicating that the ultrathin electrolyte fabricated in this work is robust under ammonia (Supplementary Figure 37c). At 600 °C, the PCEC performance on ammonia is comparable to that on H₂ (Supplementary Figure 38), indicating that the negative electrode is active for ammonia cracking, which suggests that ammonia can serve as a H₂ carrier for power generation in PCECs.

PCECs can directly utilize methane for power generation. Herein, a rationally designed internal steam methane reforming (SMR) catalyst, Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-δ}, was coated on a PCEC negative electrode to further achieve high performance using methane as the fuel at low

operating temperatures. Its catalytic activity was first evaluated in a packed bed reactor, which indicates that the synergistic effect between Ni and Ru improves the SMR activity^{15,140}. For example, as shown in Figure 3.7g, $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_2$ achieves the highest CH_4 conversion at 500 °C, which is ~35% higher than that of $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$ and ~26% higher than that of $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$. At 450 °C, the CH_4 conversion achieved over $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_2$ reaches ~27%, suggesting that the PCEC equipped with this catalyst can deliver viable power density. At 500 °C, as shown in Figure 3.7h, we demonstrate a PPD of 0.55 W cm^{-2} on methane [versus, e.g., 0.37 W cm^{-2} at 500 °C for the state-of-the-art O-SOEC; Figure 3.7i], which approaches the PPD performance of PCECs on pure H_2 (Supplementary Figure 39). The PCEC fuel cell performance on methane shows that a viable PPD is still achieved at 400 °C. The LT-PCEC fuel-cell performance using both ammonia and methane validates the fuel flexibility of PCECs operating at <450 °C.

We also evaluated the PCECs for hydrogen production in electrolysis mode at <450 °C. Figure 3.7j shows the PCECs attain a current density of -1.28 A cm^{-2} at 1.4 V and 450 °C [versus, e.g., 1.04 A cm^{-2} at 450 °C for the state-of-the-art PCECs¹¹²]. Furthermore, Figure 3.7k shows that the PCECs achieve reasonable Faradaic efficiency (%) ($FE (\%) > 80\%$, Supplementary Note 3). Moreover, at 400 °C and a current density of 0.6 A cm^{-2} , the cell-level electrical energy-to-chemical energy conversion efficiency reaches 79% (Figure 3.7l, Supplementary Figure 40), validating the feasibility of producing hydrogen with PCECs at <450 °C.

We then tested PCEC stability for power generation and hydrogen production at <450 °C. At a current density of 300 mA cm^{-2} and 400 °C, the PCEC continuously operated in fuel cell mode for 100 h, achieving a degradation rate of <0.07 mV/h (Figure 3.8a). After the stability test, there is no observable change in the microstructure and no electrolyte cracking (Figure 3.8b and

Supplementary Figure 41). The positive electrode-electrolyte interfaces show no delamination, suggesting that the interfacial bonding is good and the thermal expansions are compatible.

Figure 3.8c shows the long-term stability test data of the PCECs in electrolysis mode at 400 °C. The PCEC operated at a current density of -0.6 A cm^{-2} for >250 h, achieving a low degradation in the applied voltage ($<0.15 \text{ mV/h}$) and FE (%). These results validate the feasibility of durable H_2 production with PCECs at 400 °C, dramatically reducing the required operating temperature and exceeding previous PCEC performance. The stable terminal voltage and FE (%) suggests no noticeable degradation. Postmortem microstructural analysis shows no evidence of degradation after this long-term durability testing (Figure 3.8d). Specifically, no cracking was observed on the electrolyte, essential for high FE (%). The SEM images do not show any observable delamination between the electrolyte and positive electrode, highlighting the robustness of the PCECs for H_2 production.

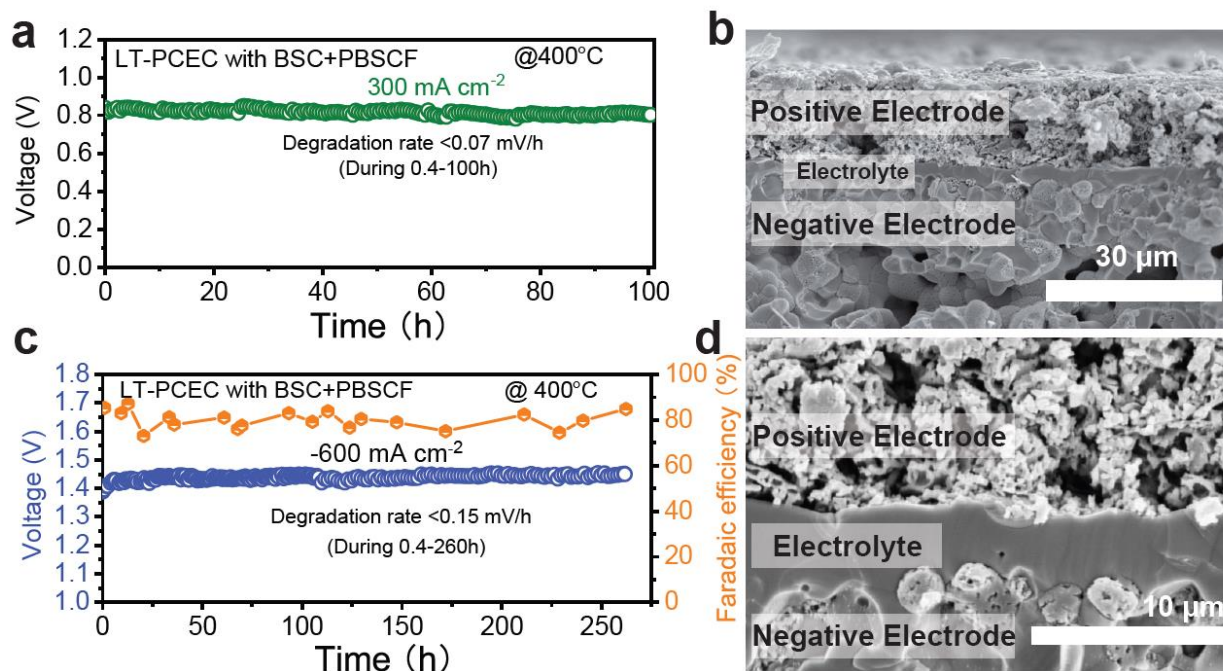


Figure 3.8. Stability of LT-PCECs with in-situ formed BSC+PBSCF as the positive electrode for power generation in fuel cell mode and green H_2 production in electrolysis mode. (a) The stability testing of the LT-PCEC on H_2 -Air at 400 °C (Cell 15). The discharging current density is 300 mA

cm^{-2} . (b) The SEM image of the LT-PCEC after stability testing on H_2 -Air (Cell 15). (c) Long-term stability testing of a LT-PCEC in electrolysis mode at $400\text{ }^\circ\text{C}$ with a charging current density of 600 mA cm^{-2} (Cell 16). (d) The SEM image of the LT-PCEC after stability testing in electrolysis mode (Cell 16).

3.5 Conclusions

By fabricating ultrathin, single-grain thick, chemically homogeneous, and low-resistance electrolytes and developing an in-situ formed composite positive electrode, we successfully fabricated high-performance PCECs capable of both power generation and hydrogen production at $<450\text{ }^{\circ}\text{C}$. The PCEC electrolyte fabricated via the simple and scalable process achieves a resistance comparable to or lower than that of PCECs prepared via costly and complicated processes. Both experimental and computational studies have revealed that this in-situ formed BSC+PBSCF positive electrode has a significantly improved electrocatalytic activity and reduced positive electrode-electrolyte contact resistance. At $450\text{ }^{\circ}\text{C}$, the PCECs developed in this work achieve exceptional performance in both fuel cell and steam electrolysis modes. The PCECs display long-term durable fuel cell performance and remarkable durability in electrolysis mode at $400\text{ }^{\circ}\text{C}$. These reproducible results further highlight the promise of using PCECs for efficient power generation and hydrogen production at a large scale.

3.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1038/s41560-023-01350-4>

Chapter 4 – Process-intensified PCFCs for power generation, chemical production, and greenhouse gas mitigation

4.1 Abstract

Here, we present protonic ceramic fuel cells (PCFCs) that achieve the internal dry reforming of methane (DRM) at 550-650 °C to simultaneously generate power, produce syngas or hydrogen as chemical building blocks, and mitigate two harmful greenhouse gases. We developed an oxide-supported *in-situ* exsolved Ni-Ru catalyst ($\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$, i.e., SDC-Ni-Ru). The *in-situ* exsolved Ru clusters favor the CO_2 activation step, while the Ni clusters promote the CH_4 activation. The synergy between Ni and Ru clusters simultaneously improves the CH_4 and CO_2 activation, enhancing the DRM activity. Additionally, we discovered that the Ru clusters altered the DRM pathway, favoring the formation of monodentate carbonate species, which subsequently accelerates the oxidization of $-\text{CH}^*$ species on Ni clusters and improves the coking tolerance. The PCFCs equipped with this SDC-Ni-Ru internal DMR catalyst attain an exceptional and durable power densities using a mixture of CH_4 and CO_2 as the fuel, setting a record for DRM-PCFCs.

4.2 Introduction

Carbon dioxide (CO₂) and methane (CH₄) are two primary greenhouse gases emitted through human activities. In 2020, CO₂ accounted for ~79% of all U.S. greenhouse gas emissions from human activities, while CH₄ accounted for ~11%¹⁴¹. Mitigating these greenhouse gases requires decreasing CO₂ and CH₄ emissions and increasing large-scale carbon fixation via chemical production from CO₂ and CH₄^{142,143}. The energy demand sectors (e.g., power generation) and raw materials/chemicals manufacturing industries lead to the highest amounts of CO₂ production and CH₄ leakage. Therefore, a technology that intensifies power generation, chemical production, and CO₂ and CH₄ utilization could serve as the “Holy Grail” for addressing these challenges associated with greenhouse gas mitigation, power generation, and chemical production.

Dry reforming of methane (DRM, $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$) utilizes two greenhouse gases to produce syngas (i.e., a mixture of H₂ and CO), which can be subsequently used for providing building blocks to chemical manufacturing industries, for producing hydrogen gas, and for generating fuels for transportation^{144,145}. In 2021, the global hydrogen demand reached 94 Mt per year, and more than 90% of it was derived from fossil fuels. If fossil fuel-derived hydrogen could be produced via DRM instead of steam methane reforming, nearly 1 Gt CO₂ per year could be utilized, achieving a Net Zero Scenario, while CO₂ and CH₄ could be converted for profitable electricity and chemical production¹⁴⁶. Additionally, the produced syngas could be further converted to CO as a valuable feedstock via the reversed water gas shift reaction (RWGS). Alternatively, DRM could also be integrated with electrolyzers, producing syngas with a wide range of H₂/CO ratios, which can be used for producing various chemicals via Fischer-Tropsch synthesis. However, the DRM reaction either yields low conversion or leads to severe coking, which also consumes extensive amounts of thermal energy. Furthermore, conventional

thermochemical reactors developed for DRM cannot concurrently generate electricity, necessitating the development of alternative reactors.

Solid oxide fuel cells based on oxygen-ion conductors (O-SOFCs) have been validated for power generation via DRM^{36,147,148}. However, O-SOFCs could further oxidize the gases fed to the anode, especially at relatively high current densities, producing CO₂ and H₂O, which lead to syngas dilution and low CO₂ conversion (Figure S1A). Additionally, Ni-based cermets are usually employed as the anode for O-SOFCs, and they typically operate at >700 °C, which favors methane pyrolysis and leads to severe coking. Therefore, O-SOFCs are not the optimal reactors for improving power generation, chemical production, and greenhouse gas mitigation. However, DRM is more thermodynamically and kinetically favorable at relatively high operating temperatures (DRM, CH₄ + CO₂ → 2CO + 2H₂, $\Delta H_{298\text{ K}}^{\circ} = 247.6\text{ kJ/mol}$; $\Delta G_{298\text{ K}}^{\circ} = 247.8\text{ kJ/mol}$; $\Delta S_{298\text{ K}}^{\circ} = -18.9\text{ J/mol/K}$). $\Delta G_{298\text{ K}}^{\circ}$ is positive, indicating that the reaction cannot occur spontaneously and requires an input of energy to proceed. In addition, the positive $\Delta H_{298\text{ K}}^{\circ}$ indicates this reaction is endothermic. The ΔG of DRM decreases with increasing the temperature, indicating DRM tends to be more favorable at high operating temperatures. Additionally, a high operating temperature enables to supply additional heat (i.e., thermal energy) for this endothermic reaction. Therefore, DRM is thermodynamically more favorable at high operating temperatures. Additionally, the DRM reaction kinetics can be improved at high operating temperatures. Increasing the operating temperature facilitates all intermediate steps of DRM reaction, which include gas diffusion, adsorption, surface reaction, and desorption.

Alternatively, protonic ceramic fuel cells (PCFCs), which employ proton-conducting oxide as the electrolyte, can address the challenges mentioned above^{9,103}. As shown in Figure 4.11A and Figure S1B, DRM occurs at the PCFC anode, where dry CO₂ reacts with CH₄ to produce H₂ and

CO. Air is fed to the PCFC cathode; thus, PCFCs function as fuel cells to generate electricity. Protons transport across the proton-conducting electrolyte and produce water at the cathode. As the electrolyte exhibits negligible oxygen-ion conduction at <650 °C, only H₂ can be utilized, which prevents the further oxidation of CO to CO₂ (Figure S1B). One unique feature of PCFCs is that water is produced at the cathode; therefore, the chemicals produced at the anode are not diluted. Moreover, during fuel cell operation, the reactor can consume H₂ gas from the DRM side and thus shift the methane reforming reaction equilibrium toward syngas production and circumvent the thermodynamic limits, allowing higher CO₂ and CH₄ conversions. Feeding water vapor to the anode of DRM-PCFC might improve the catalyst stability as water vapor can mitigate the coking ($C + H_2O \rightarrow CO + H_2$). However, supplying steam to the anode will lead to side reactions, such as water gas shift (WGS) and steam methane reforming, which reduces CO₂ conversion and decreasing syngas production rate (Figure S1C). Thus, in this work, no water vapor was fed to the anode to achieve dry reforming. Additionally, PCFCs couple endothermic DRM reactions with exothermic electrochemical processes; the overall energy efficiency of PCFCs is enhanced when they are operated near thermoneutral points because the external energy required to achieve the reaction is reduced. The DRM is a thermodynamically endothermic reaction. Its endothermic nature allows utilizing the heat, which includes the irreversible heat ($T\Delta S$) generated by this reaction and the joule heat generated by the fuel cell unit itself. Therefore, operating the PCFC near the thermoneutral point can directly and fully utilize the heat generated by the PCFC, eliminating the external heat supply, which enhances the overall energy efficiency.

As DRM-PCFC is an emerging technology, very few demonstrations of DRM-PCFCs exist^{28,149-151}. Although practical performance has been achieved, all previous DRM-PCFCs require either high operating temperatures, which can lead to the oxidation of CO, or show poor

performance or poor durability. For example, Shao et al.¹⁵¹ validated DRM-PCFCs by spray-coating a La_2NiO_4 catalyst layer on a $\text{Ni-BaZr}_{0.4}\text{Ce}_{0.4}\text{Y}_{0.2}\text{O}_{3-\delta}$ anode. At 700 °C, the PCFCs delivered a low current density of 200 mA/cm² at 0.6 V, demonstrating that the catalytic activity of the PCFC anode was low. Luo et al.²⁸ developed an internal DRM catalytic layer ($\text{Ni}_{0.8}\text{Co}_{0.2}\text{-La}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$), leading to excellent fuel cell performance, with a peak power density of 0.91 W/cm² at 700 °C. Nevertheless, the proton-conducting electrolyte exhibited considerable oxygen-ion conduction at >650 °C, which could lead to CO oxidation to CO₂ and to the production of H₂O. Due to the low activation energy of proton conduction relative to oxygen-ion conduction, PCFCs can efficiently operate at intermediate temperatures (500-650 °C). To the best of our knowledge, only one successful demonstration of DRM-PCFC has been reported at 600 °C¹⁴⁹. However, a peak power density of 0.31 W/cm² was obtained, which is much lower than the density that could be achieved with H₂. Therefore, enhancing the performance at 600 °C is considered a primary objective in DRM-PCFC development. Additionally, lowering the operating temperature of DRM-PCFCs can alleviate the stringent materials requirements and simplify thermal management, reducing the system's capital and operational costs. Therefore, tailoring a DRM catalyst that is compatible with PCFCs and can improve DRM-PCFC performance at even 550 °C is key to employing DRM-PCFCs for large-scale and simultaneous power generation, chemical production, and greenhouse gas mitigation within a single unit.

Because of the relatively high thermodynamic stability of CH₄ ($\Delta H_f^\circ = -75 \text{ kJ/mol}$) and exceptionally high thermodynamic stability of CO₂ ($\Delta H_f^\circ = -394 \text{ kJ/mol}$), as well as the chemically inert nature of CO₂, DRM is thermodynamically and kinetically unfavorable at 550-650 °C and requires a catalyst for the simultaneous activation of CH₄ and CO₂ molecules. Furthermore, due to the low O/C or H/C ratio under DRM conditions, -CH* can easily decompose

to carbon and hydrogen; thus, DRM is highly vulnerable to coking. To improve coking tolerance, DRM catalysts must also promote the oxidization of -CH^* using oxygen sourced from intermediate species formed by CO_2 adsorption. These requirements guide the rational design of DRM catalysts. First, researchers have noted that oxide-based supports exhibit high oxygen vacancy concentrations, and enhanced lattice oxygen mobility can improve CO_2 adsorption, as the oxygen vacancies could function as basic active sites¹⁵²⁻¹⁵⁶. The characteristic redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ in CeO_2 enables high oxygen storage capacity; therefore, it has been widely employed as a support for various catalytic reactions, including CO_2 hydrogenation, steam methane reforming (SMR), and DRM¹⁵⁷⁻¹⁶⁰. Therefore, engineering CeO_2 materials with increased oxygen vacancy concentrations could potentially promote CO_2 activation. Sm-doped CeO_2 (SDC) displays the smallest enthalpy of association between the dopant cations and oxygen vacancies in the fluorite lattice¹⁶¹. Thus, SDC exhibits enhanced oxygen vacancy concentration and improved lattice oxygen mobility relative to CeO_2 ; SDC could thus be a promising catalyst support. Furthermore, achieving all these requirements for SDC-supported monometallic catalysts is challenging. Leveraging the synergistic effects of two metals can reduce the activation energy of multiple catalytic steps¹⁶². For example, the synergy between Ni and Ru has been shown to improve several heterogeneous catalysis processes, including steam methane reforming, DRM, and CO hydrogenation^{140,163-165}. Therefore, we hypothesized that an SDC-Ni-Ru catalyst could concomitantly promote the activation of CO_2 and CH_4 while facilitating the subsequent oxidation of -CH^* by intermediate species formed during CO_2 adsorption and by enhancing coking tolerance. Additionally, SDC is chemically and physically compatible with PCFCs¹⁵ and can be readily integrated with PCFCs as an internal catalytic reforming layer on the anode.

This work demonstrates process-intensified DRM-PCFCs for concurrent power generation, chemical production, and greenhouse gas mitigation, with unprecedented performance at intermediate temperatures (650-550 °C). To achieve unprecedented performance, $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (SDC-Ni-Ru) was pioneered to improve DRM activity, which leads to higher fuel cell performance and higher syngas production rates than with $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$ (SDC-Ni) and $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$ (SDC-Ru) and yields enhanced coking tolerance. Comprehensive experimental and computational investigations reveal that SDC-Ni favors the activation of CH_4 , while SDC-Ru reduces the CO_2 activation energy. The synergy between Ni and Ru simultaneously facilitates CO_2 activation and CH_4 activation; thus, DRM activity is significantly improved with SDC-Ni-Ru. Moreover, CO_2 can be readily activated over SDC-Ni-Ru, which subsequently accelerates the oxidation of $-\text{CH}^*$ species formed on the Ni surface, inhibiting the decomposition of $-\text{CH}^*$ to carbon and hydrogen and consequently enhancing coking tolerance. By coating SDC-Ni-Ru on the PCFC anode as the internal DRM catalytic layer, the operating temperature of DRM-PCFCs was lowered to 550-650 °C, achieving a groundbreaking power density of $\sim 0.94 \text{ W cm}^{-2}$ at 650 °C and 0.30 W cm^{-2} at temperatures as low as 550 °C using a mixture of CH_4 and CO_2 as the fuel (compared with 0.43 W cm^{-2} at 650 °C and 0.18 W cm^{-2} at 550 °C for state-of-the-art DRM-PCFCs¹⁴⁹). Moreover, we demonstrated the durability of DRM-PCFC operation, validating that the DRM catalyst (SDC-Ni-Ru) is coking tolerant. *In situ* Raman spectroscopy, *in situ* diffuse reflectance-infrared Fourier transform spectroscopy (DRIFTS), and computational modeling studies were also conducted to confirm its excellent coking tolerance and probe the DRM mechanisms. The seminal DRM-PCFC performance demonstrated in this work highlights the potential of this technology for large-scale power generation, chemical production, and greenhouse gas mitigation.

4.3 Experimental procedures

4.3.1 Material synthesis

PCFC anode support layer powder. The anode support layer powder was composed of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20), NiO and corn starch with the weight ratio of 3:2:1. BZY20 was synthesized by a fast-heating solid-state sintering (SSS) process. First, a stoichiometric amount of BaCO_3 , ZrO_2 , Y_2O_3 and 1 wt. % NiO (the amount of NiO was based on the total weight of crystallized BZY20) was ball-milled with ethanol for 48 hours. After overnight drying, the homogeneous mixture was calcined at 1350 °C with a fast heating/cooling rate of 10 °C/min for 5 hours in air and then crushed into fine powder. The obtained BZY20 powder was then ball-milled with ethanol again. After the powder was dried at 120 °C, the as-synthesized BZY20 fine powder was ball-milled with NiO and corn starch for 48 hours. The powder was dried on a hotplate to yield the anode support layer powder. The information of all chemicals used in this work can be found in Table S7

Anode function layer powder. The anode function layer powder was composed of 60 wt.% $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) and 40 wt% NiO. No corn starch was added. The synthesis method was the same as that used for the anode support layer powder, as mentioned above.

PCFC electrolyte powder. $\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb4411) was employed as the electrolyte, which was synthesized by an improved sol-gel method¹⁰ using $\text{Ba}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, zirconyl nitrate solution (35 wt. % in diluted nitric acid), Y_2O_3 and Yb_2O_3 as the precursors. First, the required amounts of Y_2O_3 and Yb_2O_3 were dissolved in 20 wt.% dilute nitric acid solution at 120 °C to obtain clear yttrium and ytterbium nitrate solutions. Then, stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and zirconyl nitrate were subsequently added to the above nitrate solution. After the mixture was stirred for 30 mins, two complexing and chelating agents,

citric acid (CA) and ethylenediaminetetraacetic acid (EDTA), were added at a CA:EDTA:total cation molar ratio of 2:2:1, and the mixture was continuously stirred for 30 mins at room temperature for complete complexation. Then, the pH of the solution was adjusted to ~9 by the addition of aqueous NH_4OH . The obtained solution was heated at 250 °C on a hot plate until a gel was formed, which was then placed to a drying oven at 175 °C for 24 hours. The obtained chunk powder was finally calcined at 1250 °C for 5 hours in air to obtain the BCZYYb4411 electrolyte powder.

PCFC cathode powder. The cathode material was a composite made of $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BCFZY4411) and $\text{BCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BCZYYb4411) at a weight ratio of 70:30. BCZYYb4411 was prepared through the SSS method using BaCO_3 , CeO_2 , ZrO_2 , Y_2O_3 , Yb_2O_3 , and NiO (sintering aid) as the precursors, similar to the preparation of BZY20. BCFZY4411 was synthesized by an improved sol-gel method. In brief, BCFZY4411 positive electrode powder was also synthesized via a wet-chemistry method using stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, zirconyl nitrate solution (35 wt% in diluted nitric acid), and Y_2O_3 as the precursors. The calculated amount of Y_2O_3 was first dissolved in 20 wt.% dilute nitric acid solution to prepare the yttrium nitrate solution. The following steps were similar to those of the preparation of the BCZYYb4411 electrolyte, as mentioned above. After the gel was formed, it was immediately placed in a drying oven at 175 °C for 24 h and was then calcined at 600 °C for 5 hours. The obtained fine powder was finally ball-milled with ethanol for another 24 hours and then dried to obtain BCFZY4411 for the cathode ink preparation.

DRM catalyst. $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (SDC-Ni-Ru) was also synthesized via the abovementioned sol-gel method by using a stoichiometric amount of $\text{Sm}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ as the precursors. The obtained black powder was then

calcined in air at 600 °C for 5 hours to obtain the SDC-Ni-Ru catalyst. Similarly, the catalysts for the control experiments, $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$ (SDC-Ru) and $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$ (SDC-Ni), were synthesized by the same method.

4.3.2 Material ink and slurry preparation

BCZYYb4411 electrolyte ink preparation for ultrasonic spray coating. The obtained sol-gel BCZYYb4411 electrolyte powder was first mixed with 1 wt.% NiO (NiO functioned as the sintering aid and was based on the mass of BCZYYb4411), organic binders (e.g., fish oil, b-98 polyvinyl butyral and di-n-butyl phthalate) and ethanol. The ink was then ball-milled using yttria-stabilized zirconia (YSZ) beads ($d=5$ mm) for approximately 4 days, after which it was ready for the following ultrasonic spray coating.

Cathode slurry preparation. Five grams of BCFZY+BCZYYb composite powder, 1 g dispersant (20 wt.% solspere 28000 (Lubrizol) dissolved in α -terpinol), and 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved in α -terpinol) were mixed well and hand-ground by a mortar and pestle to obtain the cathode slurry.

SDC-Ni-Ru catalyst slurry preparation. Similarly, 5 grams of SDC-Ni-Ru, 1 g dispersant (20 wt.% solspere 28000 (Lubrizol) dissolved in α -terpinol), and 0.5 g binder (5 wt.% V-006 (Heraeus) dissolved in α -terpinol) were mixed well and hand-ground by a mortar and pestle to make the slurry for the DRM reaction.

Anode electrode slurry preparation. The composite anode powder BZY20 + NiO + corn starch was first mixed with organic materials (menhaden fish oil, b-98 polyvinyl butyral, polyethylene glycol 400, cyclohexanone, di-n-butyl phthalate, xylenes) and ethanol. The slurry

was then ball-milled by yttria-stabilized zirconia (YSZ) beads ($d=10$ mm) for approximately 24 hours to obtain the anode slurry.

Preparation of the anode electrode function layer slurry. The anode function layer slurry was also prepared by the same method as the anode electrode. The slurry containing BZY, NiO, organic matter and ethanol was ball-milled for approximately 24 hours.

4.3.3 DRM-PCFC half-cell manufacturing

DRM-PCFC half-cells were manufactured by combining the cotape-casting and spray-coating methods. The anode and anode functional layer (AFL) were first made by the cotape-casting method. In brief, the prepared AFL (BZY20 + NiO) was coated on Mylar via tape casting. After drying for 1 day in air at room temperature, the anode support layer slurry was then tape-cast above the AFL. The two layers obtained were then dried in air for 2 days and coprecalcined at $850\text{ }^{\circ}\text{C}$ for 30 mins to burn out all the organic materials, with a heating/cooling rate of $2^{\circ}/\text{min}$. The BCZYYb4411 electrolyte ink was then ultrasonically coated on the AFL layer side. First, the prepared BCZYYb4411 electrolyte ink solution was loaded into an automatically controlled ultrasonic syringe. The injected ink flowed through an ultrasonic nozzle, which was used for coating an ultrathin and uniform electrolyte layer. The coating parameters, such as ink injection rate, temperature, step size, etc., were carefully optimized to produce high-quality DRM-PCFC half cells. After spray-coating, the obtained half cells were cosintered at $1450\text{ }^{\circ}\text{C}$ for 5 h to crystalize the materials and densify the electrolyte.

4.3.4 DFT method

Spin-polarized periodic density functional theory (DFT) calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP)^{166,167}. The projector augmented wave (PAW) pseudopotential¹⁶⁸ and the GGA-PBE functional¹⁶⁹ were used to account for the core electrons and the electron exchange-correlation effects. The plane-wave basis set was expanded with a cutoff energy of 400 eV and Gaussian smearing ($\sigma = 0.05$ eV). The reciprocal first Brillouin zone was sampled using a $2 \times 2 \times 1$ mesh k -point mesh automatically generated from the Monkhorst-Pack scheme¹⁷⁰. We also adopted the Hubbard U method¹⁷¹ to correct the excessive delocalization of f -electrons on the Ce atoms. A $(U-J)_{\text{Ce}} = 4.5$ eV was added to the Dudarev function. The 4f electrons of Sm were treated as the core and, thus, were not corrected with the U values¹⁷². The stable CeO₂ (111) facet was chosen to construct the samarium-doped ceria (SDC) modelsm, which was also consistent with the exposure plane, as shown in Figure 4.3F. A 9-layer slab in a (2x2) supercell contained 24 Ce and 48° atoms. The top 3 layers were relaxed, while the bottom 6 layers were fixed to the optimized bulk values. The optimized lattice constant was 5.411 Å, which agreed well with experimental and calculational results¹⁷³. All displayed structures were visualized with VESTA software¹⁷⁴.

4.3.5 DRM catalyst performance evaluation in a packed bed reactor

The DRM catalytic activities were first examined at 1 atm in a packed bed reactor with an internal diameter of 0.28 inches. Then, 150 mg of each catalyst was loaded into the reactor. A thermocouple was inserted into the tube reactor close to the catalyst to determine the operating temperature. Before testing, the catalyst was first reduced under 20% H₂ balanced with Ar (total flow rate of 50 sccm) at 600 °C for 1 hour. The reactor temperature was then increased to 650 °C,

and the inlet gas composition was switched to 8 sccm CH₄ and 8 sccm CO₂. The outlet gas compositions were determined using online gas chromatography (INFICON 3000 Micro GC) from 650 to 550 °C with 50 °C intervals. Before the outlet gas compositions were measured, the reactor was held at each testing temperature for at least 30 mins to let the reactor reach equilibrium.

4.3.6 PCFC sealing and performance testing

The electrochemical button cell was sealed in an alumina tube by using a MO·SCI glass sealant (1745P/-45). The catalytic layer was painted on the anode side, covering the entire surface. For single cell testing, we used gold paste as the current collector. It was first painted on both electrodes, and then a silver grid was applied to the gold paste to strengthen the current collection. After the PCFC was sealed, the cell was reduced at 650 °C with 20% H₂ balanced with Ar (total flow rate=50 sccm) for 20 mins. The electrochemical performance was then evaluated from 650 °C to 550 °C at a cooling rate of 2.5 °C min⁻¹. The ratio of CH₄ to CO₂ fed to the anode was kept at 1:1. The total flow rate was varied with the operating temperature to maximize fuel utilization. Specifically, the total flow rates were 20 sccm, 15 sccm, and 12 sccm at 650 °C, 600 °C, and 550 °C, respectively. Before the electrochemical performance was tested, the PCFC was held at each temperature for ~15 mins to allow the PCFC to reach equilibrium. All electrochemical measurements were conducted using a Princeton applied research potentiostat.

4.3.7 Characterizations

The crystal structures of the as-synthesized and reduced catalysts were measured by using X-ray diffraction (XRD) (Rigaku MiniFlex diffractometer) with a Cu K α radiation source operated at 30 kV and 15 mA. The scan speed was 1°/min. Rietveld refinements were performed using the

open source GSAS software¹⁷⁵. The morphology of the reduced SDC-Ni-Ru powder was examined using a transmission electron microscope (FEI Tecnai Osiris). The microstructure of PCFCs was examined by using a scanning electron microscope (Hitachi/S-3400 N). X-ray photoelectron spectroscopy (XPS) was performed using a Phi 5000 VersaProbe II X-ray photoelectron spectrometer. Temperature-programmed reduction (TPR) was conducted using a ChemBET Pulsar. First, 0.1 g of the catalyst was pretreated in a U-shaped quartz tube at 120 °C for 30 mins with 50 sccm N₂. After the catalyst was cooled to 25 °C, the gas was switched to 10% H₂ balanced with Ar at a total flow rate of 100 sccm. TPR analysis was then performed with a heating rate of 10 °C/min. *In situ* Raman spectroscopy (Bruker Senterra) for SDC-Ni-Ru and SDC-Ni was conducted under 10 sccm CH₄ and 10 sccm CO₂ at 650 °C. *In situ* DRIFTS was performed using a Thermo Fisher iS50 FTIR spectrometer equipped with a Praying Mantis high-temperature reaction chamber.

4.4 Results and discussion

4.4.1 PCFCs for the dry reforming of methane (DRM-PCFCs)

Figure 4.1A displays the scenario for implementing DRM-PCFCs, which function as fuel cells that intensify DRM with electrochemical power generation. The generated power can be utilized by some energy sectors; thus, DRM-PCFCs can serve as decentralized power sources. The produced syngas or hydrogen can also be converted to value-added chemicals by chemical manufacturers. The intrinsic performance of pristine PCFCs and DRM catalysts is essential for achieving high power density. As shown in Figure 4.1B, to minimize the overpotential ascribed to the oxygen reduction reaction, a newly developed composite cathode ($\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta} + \text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$) was employed. Additionally, a PCFC electrolyte was fabricated via ultrasonic spray coating (Figure S2) to reduce its thickness to $\sim 6\ \mu\text{m}$ (Figure 4.1B), which reduced ohmic resistance. $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) + Ni was used as the anode. A DRM catalyst developed in this work, SDC-Ni-Ru, was employed as an effective catalytic layer on the anode (Figure 4.1B inserted figure). As shown in Figure 4.1C, without the DRM catalyst, the PCFC performance was poor due to the low catalytic activity of BZY20+Ni for DRM, which generates low amounts of hydrogen for power generation. The DRM catalyst developed in this work led to an ~ 2.5 -fold increase in the PCFC performance at $650\ ^\circ\text{C}$ (Figure 4.1C). Compared with literature results (Table S1), unprecedented performance for power generation was obtained. For example, at $650\ ^\circ\text{C}$, the PCFCs yield a peak power density of $0.94\ \text{W cm}^{-2}$ using a mixture of CH_4 and CO_2 as the fuel, which doubles the performance of state-of-the-art PCFCs (Figure 4.1D). Moreover, the intermediate-temperature (550 - $650\ ^\circ\text{C}$) DRM-PCFCs achieved higher performance than high-temperature (700 - $850\ ^\circ\text{C}$) DRM-SOFCs, indicating the DRM catalyst developed in this work exhibits outstanding catalytic activity at reduced operating temperatures (Table S2).

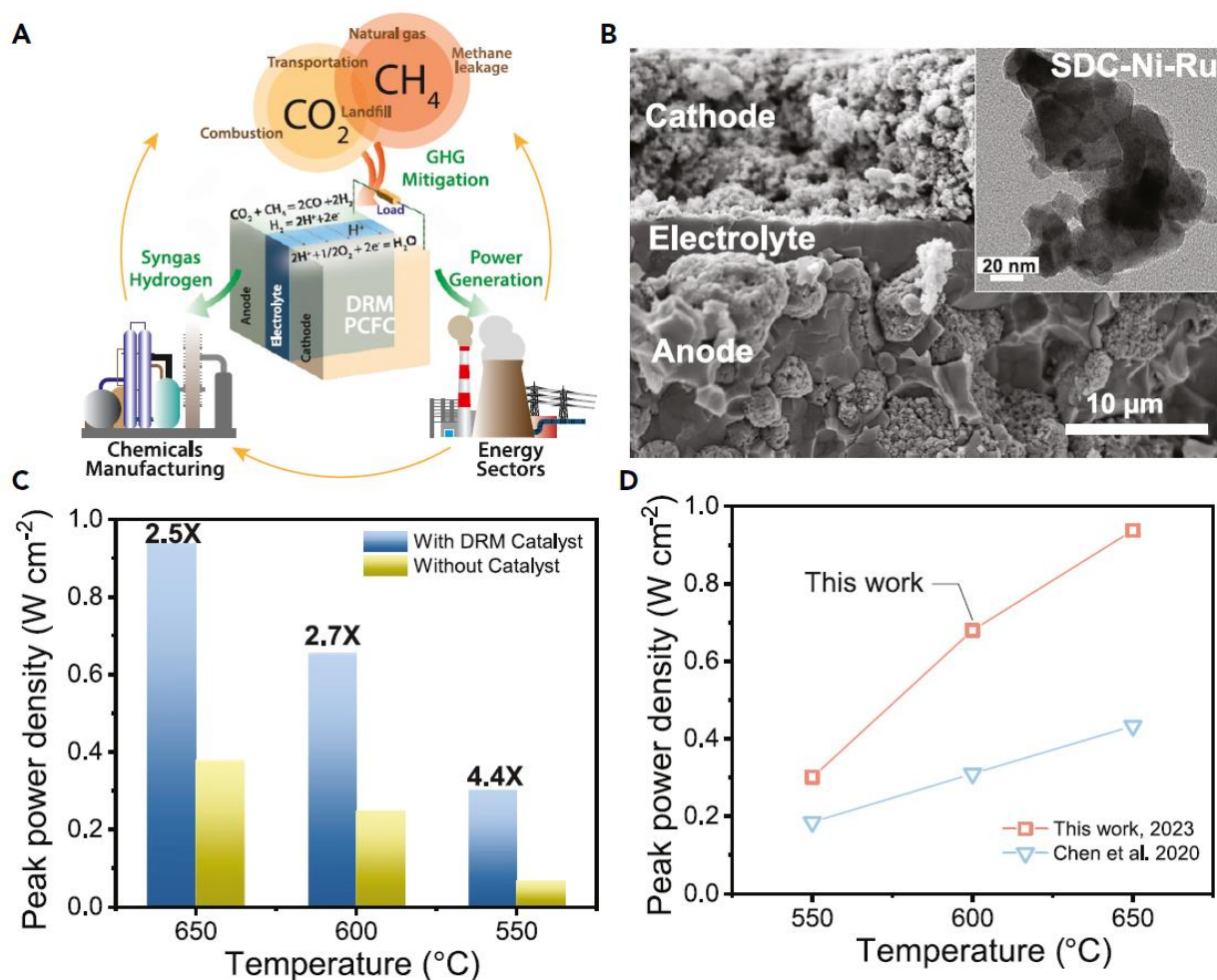


Figure 4.1. DRM-PCFCs for electrochemical power generation, chemical production, and greenhouse gas mitigation. (A) An illustration of implementing DRM-PCFCs for simultaneous power generation, chemical production, and greenhouse gas mitigation. (B) A cross-sectional SEM image of the DRM-PCFC. The inserted figure shows the TEM image of the SDC-Ni-Ru catalyst coated on the PCFC anode. (C) Comparison of peak power densities (PPDs) of DRM-PCFCs with and without the SDC-Ni-Ru catalytic layer. (D) Comparison of PPDs of our DRM-PCFCs with state-of-the-art DRM-PCFC. (Chen et al. 2020¹⁴⁹).

4.4.2 Rationally designed DRM catalyst

The DRM catalysts were synthesized via a one-pot wet-chemistry method and subsequent *in situ* exsolution. Three catalysts were synthesized and studied in this work: Sm_{0.2}Ce_{0.7}Ni_{0.15}O_{2-δ} (SDC-Ni), Sm_{0.2}Ce_{0.7}Ru_{0.15}O_{2-δ} (SDC-Ru), and Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-δ} (SDC-Ni-Ru). As shown in Figure S3, the X-ray diffraction (XRD) patterns of the as-synthesized catalysts show that SDC-

Ni consists of Ni-doped SDC, which exhibits a cubic fluorite structure and a small amount of NiO, indicating that the solubility of Ni in SDC is lower than 15 mol%. SDC-Ru is composed of Ru-doped SDC and RuO₂. However, the XRD pattern of as-synthesized SDC-Ni-Ru does not show noticeable peaks indexed to either NiO or RuO₂, implying that most of the Ni and Ru is dissolved in the SDC lattice, which could be beneficial for the creation of more metallic clusters/nanoparticles during subsequent *in situ* exsolution under a reducing atmosphere.

After reduction, as shown in Figures 4.2A-4.2C, the catalysts are reduced to SDC-supported monometallic/bimetallic clusters/nanoparticles. The reduced SDC-Ni comprises SDC and metallic Ni, while SDC-Ru contains SDC and metallic Ru. The XRD pattern for reduced SDC-Ni-Ru shows peaks associated with metallic Ni. We hypothesized that Ru also exsolves from the SDC lattice. However, the intensity of the Ru peaks is small and might have arisen from an extremely small amount of metallic Ru. As shown in Figure 4.2C and Table S3, XRD Rietveld refinement was conducted to analyze the XRD pattern of reduced SDC-Ni-Ru. The reduced SDC-Ni-Ru comprises three phases: SDC, metallic Ni, and metallic Ru. The amounts of metallic Ni and Ru are calculated as 3.0 wt.% and 2.7 wt.%, respectively, slightly lower than the maximum amounts (3.4 wt.% for Ni and 2.9 wt.% for Ru), indicating that small amounts of Ni and Ru remain in the SDC lattice. Therefore, the reduced SDC-Ni-Ru is composed of Ni and Ru-doped SDC, metallic Ni, and metallic Ru.

H₂-temperature programmed reduction (H₂-TPR) (Figure 4.2D) and TEM analysis (Figures 4.2E-4.2F) were performed to study the exsolution, microstructure, and chemical composition of the reduced catalysts. The H₂-TPR profiles shown in Figure 4.2D present the nature of Ni and/or Ru in these catalysts and also allows for investigations of the interactions between the metallic phase and the SDC support¹⁷⁶. The reduction temperature, at which the H₂-TPR profile peaks,

indicates the degree of interaction of the metallic phase with the oxide support¹⁷⁷. A relatively high reduction temperature indicates that the metallic phase strongly interacts with the oxide support¹⁵⁶. Typically, the *in situ* exsolution of Ni from the oxide support requires a higher reduction temperature than that needed to reduce bulk NiO particles, suggesting that *in situ* exsolved Ni has stronger interactions with the oxide support than interactions between bulk Ni particles and the oxide support. The H₂-TPR profile of SDC-Ni displays two overlapping peaks at approximately 265 °C and 356 °C, which could correspond to the reduction of bulk NiO particles (area c) and *in situ* exsolution of Ni (area d), respectively. The H₂-TPR profile SDC-Ru also shows two overlapping peaks with peak temperatures of 95 °C and 145 °C, which correspond to the reduction of bulk RuO₂ particles (area a) and *in situ* exsolution of Ru (area b). These H₂-TPR profiles are consistent with the XRD results. The as-synthesized SDC-Ni is composed of Ni-doped SDC and NiO, while SDC-Ru consists of Ru-doped SDC and RuO₂. Additionally, the H₂-TPR profile of SDC-Ni-Ru presents two main peaks at 143 °C and 330 °C, which are close to the temperature required to exsolve Ni and Ru from the SDC lattice, suggesting that the low-temperature peak (area b) is related to the exsolution of Ru. The high-temperature peak (area d) corresponds to the exsolution of Ni. Prior to the peak assigned to the exsolution of Ni, the H₂-TPR profile of SDC-Ni-Ru shows the reduction of small amounts of bulk NiO particles, implying that NiO is not fully dissolved in the SDC lattice and a minor amount of NiO exhibits as bulk NiO particles. Additionally, the peak corresponding to the Ni cluster of the SDC-Ni-Ru sample shifts to a lower temperature compared to that of SDC-Ni, indicating that the active H species adsorbed on the pre-reduced Ru⁰ sites could readily spillover to the neighboring Ni species in SDC lattice, and consequently promoting the exsolution of Ni from SDC bulk^{178,179}. Therefore, the reducibility of the SDC-Ni-Ru catalyst is enhanced, compared to the Ru-free SDC-Ni catalyst. Moreover, the

presence of Ru can closely interact with NiO species, resulting in a high dispersion on the SDC-Ni-Ru sample, which might also lead to the Ni exsolution at a relatively low temperature¹⁸⁰. The peak associated with the reduction of bulk RuO₂ is not clear, indicating that Ru is almost fully dissolved in the SDC lattice, which is also consistent with the XRD results. Although the XRD pattern for reduced SDC-Ni-Ru does not clearly display the peaks corresponding to Ru, the H₂-TPR profiles and XRD Rietveld refinement results suggest that Ru clusters/nanoparticles can also be created on SDC via *in situ* exsolution upon reduction.

The synergistic effect between Ni and Ru is significant for improving DRM activity. To identify the structure of *in situ* exsolved Ni and Ru, energy-dispersive X-ray spectroscopy (EDS) mapping and high-resolution transmission electron microscopy (HR-TEM) images are shown in Figures 4.2E-4.2F. In the figures, all the constituent elements of the oxide support (Sm, Ce, and O) are uniformly distributed. Ni exhibits two structures, including Ni nanoparticles and Ni clusters. The Ni nanoparticle shown in Figure 4.2D is attributed to the reduction of relatively large bulk NiO particles, while the Ni clusters are exsolved from the SDC lattice. The Ni clusters are homogeneously dispersed on the SDC. Additionally, the EDS mapping shows that Ru is uniformly distributed, and no Ru nanoparticles are observed, indicating that metallic Ru only exists as Ru clusters. These EDS mapping images are consistent with the XRD results and H₂-TPR profiles. The HR-TEM image (Figure 4.2F) shows a lattice plane with a d-spacing of 0.317 nm, corresponding to the SDC (111) plane, which matches well with the XRD Rietveld refinement results (0.315 nm).

The surface electronic structure of the reduced DRM catalysts was investigated using X-ray photoelectron spectroscopy (XPS) (Figures 4.2G-4.2J and Table S4). To present the photoemission feature of Ni 2p_{3/2} of SDC-Ni and SDC-Ni-Ru, the photoemission feature of Ni

2p_{1/2} is not shown in Figure 4.2G. The XPS spectra show that Ni displays both oxidative (Ni²⁺) and metallic (Ni⁰) states. The amount of metallic Ni is low in both catalysts (11.6 mol% for SDC-Ni-Ru and 25.3 mol% for SDC-Ni), which could be ascribed to the rapid oxidation of surface Ni clusters (Figure 4.2G)¹⁵⁶. Similar phenomena were also observed for the Ru 3p_{3/2} spectra of SDC-Ni-Ru and SDC-Ru catalysts (Figure 4.2H). The surface Ru clusters tend to be oxidized when exposed to air, leading to the formation of Ru⁴⁺. It should be noted that the SDC-Ni-Ru catalyst presents lower Ni⁰/Ni²⁺ and Ru⁰/Ru⁴⁺ ratios than SDC-Ni and SDC-Ru, respectively, suggesting that the Ni and Ru in SDC-Ni-Ru tend to form clusters that interact strongly with the SDC support, which is consistent with the H₂-TPR results. These results are combined with the XPS and H₂-TRP analysis to confirm that both Ni and Ru primarily exist as clusters on SDC-Ni-Ru.

Three types of oxygen species were identified on these catalysts (Figure 4.2I): lattice oxygen (O_L), hydroxyl species (O_{OH}), and chemisorbed H₂O (O_W)¹⁸¹. With the addition of Ru to the catalyst, the concentration of O_W increases from ~8 mol. % to ~11 mol. %, suggesting that the introduction of Ru could improve the water uptake capability of the catalyst. The amount of hydroxyl species, formed by the subsequent water molecule dissociation, on SDC-Ni-Ru and SDC-Ni is higher than that on SDC-Ru, implying the dissociation process can be promoted by

Ni. Increasing the oxygen vacancy concentration favors the formation of hydroxyl species, implying that Ni addition (acceptor dopant) could increase the oxygen vacancy concentration in SDC¹⁸¹. It has been widely recognized that a high oxygen vacancy concentration is also essential for DMR^{182,183}. Therefore, all the characterizations suggested that SDC-Ni-Ru could synergize

the advantages of both Ni and Ru, yielding enhanced DRM performance and coking tolerance.

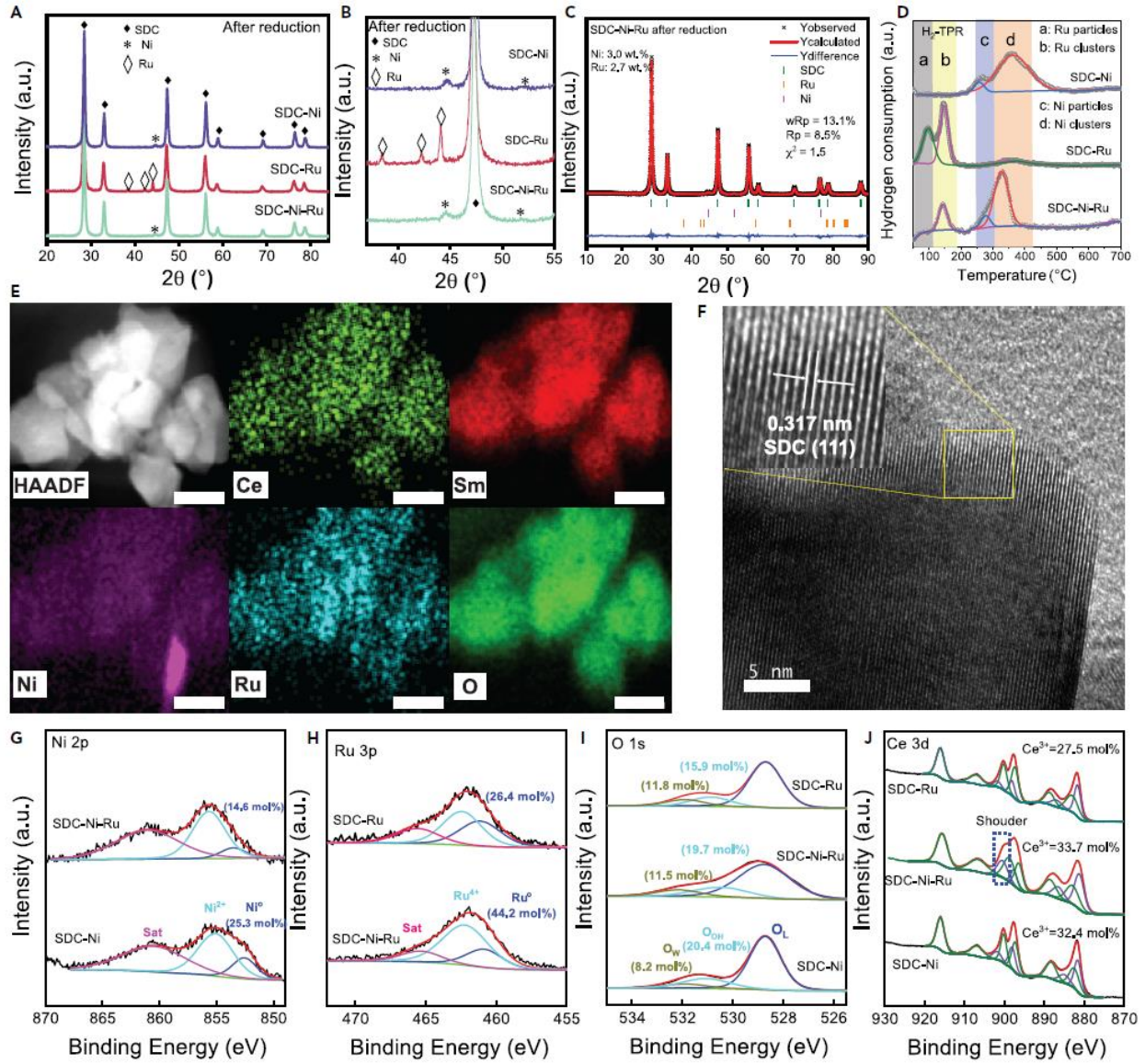


Figure 4.2. The crystal structure, microstructure, and electronic structure of DRM catalysts. (A) X-ray diffraction (XRD) patterns of SDC-Ni, SDC-Ru, and SDC-Ni-Ru after reduction. (B) Enlarge scan range from 35 to 55° of the patterns shown in (A). (C) XRD pattern of reduced SDC-Ni-Ru and refinement results. (D) H₂-temperature programmed reduction (H₂-TPR) of SDC-Ni, SDC-Ru, and SDC-Ni-Ru. (E) High-angle annular dark-field (HAADF) and EDS mapping images of reduced SDC-Ni-Ru. The scale bar is 20 nm. (F) High-resolution transmission electron microscopy (HR-TEM) image of reduced SDC-Ni-Ru. X-ray photoelectron spectroscopy (XPS) of (G) Ni 2p, (H) Ru 3p, (I) O 1s, and (J) Ce 3d for reduced SDC-Ni, SDC-Ru, and SDC-Ni-Ru. The purple line refers to Ce³⁺ and the green line corresponds to Ce⁴⁺.

4.4.3 Power generation, chemical production, and greenhouse gas mitigation

To determine the catalytic activities of the catalysts developed in this work, we first examined and compared the catalytic performance of SDC-Ni-Ru with SDC-Ru and SDC-Ni in a packed bed reactor (PBR), which is shown in Figures 4.3A-4.3C and Figures S4. SDC-Ni-Ru is much more active and coking tolerant. Both hydrogen and carbon monoxide production rates increase with increasing temperature, which might have occurred because the high operating temperatures favor the highly endothermic DRM reaction (Figure 4.3A and Figure S4A). As shown in Figures 4.3A and S4, SDC-Ni-Ru achieves the highest hydrogen and carbon production rates, indicating that Ni and Ru synergize to promote DRM. As DRM-PCFCs consume the produced H_2 to generate power electrochemically, a high hydrogen production rate is essential for a high current density (i.e., high power density). Operating the DRM-PCFCs under an enhanced current density can further promote the conversion of CO_2 and CH_4 . Therefore, obtaining a high hydrogen production rate is key to achieving high-performance power generation, chemical production, and greenhouse gas mitigation.

The Arrhenius plots of the hydrogen production rate as a function of operating temperature shown in Figure 4.3A indicate that SDC-Ni-Ru exhibits a lower activation energy (32.5 kJ/mol) than either SDC-Ru (42.0 kJ/mol) or SDC-Ni (51.7 kJ/mol), suggesting that Ni and Ru synergistically decreases the overall apparent activation energy for DRM¹⁴⁰. The lowered activation energy is vital for improving the DRM performance at <650 °C.

The second major challenge associated with DRM is its high propensity for coking. Therefore, catalyst stability is essential for integrating DRM catalysts with PCFCs. Long-term stability testing of these three catalysts was conducted at 650 °C (Figure 4.3B and Figure S4B). SDC-Ni shows severe degradation, with a nearly 50% decrease in DRM performance after 60

hours of operation. The postreaction characterizations show a considerable amount of carbon formed on SDC-Ni (Figure S5). On the other hand, SDC-Ni-Ru and SDC-Ru retain stable operations for ~120 hours, suggesting that Ru is critical for enhancing coking tolerance. The PBR outlet gas compositions were also monitored as a function of time to confirm the stability of SDC-Ni-Ru. As shown in Figure 4.3C, the total concentration of unreacted CH₄ and CO₂ remain at ~10% for 110 hours, indicating that SDC-Ni-Ru is stable during DRM.

DRM-PCFCs were then built by coating SDC-Ni-Ru on our PCFCs (Figure S6). The performance of the DRM-PCFCs was evaluated with a CH₄ and CO₂ mixture (CH₄ to CO₂ ratio = 1) that was fed to the anode, and ambient air was fed to the cathode. Figures 4.3D-E and S6-S7 compare the performance of the DRM-PCFCs equipped with SDC-Ni-Ru catalyst and without catalyst, which clearly shows that the DRM-PCFCs with SDC-Ni-Ru has significantly enhanced power density at 550-650 °C. For example, at 650 °C, SDC-Ni-Ru shows an increase in the peak power density from 380 mW cm⁻² to 940 mW cm⁻², outperforming state-of-the-art DRM-PCFCs reported in the literature (Figure 4.1D and Table S1). Additionally, as SDC-Ni-Ru displays a relatively low activation energy for DRM (Figure 4.3A), it is expected that SDC-Ni-Ru could lead to more significant improvement at low operating temperatures. As shown in Figure 4.1C, at 550 °C, the DRM-PCFCs with SDC-Ni-Ru achieve a practical PPD of 300 mW cm⁻², which is more than four times higher than that of pristine DRM-PCFCs. The open circuit voltage (OCV) of DRM-PCFCs with SDC-Ni-Ru, especially at 550 °C, still reaches ~950 mV (versus 750 mV for the pristine PCFC), suggesting that the SDC-Ni-Ru catalyst layer effectively converts CH₄ and CO₂ to syngas, which is consistent with the DRM performance demonstrated in PBRs. The corresponding EIS spectra (Figure S7A and Figure S8A) show that both ohmic resistance (Figure S9) and electrode polarization resistance (Figure 4.3F) are substantially reduced on SDC-Ni-Ru,

suggesting that such a catalytic layer enables an anode atmosphere that has a high H_2 concentration. To better visualize and differentiate the processes that occur in the DRM-PCFCs, distribution of relaxation time (DRT) analysis of EIS spectra was conducted and is presented in Figure S10. The DRT plots are divided into three main regions, the low frequency (LF, 100-1000 Hz), intermediate frequency (MF, 5000-50000 Hz), and high frequency (HF, >50000 Hz) regions, corresponding to mass transport, surface exchange kinetics, and the charge transfer process, respectively^{50,127,184}. First, the LF peak substantially decreases when SDC-Ni-Ru is used as the internal DRM catalyst, indicating that the gas diffusion process is significantly accelerated, which is attributed to the fact that SDC-Ni-Ru enhances CH_4 and CO_2 conversion and produces more H_2 . Second, the DRM-PCFC with SDC-Ni-Ru also exhibits smaller MF peaks, indicating that surface exchange processes could also be promoted by SDC-Ni-Ru. Additionally, the catalytic layer could also improve the charge transfer steps. At 550 °C, the HF peak in the DRM-PCFC without the catalytic layer split into two peaks, implying that an additional charge transfer barrier exists, which suggests that the BZY-Ni anode is not active for DRM at 550 °C¹⁸⁵. The stability of the optimized DRM-PCFCs was then examined for simultaneous power generation, chemical production, and greenhouse gas mitigation. Figure 4.3G shows that both DRM-PCFCs decorated with SDC-Ni-Ru and pristine PCFCs were tested at a constant current density of 500 mA cm⁻². The SDC-Ni-Ru-decorated DRM-PCFC attains a terminal voltage that stabilized at ~ 0.8-0.75 V, with slight degradation. The DRM-PCFC continuously generate electricity with a power density as high as 400 mW cm⁻², converting CO_2 and CH_4 to syngas (Figure S11A). However, the pristine PCFC shows severe degradation, with the terminal voltage decreasing from 500 mV to nearly 0 mV within 2 hours. This PCFC achieves much lower CH_4 and CO_2 conversion, while the produced H_2 concentration drops to 5% (Figure S11B). The severe degradation could be ascribed to coking, which blocks active sites for

DRM. Due to the SDC-Ni-Ru catalytic layer, the SEM images of DRM-PCFCs do not show noticeable microstructural changes or carbon deposits on the anode of SDC-Ni-Ru-decorated DRM-PCFC (Figure S12), indicating that SDC-Ni-Ru improves the coking tolerance of the PCFC anode. Conversely, a considerable amount of carbon was observed on the anode of pristine PCFCs (Figure S13). Additionally, we have conducted the second DRM-PCFC stability testing (Figure 4.3H), which achieves >85 hours of stable operation at 650 °C, further confirming the improved durability of DRM-PCFC equipped with the SDC-Ni-Ru catalyst. To the best of our knowledge, we have for the first time lowered the operating temperature of DRM-PCFC stability testing to 650 °C^{28,36,149,151}. As CO is produced at the anode, decreasing the operating temperature tends to favor the coking via Boudouard reaction. Therefore, all previous DRM-PCFC stability were evaluated at 700 °C to avoid coking and achieve durable operation. Despite the stability testing was not performed for an extremely long period (e.g., >1000 hours), the stability demonstrated in this work is much longer than all previously reported DRM-PCFCs and DRM-SOFCs^{28,149,151,186-}

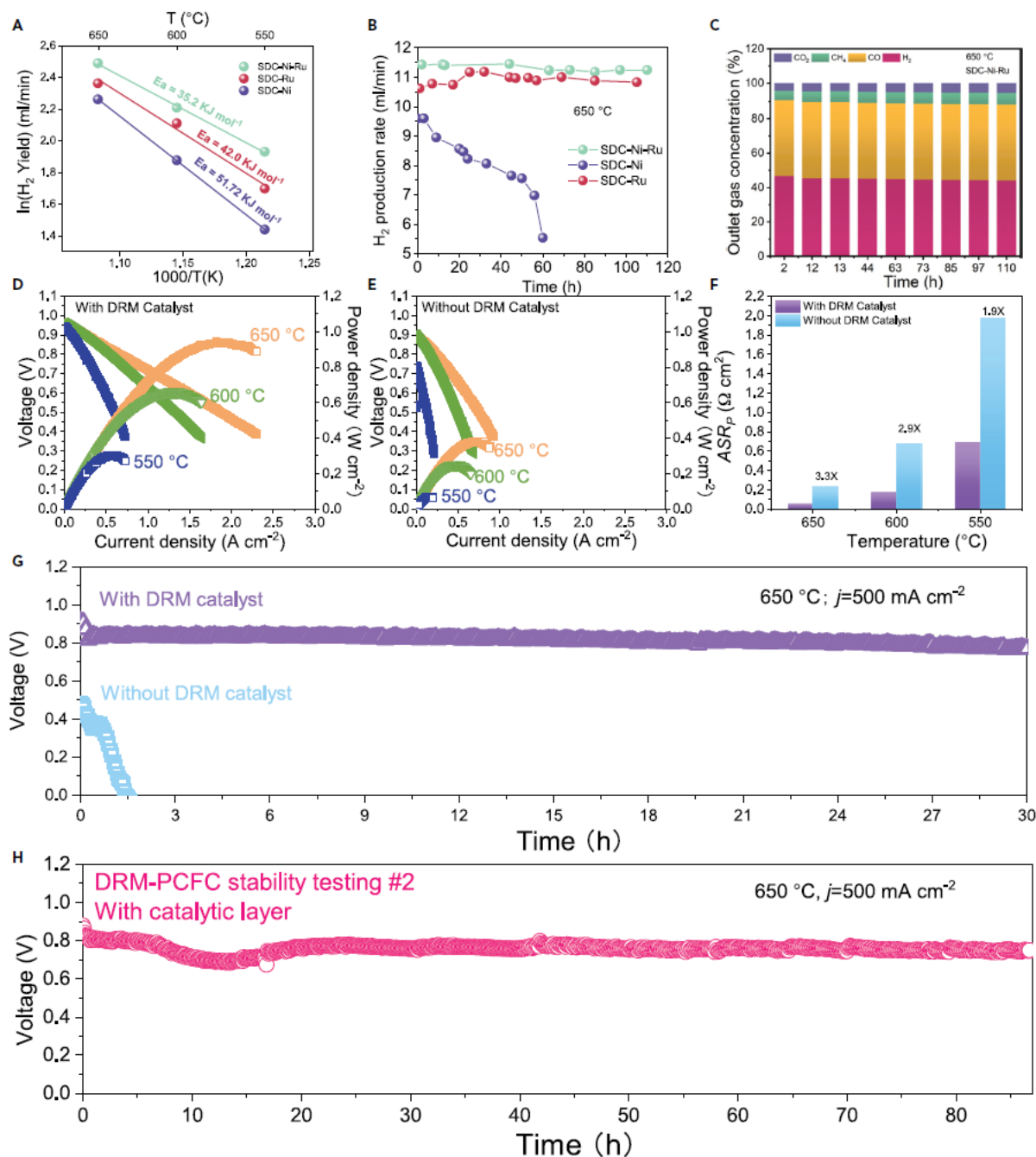


Figure 4.3. DRM-PCFCs equipped SDC-Ni-Ru internal DRM catalyst for power generation, chemical production, and greenhouse gas mitigation. (A) Arrhenius plots for H_2 production rate achieved on SDC-Ni, SDC-Ru, and SDC-Ni-Ru in packed bed reactors. (B) The H_2 production rate as a function of operation time obtained on SDC-Ni, SDC-Ru, and SDC-Ni-Ru in packed bed reactors. (C) The packed bed reactor outlet gas concentration as a function of operation time for SDC-Ni-Ru at 650 °C. (D) I - V and I - P curves of a DRM-PCFC decorated with the SDC-Ni-Ru as the internal DRM catalytic layer at 650-550 °C. A mixture of CH_4 and CO_2 with a CH_4 : CO_2 ratio of 1:1 was fed to the anode and ambient air was fed to the cathode. (E) I - V and I - P curves of a DRM-PCFC without catalytic layer applied at 650-550 °C. The testing conditions are the same as

the PCFCs shown in Figure 4.3D. (F) Comparison of the area specific electrode polarization resistance (ASR_p) of DRM-PCFCs with and without the SDC-Ni-Ru catalyst. (F) Comparison of electrochemical stability of DRM-PCFCs with and without the SDC-Ni-Ru catalyst at 650 °C. The PCFCs were tested under a constant discharging current density of 500 mA cm⁻². (H) The second stability testing of DRM-PCFCs with the SDC-Ni-Ru catalyst at 650 °C and a current density of 500 mA cm⁻², which further validates the durability of DRM-PCFCs. Fuel utilization=4.4%.

4.4.4 In situ spectroscopy studies of the DRM catalyst

In situ DRIFTS experiments were conducted to probe the active intermediate species involved in DRM and understand the DRM mechanisms. As shown in Figures 4.4A-4.4C, time-resolved DRIFTS spectra over three catalysts were collected upon changing the atmosphere from ultrahigh purity (UHP) Ar to CO₂ gas in a high-temperature DRIFTS cell chamber to identify the reactive absorbed species^{190,191}. After the gas was switched, peaks for gaseous CO₂ (~2353.5 cm⁻¹) quickly emerged. Concomitantly, the intensity of the bands belonging to monodentate and bidentate carbonate species gradually increase, implying that they are involved in the CO₂ absorption process (Figure 4.4A-C). Monodentate carbonate was observed on SDC-Ni-Ru and SDC-Ru, while only bidentate carbonate was formed on SDC-Ni. To confirm that the monodentate and bidentate carbonates are the intermediate species chemically adsorbed on the catalysts, DRIFTS spectra were acquired during CO₂ desorption by switching the CO₂ gas to UHP Ar. As shown in Figure S14, the bands assigned to gaseous CO₂ quickly disappeared. At the same time, the carbonate species remained unchanged, confirming that the monodentate and bidentate carbonates could serve as the actively adsorbed species for DRM. After all gaseous CO₂ was removed from the reactor, the reactor atmosphere was changed to CH₄ (Figure 4.4D-F). Upon exposure to CH₄, formyl (~1750 cm⁻¹) was observed on SDC-Ni-Ru and SDC-Ru¹⁹², while CO species were simultaneously produced on these two catalysts. When SDC-Ni-Ru and SDC-Ru were exposed to CH₄ for longer periods of time, the carbonate species (i.e., monodentate carbonate)

gradually decrease, and the CO band tends to decrease, indicating that the carbonate species are consumed and converted to CO. Nevertheless, neither formyl nor CO was detected over the SDC-Ni catalyst. Furthermore, the bands associated with bidentate carbonate remained unchanged after the atmosphere was changed to CH₄, indicating that the carbonate species (i.e., bidentate carbonate) on SDC-Ni react slowly with CH₄ and produce an undetectable amount of CO, which is consistent with the PBR results, which shows that SDC-Ni displays poor DRM activity.

In situ Raman spectroscopy was conducted on both catalysts to study the coking tolerance of SDC-Ni-Ru and SDC-Ni. Compared with postreaction characterization, this *in situ* characterization approach reveals practical information about the dynamic interactions between the reacting gaseous species and catalysts. As shown in Figures 4.4G-H, Raman spectra were collected as a function of time after the catalysts were exposed to a CO₂-CH₄ mixture. The D-band (1350 cm⁻¹) and G-band (1580 cm⁻¹), signs of coking, appeared quickly on SDC-Ni after ~35 mins. Therefore, SDC-Ni is prone to coking, which is consistent with the PBR results. With increasing operating time, the intensity of both peaks increases. An additional 2D band evolved at 2680 cm⁻¹ after 50 mins, indicating continuous coke accumulation and graphene formation. In contrast, no clear signs of coking were observed on the SDC-Ni-Ru catalyst even after 1000 mins of treatment, further validating that SDC-Ni-Ru has significantly enhanced coking tolerance relative to SDC-Ni.

Figure 4.4I presents the proposed DRM mechanism with SDC-Ni-Ru, which shows how Ni and Ru synergize to enhance DRM activity and promote coking tolerance. Ni favors the activation of CH₄, and CH₄ molecules dehydrogenate to CH₃*, CH₂, and CH*, consequently producing H₂. Without the oxidation of CH* to CHO*, further dehydrogenation can lead to coking. However, the bidentate carbonate formed on SDC-Ni does not actively react with CH*. Therefore,

SDC-Ni is unfavorable for the oxidation of CH* and subsequent CO production. Additionally, SDC-Ni is more prone to coking. On the other hand, the addition of Ru accelerates the activation of CO₂ while altering CO₂ activation, forming monodentate carbonate, which is more active in oxidizing CH*. Therefore, CHO* readily forms on SDC-Ni-Ru and SDC-Ru, leading to CO production and enhanced coking tolerance.

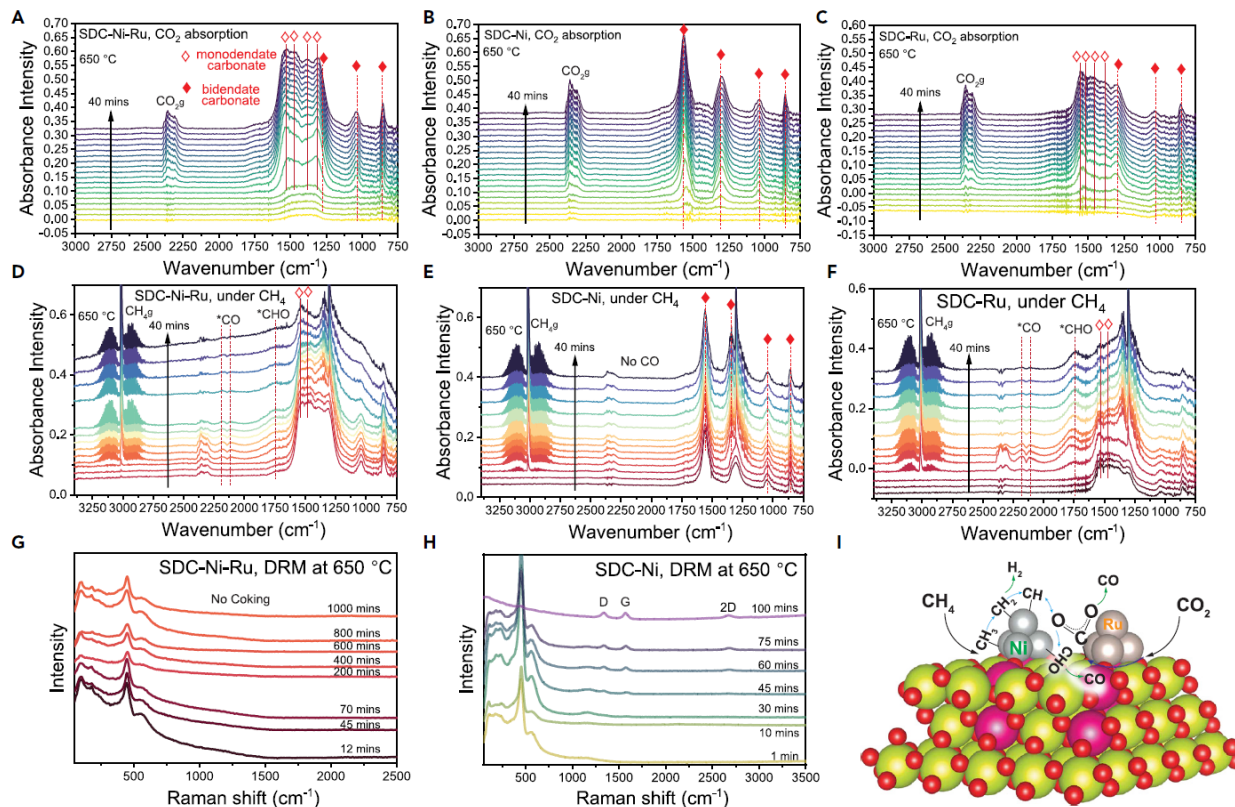


Figure 4.4. *In situ* DRIFTS and Raman spectroscopy to probe the intermediate species and coking tolerance for DRM. *In situ* DRIFTS spectra of CO₂ absorption on (A) SDC-Ni-Ru, (B) SDC-Ni, and (C) SDC-Ru at 650 °C. All samples were first reduced at 650 °C for 1 h and cooled down to 25 °C under H₂. The atmosphere was then changed to ultrahigh purity (UHP) Ar to collect the background. Upon changing the feeding gas from UHP Ar to 20 sccm CO₂ and 20 sccm Ar, the spectra were collected as a function of operation time. *In situ* DRIFTS spectra of dry reforming of methane by chemically adsorbed species on (D) SDC-Ni-Ru, (E) SDC-Ni, and (F) SDC-Ru at 650 °C. After purging 100 sccm UHP Ar for CO₂ desorption, the atmosphere was then switched to 20 sccm CH₄ and 20 sccm Ar. *In situ* Raman spectroscopy of DRM on (G) SDC-Ni-Ru and (H) SDC-Ni at 650 °C. The gas fed to the high-temperature Raman cell was 10 sccm CH₄ and 10 sccm CO₂. D indicates disordered carbon. G corresponds to the graphite. 2D is attributed to the 2-dimentional graphene. (I) Proposed DRM mechanism on SDC-Ni-Ru. The Ce, O, Sm, Ni, and Ru atoms are in yellow, red, wine, grey, and brown, respectively.

4.4.5 Density functional theory (DFT)

Model SDC-Ni and SDC-Ru catalysts consisting of Ni₄ and Ru₄ clusters supported on SDC substrates were employed for DFT modeling to elucidate the conversions of CH₄ and CO₂ at different active sites. XRD Rietveld refinement (Figure 4.2C) and HAADF-EDS mapping results (Figure 4.2E) indicated that Ni and Ru clusters coexist independently on the SDC support. Therefore, the reactions taking place on Ni and Ru clusters were modeled individually. SDC-supported pyramidal Ni₄ and Ru₄ clusters were chosen since these are the simplest 3D metal catalyst clusters consisting of both interfacial metal sites and free metal sites. This configuration has been widely adopted to represent supported metal catalysts for DFT calculations¹⁹³⁻¹⁹⁷. The optimized catalyst models are illustrated in Figures 4.5A-D. For the SDC substrate, 4 Ce atoms in the CeO₂ (111) slab were replaced with Sm atoms. The lattice constant of the optimized SDC is 5.411 Å, in good agreement with the XRD measurements reported in Table S3 (5.448 Å). The Sm doping sites were determined according to a report by Ren and coworkers¹⁷². Because of the valence state difference between Ce and Sm, Sm doping is expected to promote oxygen vacancy formation. The most stable oxygen vacancy positions are indicated by black circles in Figure 4.5C-5D. Both the Ni₄ and Ru₄ clusters bond with three surface lattice oxygen atoms. Upon optimization, the top Ru atom in Ru₄ displays slight tilting toward one of the surface Ce atoms.

Free energy profiles. The free energy profiles depicting DRM on different active sites are shown in Figure 4.5E. All Gibbs free energies were estimated at 873 K (600 °C) and 1 bar using the standard statistical mechanical approach¹⁹⁸. The gas phase reactants (CH₄ and CO₂) and the clean surface were used as the free energy reference state. Free energy changes and energy barriers of elementary steps are shown in Table S5. The binding energies (BE) of the intermediate species reported in Table S6 are defined according to Eqn. 1:

$$BE = E_{total} - E_{adsorbate(g)} - E_{surface} \quad (1)$$

where E_{total} , $E_{adsorbate(g)}$, and $E_{surface}$ represent the total energies of the adsorbed surface species, adsorbate in the gas phase, and clean surface, respectively. The optimized structures of the intermediate species on the SDC-Ni and SDC-Ru surfaces are illustrated in Figure S15 and Figure S16, respectively.

Activation of CH₄ and CO formation routes. The initial C-H bond activation is a rate-limiting step in the DRM process, which usually takes place at metal sites^{15,140,199}. As shown in Figure 4.5E, the first C-H bond activation is exothermic on both Ni₄ and Ru₄. The energy barrier on Ni₄ is 0.58 eV, which is lower than that on Ru₄ (1.04 eV). The dissociated CH₃* then undergoes stepwise decompositions to yield CH*. On Ni₄, the formation of CH* is facile, with negligible energy barriers. Overall, CH₄ decomposition is favored on Ni sites. On Ru₄, the conversion of CH₃* into CH₂* is more hindered. Moreover, *in situ* DRIFTS reveals the presence of the CHO intermediate only on the SDC-Ru and SDC-Ni-Ru surfaces. Hence, we can conclude that on SDC-Ni, the CH* → C* → CO* pathway is favored.

Adsorption and conversion of CO₂. *In situ* DRIFTS also suggests different configurations for the carbonates formed on SDC-Ni and SDC-Ru. All the corresponding structures were optimized using DFT calculations and used for free energy calculations. As shown in Figure S15, on SDC-Ni, the carbon in CO₂ binds the surface lattice oxygen of SDC, with one of the O atoms in CO₂ located near the oxygen vacancy site and the other anchored by Ni₄. On SDC-Ru, as shown in Figure S16, the C in CO₂ binds a surface SDC lattice oxygen, while one of the CO₂ oxygens is anchored by Ru₄. Both configurations have been identified on the CeO₂ surface in previous research by *in situ* DRIFTS and DFT calculations^{191,200}. The adsorbed CO₂ has lower free energy on Ru₄. As shown in Table S6, the binding energies of CO₂ on SDC-Ni₄ and SDC-Ru₄ are -1.47

eV and -1.72 eV, respectively. The CO₂ dissociation energy on the Ru₄ site is also much lower than that on the Ni₄ site (1.66 eV lower), which makes the CO₂ activation process exothermic on the Ru₄ site but endothermic on the Ni₄ site. Therefore, CO₂ activation is favorable on the Ru₄ site. Combined with CH₄ decomposition, CH* is more likely to utilize the O atoms from CO₂ dissociation, producing CHO* as the intermediate for CO* production.

Synergistic effect between Ni and Ru. The DFT calculations performed on SDC-Ni and SDC-Ru yielded findings consistent with *in situ* DRIFTS and enabled us to elucidate the reaction pathways at different active sites in SDC-Ni-Ru. It was found that Ni₄ is more active for the activation of CH₄, which works as a carbon and hydrogen supply for DRM, while Ru₄ plays a larger role in enhancing CO₂ adsorption and activation. As shown in Figure 4.4I, in the absence of Ru, stronger CH₄ activation may result in excessive carbon formation and make the C to CO conversion less efficient. Overall, this limits the performance of the entire DRM process. In a dual-site system, the Ru component contributes the necessary oxygen source. In this work, we demonstrated that the unique ability of Ni and Ru could be utilized simultaneously in a unified SDC-Ni-Ru system. The Ni sites provide high CH₄ activation capacity, while the Ru sites could activate CO₂ effectively, which significantly improves DRM performance. A similar synergistic effect was also revealed on a CeO₂-Ni-Ru catalyst for the DRM reaction¹⁴⁰. The free energy of SDC-Ni-Ru is plotted in Figure 4.5E with the solid green line and shows that the energy barriers are mitigated significantly through the simultaneous use of Ni and Ru, especially for activating the first C-H bond of CH₄, CH* → CO* formation, and CO₂ activation.

Coke formation. The different characteristics of the Ni and Ru sites and the synergic effect also account for the coking resistance of SDC-Ru and SDC-Ni-Ru. On the SDC-Ni surface, the high capacity for CH₄ activation provides abundant carbon. However, the lack of an oxygen supply

led to an accumulation of carbon on the surface, which is responsible for the poor coking resistance of SDC-Ni. For the SDC-Ru catalyst, a weaker carbon supply and abundant oxygen atoms from CO₂ activation make carbon accumulation on the surface more difficult. On the SDC-Ni-Ru surface, even though Ni sites boost the carbon supply, the accumulated carbon could be removed efficiently by coupling with oxygen supplied by the strong CO₂ activation on the Ru sites.

Besides, the free energy changes and energy barriers for C-C coupling on Ni₄ and Ru₄ were calculated, as shown in Figure S17 and Table S5. Both the activation energy barrier and free energy change in C-C coupling are higher on Ru₄ in Figure S17 (1.08 eV higher of energy barrier, 1.26 eV higher of free energy change), consistent with the observation that the Ru sites are more durable during DRM.

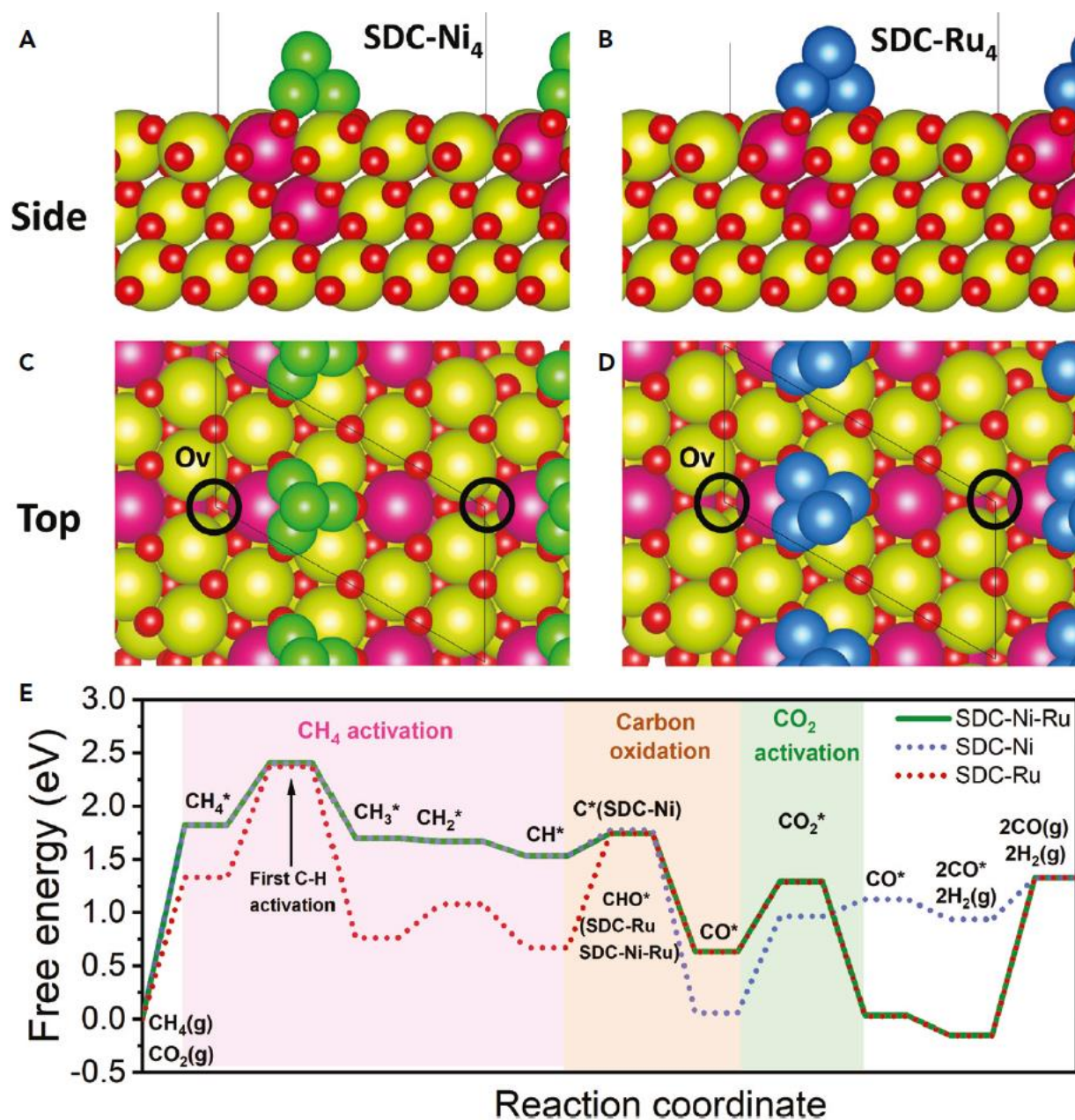


Figure 4.5. DFT calculations to study the synergistic effects between Ni and Ru for DRM. (Optimized SDC-Ni₄ (A, C) and SDC-Ru₄ (B, D) surfaces. Solid black lines indicate the supercell boundaries. Positions of oxygen vacancies are indicated with black circles. The Ce, O, Sm, Ni, and Ru atoms are in yellow, red, wine, green, and blue, respectively. (E) Free energy diagram depicting DRM performance on SDC-Ni, SDC-Ru, and SDC-Ni-Ru generated at 873 K and 1 bar. Key pathways include CH₄ activation, carbon oxidation, and CO₂ activation.

4.5 Conclusions

Herein, the operations of high-performance PCFCs, which intensify electrochemical power generation through DRM, were successfully demonstrated for power generation, chemical production, and greenhouse gas mitigation. A rational designed DRM catalyst, SDC-Ni-Ru, was developed for the PCFCs, which simultaneously accelerates CH₄ activation, CO₂ activation, and mitigation of coking, leading to exceptional DRM performance and coking tolerance. The PCFCs decorated with the SDC-Ni-Ru internal DMR catalyst achieve groundbreakingly high power densities of 0.94, 0.65, and 0.30 W cm⁻² at 650 °C, 600 °C, and 550 °C, respectively, and outperform all previous DRM-PCFCs. Both experimental and computational studies were conducted to probe the DRM mechanisms and understand how the synergistic effect between Ni and Ru facilitates DRM and improves coking tolerance. The results of this work highlight the potential of DRM-PCFCs to address the challenges associated with power generation, chemical manufacturing, and greenhouse gas mitigation.

4.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1016/j.joule.2023.05.009>.

Chapter 5 – Direct CH₄-fed SOFCs for vehicle applications

5.1 Nanocomposite catalyst for high-performance and durable intermediate-temperature methane-fueled metal-supported solid oxide fuel cells

5.1.1 Abstract

CH₄-fueled metal-supported solid oxide fuel cells (CH₄-MS-SOFCs) are propitious as CH₄ is low-priced and readily available, and its renewable production is possible, such as biomethane. However, the current CH₄-MS-SOFCs suffer from either poor power density or short durable operation, which is ascribed to the low catalytic activity and poor coking tolerance of the metallic anode support. Herein, we have deliberately designed and synthesized a highly active nanocomposite catalyst, Sm-doped CeO₂-supported Ni, as the internal steam methane reforming catalyst, to optimize CH₄-MS-SOFCs. Both power densities and durability of optimized CH₄-MS-SOFCs have been dramatically enhanced compared to the pristine CH₄-MS-SOFCs. The optimized CH₄-MS-SOFCs deliver the highest performances among all zirconia-based CH₄-MS-SOFCs. Furthermore, the operating temperature has been reduced to 600 °C. At 600 °C, a viable peak power density of >350 mW/cm² is achieved, which is more than three times as high as the pristine CH₄-MS-SOFCs. Furthermore, the optimized CH₄-MS-SOFC achieves >1000 hours of stable operation.

5.1.2 Introduction

Metal-supported solid oxide fuel cells (MS-SOFCs) have attracted growing attention in recent decades, which is attributed to their unique advantages over ceramic/cermet-supported SOFCs. These advantages include fast start-up capability, high robustness, exceptional tolerance to aggressive thermal excursions, and utilization of low-cost alloys as the anode support²⁰¹⁻²¹⁰. Compared to the batteries, it is much faster to refuel or recharge the fuel cell system. Furthermore, solid oxide fuel cells (SOFCs), including MS-SOFCs, can directly use various fuels, such as natural gas, for power generation²¹¹⁻²¹³. As the natural gas transportation and storage

infrastructures have been well-established, natural gas could be readily available to refuel MS-SOFC systems without extensive modification to the current natural gas infrastructures. Therefore, methane-fueled fuel cells offer a bright future for near- to mid-term, high-efficiency power generation. Among all technologies that could provide power for electric vehicles (EVs), the CH₄-MS-SOFC has been considered as one of the most promising power generators and range extenders, which can power EVs with a prolonged driving range. Moreover, the CH₄-MS-SOFC systems could be widely implemented in the power generation sector, ranging from 500W systems deployed in remote areas as backup power supplies to hundreds of MW systems that could serve as stationary power plants.

In the last two decades, there have been astonishing demonstrations of high-performance MS-SOFCs for power generation. For example, Tucker et al. have devoted extensive efforts to optimizing the MS-SOFC manufacturing processes and pioneered a unique approach to fabricating scalable and low-cost MS-SOFCs that exhibit exceptional performance under H₂^{205,214,215}. Commercially relevant MS-SOFCs have been demonstrated by the Technical University of Denmark for automotive applications, which deliver outstanding power densities (e.g., 1.9 W/cm² at 750 °C)²¹⁶. Most recently, a new generation of H₂-MS-SOFC with an impressive power density of 3.13 W/cm² at 800 °C has been reported by David et. al.²¹⁷. Moreover, intermediate-size (~25 cm²) and large-area (up to 300 cm²) MS-SOFCs have been successfully manufactured^{202,203}. For example, an MS-SOFC short stack with an active area of 80 cm² was built and tested upon rapid thermal cycling. Despite the cell showing a temperature gradient of 30 °C/cm², no gas leakage or cracking is observed, validating the robustness of MS-SOFCs²¹⁸. Additionally, MS-SOFCs have attracted attention from industries^{219,220}. Ceres Power has pioneered an advanced MS-SOFC technology, namely SteelCell[®], which displays high robustness, enhanced energy efficiency, and

reduced manufacturing cost²²¹. The research, development, and deployment activities in both research institutes and industries have dramatically accelerated the global development and commercialization of MS-SOFCs²²².

H₂-MS-SOFCs have been widely studied and demonstrated for efficient and durable power generation. A peak power density (PPD) of >1.2 W/cm² could be readily achieved at 750 °C. Furthermore, >3000 hours of stability testing have been validated^{223,224}, indicating H₂-MS-SOFCs exhibit comparable or even higher performances than conventional SOFCs. Methane possesses a much higher volumetric energy density (~230 MJ/m³) than that of H₂ (~10.1 MJ/m³), allowing the use of smaller fuel tanks, which is essential for vehicular applications. The low transportation and storage cost of methane could further enhance its economic viability. Moreover, it has been recognized that the fuel cell system powered by methane enables the realization of higher “well-to-wheels” fuel conversion efficiencies^{225,226}. However, prior research on MS-SOFCs centers on either optimizing manufacturing processes or developing H₂-MS-SOFCs, while a limited amount of work has been conducted on CH₄-MS-SOFCs, which is ascribed to the poor performance and poor durability of MS-SOFCs under methane^{213,227,228}. Poor performance and durability are ascribed to the catalytically inactive metallic support that functions only as mechanical support without contributing to the reforming of methane. Furthermore, in this work, we recognize that MS-SOFCs are very prone to coking, even at a relatively high steam to carbon ratio of 1:1. Therefore, internal steam methane reforming (SMR) catalysts that could be physically and chemically compatible with the MS-SOFCs are critical needs for enhancing both fuel cell performances and achieving long-term durable operation. Decorating the anode with catalysts via impregnation and applying a reforming layer have been demonstrated for improving performance

and stability of conventional SOFCs²²⁹⁻²³². However, as the development of CH₄-MS-SOFCs is in early stage, there are few works reported on decorating the metallic anode of CH₄-MS-SOFCs.

In this work, an effective and scalable approach has been validated to optimize the anode of CH₄-MS-SOFCs, which significantly improves their performance and stability at intermediate operating temperatures. A highly active nanocomposite internal SMR catalyst, Sm-doped CeO₂-supported Ni, was carefully designed and synthesized, which was subsequently applied over the metallic anode support as the internal SMR catalytic layer. Both power densities and durability of optimized CH₄-MS-SOFCs have been dramatically enhanced. For example, the operating temperature of CH₄-MS-SOFCs can be reduced to 600 °C. Additionally, a viable peak power density of >350 mW/cm² and >1000 hours stability testing has been demonstrated at 600 °C under CH₄. The degradation rate is <0.1mV/h. No coking was observed after >1000 hours operation with CH₄ as the fuel.

5.1.3 Methods and materials

5.1.3.1 Material and catalyst preparation

Sm_{0.25}Ce_{0.75}O_{2-δ}-supported Ni catalysts (SDC-Ni) were synthesized through three different methods, including SDC-Ni Wet-Chemistry, SDC-Ni-Anode, and SDC-Ni-Impregnation. The Ni loading of these three catalysts is 40 wt. %. The one-pot wet-chemistry method was used to prepare the SDC-Ni Wet-Chemistry catalyst. A stoichiometry amount of samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was firstly dissolved in distilled water. Then the ethylene glycol (EG) and citric acid (CA) were added into the above metal salt solution with a mole ratio of 0.1:0.1:1 (EG : CA : total metal ions). The above solution was subsequently stirred to get a

homogeneous mixture and then heated at 250 °C until a gel was formed. The gel was immediately moved to a drying oven at 175 °C for 24 h. The gel turned into black powder, which was then calcined under air at 600 °C for 5 hours to obtain the unreduced SDC-Ni Wet-Chemistry catalyst.

SDC-Ni-Impregnation was prepared by using the conventional wet impregnation method, which has been widely used for synthesizing heterogenous catalysts²³³. The oxide support, $\text{Sm}_{0.25}\text{Ce}_{0.75}\text{O}_{2-\delta}$, was first synthesized by using the same method for synthesizing SDC-Ni Wet-Chemistry without adding Ni precursor. After drying in the oven and calcination at 600 °C for 5 hours, wet impregnation was conducted by adding DI water and a stoichiometric amount of nickel (II) nitrate hexahydrate. After continuous stirring and heating at 250 °C, the dry composite powder was then calcined in air at 600 °C for 5 hours to obtain unreduced SDC-Ni-Impregnation.

SDC-Ni Anode and Ytria-stabilized zirconia supported Ni (YSZ-Ni) Anode catalysts were prepared through a physical mixing approach, which is the same as the SOFC anode powder preparation processes. Here, the $\text{Sm}_{0.25}\text{Ce}_{0.75}\text{O}_{2-\delta}$ (SDC), was synthesized by using the same method of the SDC powder prepared for the SDC-Ni-Impregnation catalyst. Commercial YSZ powder was purchased from TOSOH corporation. Firstly, SDC or YSZ powder was mechanically mixed with NiO to meet the desired 40 wt.% metallic Ni loading. This composite mixture was ball-milled in ethanol with 10 mm YSZ beads for 12 hours, followed by drying at 80 °C overnight to get the final catalysts.

5.1.3.2 Catalyst characterization

The X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2 θ : 20-80°, scanning speed: 1°/min). The as-fired catalysts were reduced under 40% H₂ balanced with N₂ (20 sccm H₂+30 sccm N₂) at 600 °C for 2 hours. X-ray photoelectron spectroscopy (XPS) was performed

by using Phi 5000 VersaProbe II X-ray Photoelectron Spectrometer. Transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were performed with an FEI Talos F200X TEM/STEM using a 200 keV accelerating voltage.

The morphology of reduced catalysts was examined using transmission electron microscopy (TALOS F200X, Thermo Fisher Scientific)).

H₂-temperature-programmed reduction (H₂-TPR) was conducted using a ChemBET Pulsar. 0.1 g of the catalyst was pretreated in a U-shaped quartz tube at 140 °C for half an hour under flowing of N₂ (100 sccm) to remove any moisture and impurities. After cooling down to 25 °C, the gas was switched from N₂ to 15 % H₂ balanced with Ar under a flow rate of 100 sccm. The TPR analysis was then performed with a heating rate of 10 °C/min.

The metallic Ni surface area and Ni dispersion were measured by performing H₂ pulse chemisorption. H₂ pulse chemisorption was also conducted using a ChemBET Pulsar. 0.1 g of the catalyst was loaded in a U-shaped quartz tube and reduced at 600 °C for two hours under 40% H₂ balanced with N₂ (the same reduction procedure with catalyst testing in a fixed bed reactor). At 600 °C, the atmosphere was then changed to ultra-high purity (UHP) nitrogen for 2 hours to remove the gaseous and adsorbed hydrogen. After cooling the temperature to 25 °C under UHP nitrogen, 50 µL H₂ was repeatedly injected into the reactor until the H₂ chemisorption on Ni reaches equilibrium. The metallic Ni surface area and dispersion were analyzed by using Quantachrome TPRwin v4.1.

5.1.3.3 Catalyst testing

The steam methane reforming catalytic activities were evaluated in a continuous flow fixed bed (quartz) tubular reactor (0.28-inch i.d.) at 0.1MPa. 80 mg of each catalyst was loaded into the reactor. A thermocouple was inserted into the tube reactor close to the catalyst to measure the

temperature. The catalyst was first reduced under 40% H₂ balanced with Ar (50 sccm) at 600 °C for two hours. After reduction, the reactor temperature was decreased to 550 °C and 10 sccm CH₄ gas was flowed through a heated water bubbler with a steam to carbon (S/C) ratio of 1:1 to the reactor (GHSV= 15000 ml h⁻¹g⁻¹). The outlet gas compositions were determined using online gas chromatography (INFICON 3000 Micro GC) from 550 to 650 °C with 25 °C intervals. Before measurement, the reactor was kept at each temperature for around 40 min to reach equilibrium. The CH₄ conversion (X_{CH_4}), H₂ production rate (PR_{H_2}) are calculated as follows:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (1)$$

$$PR_{H_2} = \frac{F_{H_2,out}}{W_g} \times 100\% \quad (2)$$

Where F_{in} or F_{out} represents the flow rate of inlet gas or outlet gas, respectively. W_g refers to the catalyst weight, which is 80 mg.

5.1.3.4 MS-SOFC structure and testing

All MS-SOFCs tested in this work were manufactured by Nissan Technical Centre North America and Nissan Research Centre, Nissan Motor Corporation Limited. A porous Fe-Cr alloy was employed as the metallic anode support. A composite of ScYSZ and Ni (40 wt% ScYSZ + 60 wt% NiO) was used as the anode function layer. The electrolyte is ScYSZ. Its thickness is ~8 µm. A gadolinia doped ceria (GDC) barrier layer with a thickness of 1 µm was applied on the electrolyte. The half-cell, including the Fe-Cr alloy support, a composite ScYSZ+Ni anode functional layer, ScYSZ electrolyte and GDC barrier were made by tape casting methode^{234,235}. A conventional La_{0.6}Sr_{0.4}CoO₃ (LSC) made by sol-gel method²³⁶ was screen painted as the cathode. The pristine CH₄-MS-SOFCs studied in this work were preliminary optimized by Nissan by infiltrating a certain amount of SDC-supported Ni. However, the preliminary optimization does

not lead to outstanding performance. The optimized CH₄-MS-SOFCs was modified by using the SDC-Ni Wet-Chemistry catalyst. To optimize the MS-SOFCs, the SDC-Ni Wet-Chemistry catalyst was mixed with binder and dispersant to prepare the catalyst ink, which was then coated on the anode of MS-SOFC. The cell was sealed on an alumina tube using a glass sealant (MO·SCI: 1709P/-45). The gold paste was used as the current collector. Their electrochemical performances were evaluated at 700, 650, and 600 °C using a Gamry 3000 Potentiostat. Dry H₂ was used in this work to first evaluate the performance of MS-SOFCs. A S/C ratio of 1 is used for testing the performance of CH₄-MS-SOFCs. The CH₄ flow rate is 10 sccm. The steam concentration was controlled by bubbling CH₄ gas through a custom designed bubbler unit. An Agilent GC 6890 gas chromatography equipped with a thermal conductivity detector was used to measure the anode outlet gas compositions. Bruker Senterra Raman Microscope is used for performing Raman spectroscopy. The effective electrode area of the cell is 0.7 cm².

5.1.4 Results and discussion

5.1.4.1 Current research and development status of CH₄-MS-SOFCs

As illustrated in Figure 5.1A, MS-SOFCs demonstrated in this work are composed of multiple layers with a porous Fe-Cr alloyed support. This porous metallic support is the key to MS-SOFCs, which greatly enhances the thermal cycling stability that is essential for automotive applications. Additionally, the metallic support is mechanically robust, which significantly improves the resistance to vibration, allowing MS-SOFCs to provide resilient power for the vehicles. It has been suggested that porous stainless steel manufactured via powder metallurgy could be the optimal metallic support^{202,237}. However, the porous stainless steel is catalytically inactive, which leads to low methane conversion and cell performances under methane^{213,227}.

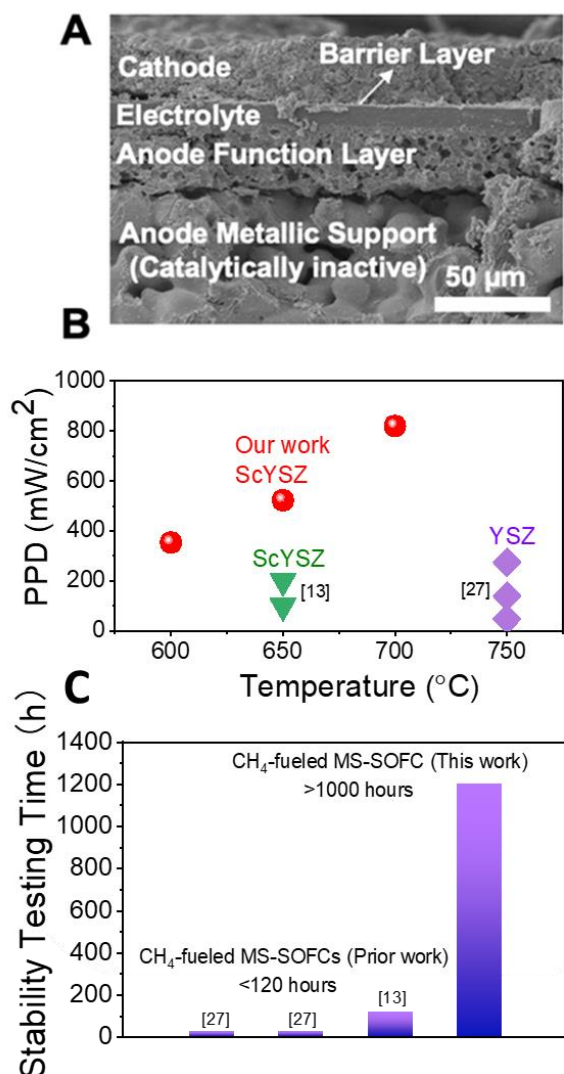


Figure 5.1. Methane-fueled metal-supported solid oxide fuel cells. (A) A scanning electron micrograph of a single cell. (B) Peak power densities (PPD) of methane-fueled MS-SOFCs. (C) Demonstrated stability testing time of methane-fueled MS-SOFCs.

Figures 5.1B and 5.1C, and Table S1^{213,227} summarize the previous decades of progress in CH_4 -MS-SOFCs that are equipped with zirconia-based electrolytes, including ScYSZ and Y_2O_3 stabilized ZrO_2 (YSZ). CH_4 -MS-SOFCs deliver much lower power densities than H_2 -MS-SOFCs. For instance, ScYSZ-based CH_4 -MS-SOFCs achieve a PPD of $<200 \text{ mW}/\text{cm}^2$ at 650°C while a PPD of $<300 \text{ mW}/\text{cm}^2$ has been demonstrated using YSZ-based CH_4 -MS-SOFCs at 750°C , which are much lower than the performance under H_2 . The long-term stability testing is limited to <200

hours of operation (Figure 5.1C), suggesting the durability of CH₄-MS-SOFCs lags far behind conventional direct-methane SOFCs. Poor performance and durability are ascribed to the catalytically inactive metallic support that functions only as mechanical support without contributing to the reforming of methane. Therefore, internal SMR catalysts are critical needs for enhancing both fuel cell performances and achieving long-term durable operation. It is expected CH₄-MS-SOFCs equipped with the internal SMR catalyst could improve the PPD to >500 mW/cm² at 650 °C and achieve >1000 hours of stable operation, which is essential for the implementation of CH₄-MS-SOFCs.

5.1.4.2 Rationally design and synthesize SMR catalyst for CH₄-MS-SOFCs

Despite the few reports of CH₄-MS-SOFCs, the strategies that have been established for improving internal SMR activities and coking tolerance of direct-methane ceramic/cermet-supported SOFCs can be leveraged for modifying MS-SOFCs. Figure S1 illustrates two primary approaches to improving the catalytic activities of CH₄-MS-SOFCs, which include decorating the porous anode scaffold with nanosized catalysts and applying a catalyst layer over the metallic anode support. However, decorating the porous metallic anode scaffold with nanosized catalysts is time-consuming, costly, and unscalable. It is therefore not expected that this approach can be directly adopted to decorate the anode of CH₄-MS-SOFCs. Alternatively, applying a thin catalyst layer over the anode is straightforward, which can internally and efficiently reform CH₄ and convert CH₄ to H₂ and CO for power generation. Additionally, this thin catalyst layer, which is similar to the thin cathode layer applied on the electrolyte, does not reduce the thermal cycling stability of MS-SOFCs. Therefore, it is suggested that applying a catalyst layer over the metallic anode support could be a better approach.

To build high-performing and durable CH₄-MS-SOFCs, this catalyst layer must concurrently exhibit high catalytic activity, electronic conductivity, and coking tolerance. Herein, we center on deliberately designing and synthesizing the internal SMR catalyst. As shown in Figures 5.1B and 5.1C, a SMR catalyst, which is a composite of Sm-doped CeO₂ and Ni (see method), has been developed and applied as the internal SMR catalyst, achieving the highest peak power densities and longest stability operation among all zirconia-based CH₄-MS-SOFCs. The validated performances and durability indicate that modifying the metallic anode support with a catalytic layer can be an effective approach.

Sm-doped CeO₂ (SDC) is widely used as the component of conventional SOFC anodes, which has been validated with excellent catalytic activity and coking tolerance for direct-methane SOFCs²³⁸⁻²⁴⁰. Despite SDC-supported Ni having been used as the anode of conventional SOFCs, it has not been adopted as the internal SMR layer of CH₄-MS-SOFCs. As the metallic support does not conduct oxygen ions, this catalytic layer will not exhibit electrochemically active interfaces that could partially oxidize the methane, which is different from the SDC-Ni cermet anode of conventional SOFCs. Therefore, careful engineering of SDC-supported Ni to fine-tune the interactions between SDC and Ni is essential for the conversion of methane to syngas. We have synthesized SDC-Ni via three approaches, including the wet-chemistry method (SDC-Ni Wet-Chemistry), impregnation that is typically used for preparing thermochemical catalysts (SDC-Ni impregnation), and physically mixing SDC with NiO that is used for preparing the cermet anode of conventional SOFCs (SDC-Ni anode). Additionally, we also synthesized and characterized YSZ-Ni which is a well-known anode of SOFCs (YSZ-Ni anode).

The catalytic activity and properties of these four catalysts were first measured in a packed bed reactor (Figures 5.2A-5.2B). We then correlate the SMR performance with their chemical

compositions, crystal and electronic structure, oxide-Ni interactions, and microstructure. A composite of SDC and NiO could be obtained via all these three approaches (Figure S2), suggesting these three approaches can all produce SDC-supported NiO. Upon reduction under H₂, NiO can be reduced to metallic Ni (Figure S3), creating interfaces between SDC and metallic Ni that serve as the active sites for SMR. It has been recognized that the catalyst synthesis processes can modulate these interfaces and tune the interactions between SDC and Ni²⁴¹⁻²⁴³. As shown in Figures 5.2A-5.2B, SDC-Ni Wet-Chemistry delivers the highest methane conversion and H₂ production rate among all three SDC-supported Ni catalysts. Additionally, SDC-Ni Wet-Chemistry achieves better performances than YSZ-Ni anode, suggesting SDC-Ni Wet-Chemistry can lead to higher internal SMR activity than that of YSZ-Ni cermet SOFCs. Furthermore, the highest amount of H₂ is produced over SDC-Ni Wet-Chemistry (Figure 5.2B). The outstanding SMR activity of SDC-Ni Wet-Chemistry suggests SDC-Ni Wet-Chemistry can be used to enhance CH₄-MS-SOFCs.

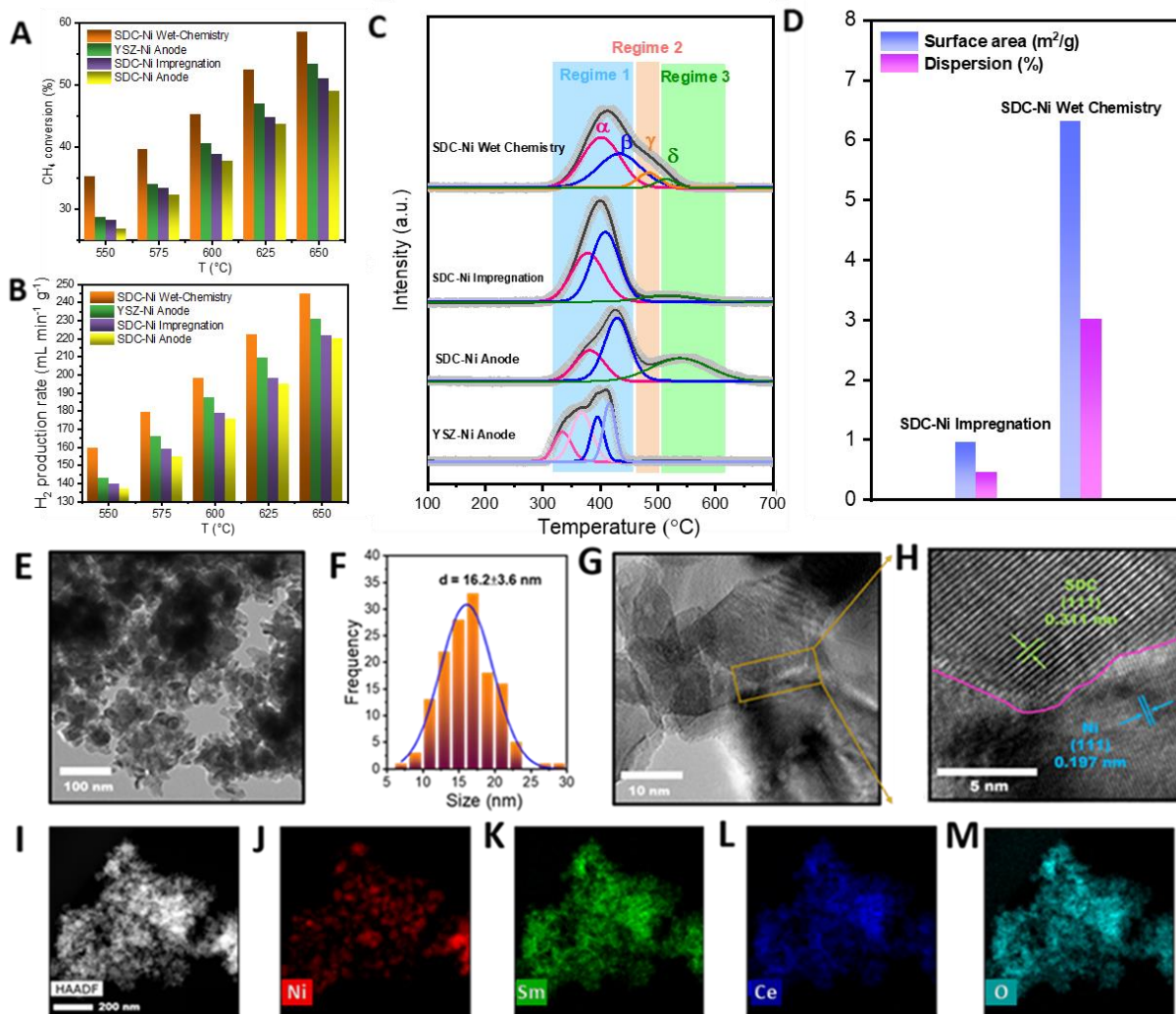


Figure 5.2. Rationally develop internal steam methane reforming catalysts. (A) The CH_4 conversion over four SMR catalysts in packed bed reactors (GHSV=15000 mL/h/g, S/C=1). (B) The H_2 production rate over four SMR catalysts in packed bed reactors (GHSV=15000 mL/h/g, S/C=1). (C) H_2 -temperature-programmed reduction profiles of four catalysts. (D) The active metallic Ni surface area and dispersion determined by pulsed H_2 chemisorption. (E) Bright-field TEM image of reduced SDC-Ni Wet-Chemistry. (F) Particle size distribution of reduced SDC-Ni Wet-Chemistry. (G-H) High-resolution TEM images of reduced SDC-Ni Wet-Chemistry. (I) High-angle annular dark-field (HAADF) image of reduced SDC-Ni Wet-Chemistry. (J-M) Energy-dispersive X-ray spectroscopy (EDS) mapping of reduced SDC-Ni Wet-Chemistry.

The H_2 temperature-programmed reduction (H_2 -TPR) profiles of these four catalysts (Figure 5.2C) present the reducibility of Ni and the interactions between oxide support and metallic Ni. The reduction peaks fall into three temperature ranges, which correspond to different extents

of oxide support-Ni interactions^{176,177}. In Regime 1, the peaks denoted as α and β are attributed to the reduction of bulk NiO. Both α and β peaks of SDC-Ni Wet-Chemistry shift to higher temperatures than SDC-Ni impregnation and SDC-Ni anode, indicating the wet-chemistry method leads to stronger oxide support-Ni interactions. As enhancing oxide support-metal interactions can be a promising approach to improving the catalytic performance and stability²⁴⁴, the excellent catalytic performances of SDC-Ni Wet-Chemistry can be due to strong oxide support-Ni interactions.

SDC-Ni Wet-Chemistry possesses an α peak that is larger than the β peak, while the α peaks of other catalysts are smaller than their β peaks. The α peak represents the NiO with smaller particle size and the β peak shows the reduction of NiO with bigger particle size^{245,246}, indicating that the wet-chemistry method could produce a higher amount of small-size NiO particles. The transmission electron microscopy (TEM) images (Figure S4) and pulsed H₂ chemisorption results (Figure 5.2D) also show that SDC-Ni Wet-Chemistry possess the smallest Ni particle and the highest dispersity, creating large active interfaces and consequently achieving high SMR performances.

The γ peak in Figure 5.2C can be attributed to the *in-situ* exsolution of Ni nanoparticles from the SDC lattice, which requires a higher reduction temperature and driving force to reduce the NiO trapped into SDC lattice. As the wet-chemistry approach can mix the ions, including Sm³⁺, Ce³⁺/Ce⁴⁺, Ni²⁺, at an atomic level, SDC traps a certain amount of Ni. Therefore, only the H₂-TPR profile of SDC-Ni Wet-Chemistry displays the γ peak. The exsolution of Ni nanoparticles creates Ni vacancies in the SDC lattice, which subsequently reduces a number of the Ce⁴⁺ ions to Ce³⁺ ions to maintain charge neutrality. In Regime 3, the peak denoted as δ is associated with the reduction of Ce⁴⁺ to Ce³⁺ by gaseous H₂. The SDC-Ni Wet-Chemistry catalyst possesses the smallest δ peak

area, confirming the *in-situ* exsolution of Ni nanoparticles. The TEM image of reduced SDC-Ni Wet-Chemistry shows Ni particles are uniformly dispersed on the SDC support (Figure 5.2E). The average particle size is around 16.2 nm (Figure 5.2F). Ni and SDC are in close contact with each other, forming a metal-support active interface (Figures 5.2G-5.2H). The SDC (111) interplanar spacing of SDC-Ni Wet-Chemistry is 0.311 nm, which is smaller than that of SDC-Ni Anode (0.319 nm) and SDC-Ni Impregnation (0.319 nm). As the radius of Ni^{2+} (55 pm) is smaller than that of Sm^{3+} (95.7 pm) and Ce^{4+} (87 pm)²⁴⁷, the larger lattice spacing of SDC (Figure S5) further affirms that the wet-chemistry method could enhance the amount of Ni doped into the SDC lattice. In addition, the EDS mapping (Figures 5.2I-5.2M) shows that all the elements were uniformly distributed in the SDC-Ni Wet Chemistry processed sample.

The electronic structure of three SDC-supported Ni catalysts was evaluated using X-ray photoelectron spectroscopy (XPS). As shown in Figures 5.3A and Table S2, SDC-Ni Wet-Chemistry exhibits a metallic Ni amount of 9.46%, which is lower than that of SDC-Ni anode and SDC-Ni impregnation (~17.01%). This observation is due to the quick oxidation of nano-sized Ni on SDC-Ni Wet-Chemistry. The high-resolution spectra of Ni 2P_{3/2} were collected after 5 mins of Ar sputtering to remove the oxidized layer (Figure S6). Despite SDC-Ni Wet-Chemistry showing a higher amount of metallic Ni, it is still lower than that of SDC-Ni anode and SDC-Ni impregnation, suggesting the Ni is strongly interacting with the SDC support, which is consistent with the H₂-TPR profiles. Four types of oxygen species can be probed on SDC-Ni (Figure 5.3B). It has been revealed that increasing the concentration of oxygen vacancies can enhance the SMR performance²⁴⁵. Figure 5.3B shows that the wet-chemistry method enables the creation of additional oxygen vacancies, suggesting the outstanding SMR performance of SDC-Ni Wet-Chemistry could be correlated with its high oxygen vacancy concentration. Additionally, the

concentration of oxygen originating from H₂O molecules is much higher on SDC-Ni Wet-Chemistry, suggesting SDC-Ni Wet-Chemistry has a high water uptake capability, which also contributes to enhanced SMR performance²⁴⁸. The concentration of Ce³⁺ also depends on the catalyst manufacturing processes. As determined by the H₂-TPR, SDC-Ni Wet-Chemistry has a higher amount of Ce³⁺ than SDC-Ni impregnation while the SDC-Ni anode exhibits the lowest amount of Ce³⁺. Additionally, SDC-Ni Wet-Chemistry exhibits a higher amount of oxygen vacancies to balance Ce³⁺ ions and keep electrostatic neutrality. Therefore, according to the catalytic properties measurements and the detailed characterization results, it has been identified that SDC-Ni Wet-Chemistry can be one promising internal SMR catalyst for intermediate-temperature CH₄-MS-SOFCs.

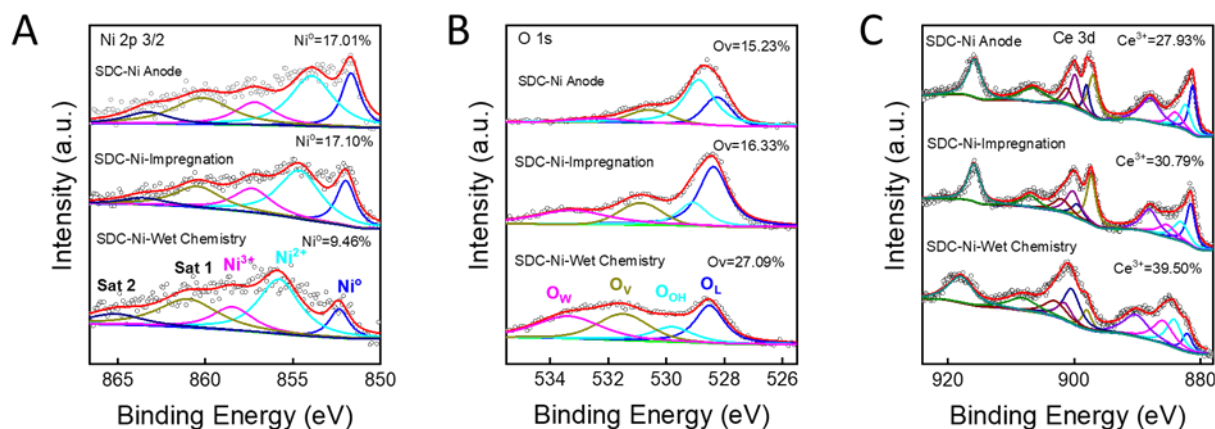


Figure 5.3. X-ray photoelectron spectroscopy (XPS) of (A) Ni 2p3/2, (B) O 1s, and (C) Ce 3d for three representative SDC-Ni catalysts.

5.1.4.3 MS-SOFC performance and stability evaluation

SDC-Ni Wet-Chemistry catalyst is then applied over the metallic anode as the internal SMR catalytic layer. These MS-SOFCs with the catalytic layer are named optimized MS-SOFCs. The MS-SOFCs manufactured by Nissan, which have been preoptimized by infiltrating the metallic support with SDC-Ni catalyst, are named pristine MS-SOFCs. The performances of

pristine MS-SOFCs under hydrogen were first measured, which are shown in Figure 5.4A. A peak power density of 1009, 681, and 468 mW/cm² is achieved at 700, 650, and 600 °C, respectively. Figure 5.4B presents the electrochemical performance of pristine MS-SOFCs under methane with a steam to carbon (S/C) ratio of 1. The PPDs under methane are much lower than that under hydrogen, indicating the anode that is preoptimized is not highly active for methane reforming. At 600 °C, its PPD is <0.1 W/cm², which is practically valueless. Additionally, the *I-V* curves of the pristine CH₄-MS-SOFC show a severe mass transport loss, suggesting the anode cannot efficiently reform methane. Furthermore, the poor performance of the pristine CH₄-MS-SOFC confirms that decorating the metallic scaffold with a nanosized catalyst, as shown in Figure S1A, might not be an effective method for optimizing MS-SOFCs.

The optimized CH₄-MS-SOFCs were tested under the same conditions, as shown in Figure 5.4C, the performances are drastically improved. The PPDs of the optimized CH₄-MS-SOFC under methane are close to H₂-MS-SOFCs, indicating the catalytic layer significantly enhances the internal SMR activity. As shown in Figure 5.4D, by applying this catalytic layer, the PPD is improved from 0.42 W/cm² to 0.82 W/cm² at 700 °C. At 600 °C, the PPD of the optimized CH₄-MS-SOFC is more than two times higher than that of the pristine CH₄-MS-SOFC. The OCV of the optimized CH₄-MS-SOFC, especially at 600 °C, is higher than that of the pristine CH₄-MS-SOFC (Figure 5.4E), suggesting the catalyst layer is highly active at intermediate operating temperatures. Figure 5.4E shows *I-V* curves of the optimized CH₄-MS-SOFC and the pristine CH₄-MS-SOFC, it is clear that SDC-Ni Wet Chemistry layer can actively convert methane to syngas that is subsequently used to generate power. The *I-V* curve of the optimized CH₄-MS-SOFC does not show obvious mass transport limitations, further confirming the excellent catalytic activity of SDC-Ni Wet-Chemistry layer.

Figure S7 presents the electrochemical impedance spectra (EIS) of the optimized CH₄-MS-SOFC and the pristine CH₄-MS-SOFC at 600 °C at a terminal voltage of 0.8 V, which shows the ohmic area-specific resistance (ASR_{ohmic}) of these two cells is similar while the electrode polarization area-specific resistance (ASR_p) is substantially different, indicating the catalytic layer is highly conductive and catalytically active. At a terminal voltage of 0.8V, the ASR_p is greatly reduced by employing the catalytic layer (Figure 5.4I). The beneficial impact of the catalytic layer is more significant at lower operating temperatures. With reducing the terminal voltage to 0.75V (i.e., increasing the polarization current density), the ASR_p of pristine CH₄-MS-SOFCs tends to dramatically increase at 600 °C, which is due to the poor catalytic activity of pristine anode and the produced syngas is insufficient for power generation, leading to exacerbated mass transport loss. However, the ASR_p of optimized CH₄-MS-SOFCs tends to decrease with increasing the polarization current, indicating the optimized CH₄-MS-SOFCs have negligible mass transport loss. The reduced ASR_p can be ascribed to the enhanced H₂ concentration and mass transport under a high current density that results in high steam concentration. An enhanced steam concentration can convert methane and CO to additional H₂. Furthermore, increasing the steam concentration can improve the gas diffusion in the anode and reduce the ASR_p .

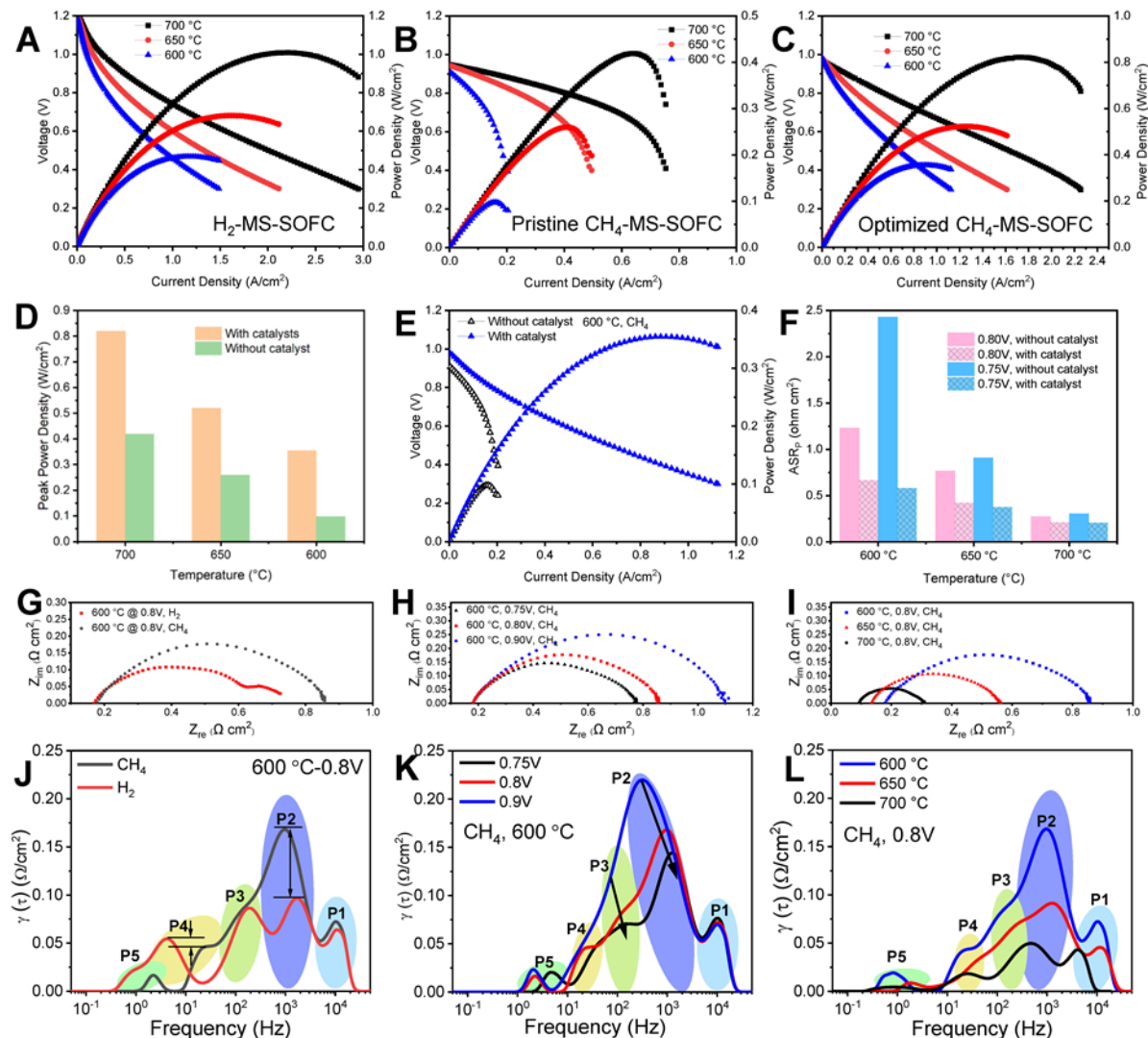


Figure 5.4. Performances of methane-fueled MS-SOFCs. (A) *I*-*V* and *I*-*P* curves of pristine MS-SOFCs under H_2 . (B) *I*-*V* and *I*-*P* curves of pristine MS-SOFCs under CH_4 . (C) *I*-*V* and *I*-*P* curves of optimized MS-SOFCs under CH_4 . (D) The peak power densities (PPDs) of pristine and optimized MS-SOFCs under CH_4 . (E) *I*-*V* and *I*-*P* curves of pristine and optimized MS-SOFCs under CH_4 at 600 °C. (F) ASR_p comparison of optimized MS-SOFCs under CH_4 at 600-700 °C. (G) Nyquist plots of pristine and optimized H_2 -fed and CH_4 -fed MS-SOFC at 600 °C and an applied voltage of 0.8 V. (H) Nyquist plots of optimized CH_4 -fed MS-SOFC at a terminal voltage of 0.9, 0.8, and 0.75 V at 600 °C. (I) Nyquist plots of optimized CH_4 -fed MS-SOFC operated at 600-750 °C at a terminal voltage of 0.8 V. (J-L) DRT analysis of EIS results shown in Figures G-I.

Figures 5.4G-5.4L present the associated EIS results and distribution of relaxation time analysis (DRT)²⁴⁹. Figure 5.4G shows that the ASR_p slightly increases with changing the fuel from H_2 to CH_4 at 600 °C and 0.8V, indicating the anode converts a considerable amount of methane to

syngas. Therefore, changing the fuel fed to the anode does not lead to a significant difference in ASR_p . The corresponding DRT is performed to visualize and differentiate the polarization resistances attributed to the processes that occur in the anode and cathode^{250,251}. Figure 5.4J displays five peaks, which correspond to five different processes. P1, P3, and P5 are associated with the processes that occur in the cathode. They represent gas diffusion in the cathode, oxygen surface exchange and oxygen reduction reaction in the cathode, and oxygen ion conduction at the cathode-electrolyte interface, respectively. Therefore, P1, P3, and P5 show similar resistance under H_2 and CH_4 as the fuel fed to the anode will not impact the processes in the cathode.

The peak of P4 at a low frequency (5-50 Hz) is noted as the gas diffusion in the anode²⁵⁰. Figure 5.4J shows H_2 -MS-SOFCs exhibit a higher anode gas diffusion resistance than that of CH_4 -MS-SOFCs, which is due to the higher amount of steam fed to the anode of CH_4 -MS-SOFCs. The steam could accelerate the gas diffusion in the anode, leading to lower P4 resistance of CH_4 -MS-SOFCs²⁵². The process of P2 that occurs at a high-frequency range ($\sim 10^3$ Hz) represents the fuel oxidation kinetics at the anode triple-phase boundaries, which dominates the ASR_p , especially for CH_4 -MS-SOFCs. Therefore, the fuel oxidation reaction that occurs in the anode could determine the performance of CH_4 -MS-SOFCs. The impacts of terminal voltage and operating temperature on the optimized CH_4 -MS-SOFC were also evaluated. The ASR_{ohmic} remains constant with reducing the terminal voltage (i.e., increasing the polarization current), while the ASR_p decreases (Figure 5.4H), which is consistent with results shown in Figure 5.4F. As shown in Figure 5.4K, the terminal voltage significantly affects fuel oxidation. Increasing the current density improves the fuel oxidation process (P2), consequently, reducing the overall ASR_p . The outlet gas compositions were determined as a function of polarization current. As shown in Figures 5.5A-5.5C, increasing the current density could improve the oxidation of fuel and enhance methane

conversion. The operating temperature greatly impacts the ASR_p (Figures 5.4I and 5.4L). At an intermediate temperature (e.g., 600 °C), the electrode polarization loss dominates the total losses. The resistance of fuel oxidation reaction (P2) dominates the ASR_p at 600 °C, suggesting the catalytic layer could be further improved in subsequent work to enhance the CH₄-MS-SOFCs.

The long-term durability of CH₄-MS-SOFCs is critical for their implementation. As shown in Figure 5.1C, prior research has demonstrated the MS-SOFCs are unstable under methane. The stability of the optimized CH₄-MS-SOFCs is comprehensively evaluated. At 700 °C, the short-term stability of the optimized CH₄-MS-SOFCs is determined (Figure 5.5A). Additionally, the outlet gas compositions were determined to quantify the methane conversion as a function of current density. The terminal voltage under various current densities is constant, indicating the optimized CH₄-MS-SOFCs are stable. Furthermore, at 700 °C, the optimized CH₄-MS-SOFC enables a methane conversion of ~70% without any current applied. Increasing the discharge current density can enhance methane conversion as fuels are consumed and H₂O is produced, which shifts the reaction equilibrium towards higher methane conversion. Under a current density of 857 mA/cm², the methane conversion is enhanced to ~90%. It, therefore, confirms the optimized CH₄-MS-SOFC exhibits outstanding internal SMR activity. Moreover, the CO₂/CO ratio as a function of current density is quantified. A high CO₂/CO ratio can thermodynamically suppress the coking ascribed to the Boudouard reaction. Figure 5.5C shows that increasing the current density can greatly increase the CO₂/CO ratio, suggesting the CH₄-MS-SOFC could be more stable under a relatively high current density.

The pristine CH₄-MS-SOFC was also tested under an S/C ratio of 1 at 600 °C (Figure 5.5D), which shows the pristine CH₄-MS-SOFC degrades within five hours. We then performed Raman spectroscopy on the anode to probe its degradation mechanism. As shown in Figure 5.5E,

the pristine CH₄-MS-SOFCs show substantial carbon in the anode. Therefore, the fast degradation of the pristine CH₄-MS-SOFC is ascribed to its poor coking tolerance. We then tested the stability of a CH₄-MS-SOFC modified with the SDC-Ni Wet-Chemistry catalyst under the same conditions. As shown in Figure 5.5F, the optimized CH₄-MS-SOFC delivers a much higher current density. Additionally, >1000 hours of operation is achieved, which realizes a much longer operation time than other CH₄-MS-SOFCs (Figure 5.1C). The degradation rate is <0.1mV/h. After >1000 hours of operation, Raman spectroscopy is performed on the anode, as shown in Figure 5.5E, and no notable carbon is observed, indicating the internal SMR catalytic layer greatly enhances the coking tolerance. Post-mortem SEM images (Figure S8) of the optimized CH₄-MS-SOFC after >1000 hours of operation show that no coking has been observed.

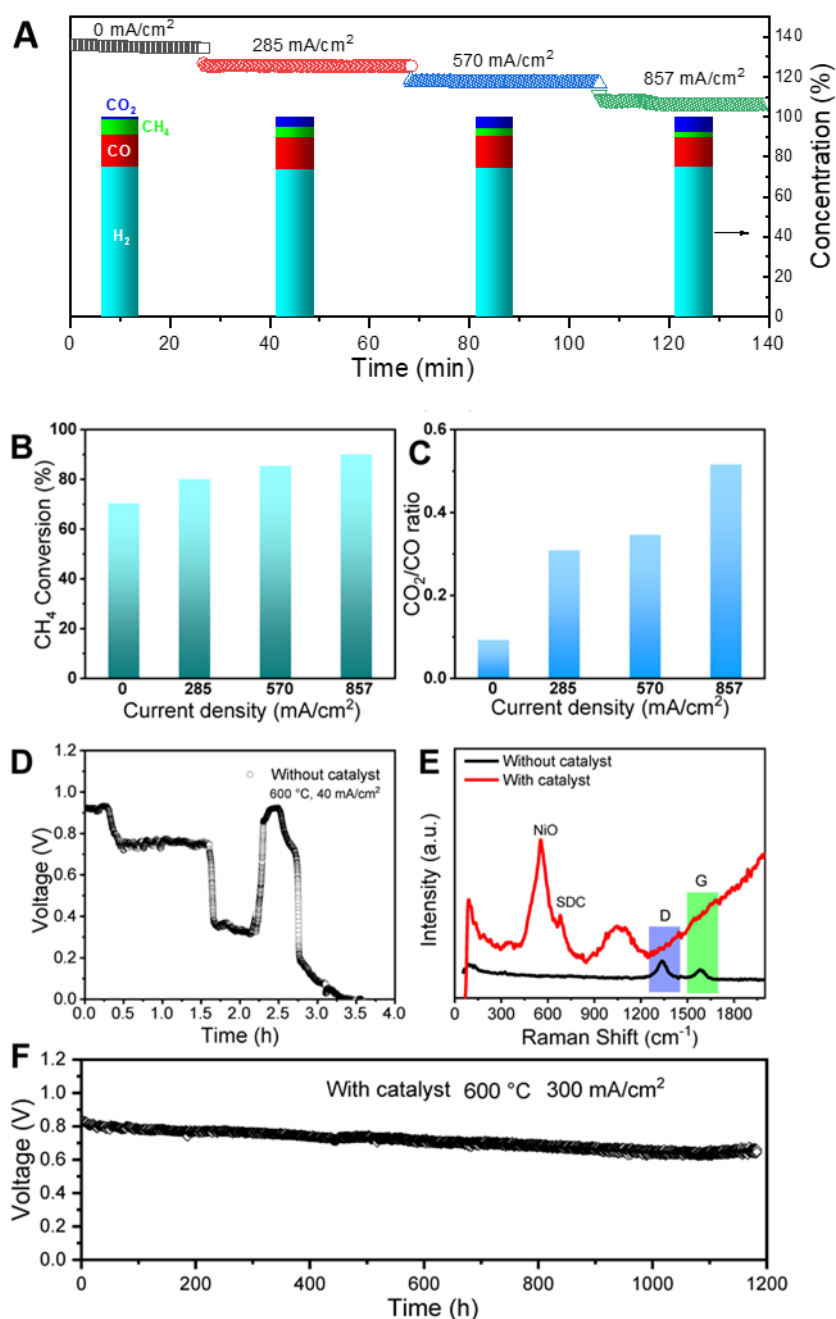


Figure 5.5. Stability testing of CH₄-MS-SOFCs. (A) Voltage and outlet gas compositions of the optimized CH₄-MS-SOFC as a function of applied current densities at 600 °C. (B) CH₄ conversion and (C) CO₂/CO ratio in anode outlet gas stream of the optimized CH₄-MS-SOFC as a function of the applied current density at 600 °C. (D) Short-term stability of pristine CH₄-MS-SOFC at 600 °C under a S/C ratio of 1. (E) Raman spectra of the anode of pristine CH₄-MS-SOFC and optimized CH₄-MS-SOFC after stability testing under CH₄. (F) Long-term stability of an optimized CH₄-MS-SOFC at 600 °C under a S/C ratio of 1.

5.1.5 Conclusion

By optimizing the MS-SOFCs with an internal SMR catalyst layer, both the power density and long-term durability have been significantly enhanced, especially at an intermediate operating temperature (e.g., $>0.35 \text{ W/cm}^2$ at $600 \text{ }^\circ\text{C}$). The optimized CH_4 -MS-SOFCs attain the highest power densities at $600\text{--}700 \text{ }^\circ\text{C}$ among all zirconia-based MS-SOFCs. Furthermore, the modified CH_4 -MS-SOFCs demonstrate excellent stability for >1000 hours, underscoring the promise of modifying MS-SOFCs with a catalyst layer. The results demonstrated in this work highlight the potential of methane-fueled MS-SOFCs for high-efficiency, durable, and resilient power generation.

5.1.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1021/acsami.2c16233>

5.2 Synergistic effects of in-situ exsolved Ni–Ru bimetallic catalyst on high-performance and durable direct-methane solid oxide fuel cells

5.2.1 Abstract

Direct-methane solid oxide fuel cells (CH₄-SOFCs) have gained significant attention, as methane, the primary component of natural gas (NG), is cheap and widely available, and the natural gas infrastructures are relatively mature. However, at intermediate temperatures (e.g., 600–650 °C), current CH₄-SOFCs are suffering from low performance and poor durability under a low steam-to-carbon ratio (S:C ratio), which is ascribed to the Ni-based anode that is of low catalytic activity and prone to coking. Herein, with the guidance of density functional theory (DFT) studies, a highly active and coking tolerant steam methane reforming (SMR) catalyst, Sm-doped CeO₂-supported Ni-Ru (SCNR), was developed. The synergy between Ni and Ru lowers the activation energy of the first C-H bond activation and promotes the following CH_x decomposition. Additionally, Sm doping increases the oxygen vacancy concentration in CeO₂, facilitating H₂O adsorption and dissociation. The SCNR can therefore simultaneously activate both CH₄ and H₂O molecules, while oxidizing the CH* and improving coking tolerance. We then applied SCNR as the CH₄-SOFC anode catalytic reforming layer. A peak power density of 733 mW cm⁻² was achieved at 650 °C, representing a 55% improvement compared to pristine CH₄-SOFCs (473 mW cm⁻²). Moreover, long-term durability testing, with >2000 h continuous operation, was performed under almost dry methane (5% H₂O). These results highlight that CH₄-SOFCs with SCNR catalytic layer can convert NG to electricity with high efficiency and resilience.

5.2.2 Introduction

Solid oxide fuel cells (SOFCs) are promising electrochemical energy conversion devices that directly convert chemical energy to electricity with high efficiency and low emissions^{109,253}. Compared to their low-temperature counterparts, polymer membrane electrolyte fuel cells that utilize high-purity H₂, the fuel flexibility of SOFCs significantly broadens their potential applications^{42,254}. Among all fuel-flexible SOFCs, direct-methane SOFCs (CH₄-SOFCs) are of high interest as methane is much cheaper than other commercially available fuels^{15,255,256}. Additionally, liquified natural gas (LNG) exhibits a relatively high volumetric energy density, which is essential for vehicular applications. Therefore, CH₄-SOFCs have great potential to be employed to power long-range heavy-duty trucks^{220,221}.

Implementing CH₄-SOFCs in transportation sectors requires CH₄-SOFCs running at relatively low operating temperatures (e.g., <650 °C), at which the risks associated with thermal cycling could be minimized. Additionally, the fuel stream fed to the CH₄-SOFCs, typically a mixture of CH₄ and steam, should exhibit a low steam-to-carbon (S:C) ratio²⁵⁷. A high steam concentration requires a complicated system to generate and manage the steam supply while consuming extensive thermal energy. Moreover, the steam can dilute the fuel, leading to relatively poor fuel cell performance. Alternatively, a mixture of CH₄ and air can be fed to the fuel cell to generate power via internal catalytic partial oxidation (CPOX) of methane²⁵⁸. However, the overall energy efficiency is lower under CPOX conditions than that under SMR conditions. Therefore, the utilization of CH₄-SOFCs for powering vehicles necessitates running CH₄-SOFCs under a low S:C ratio and <650 °C.

Significant progress has been made in lowering the operating temperature of H₂-fueled SOFCs^{3,106,113,259,260}. Unfortunately, developing intermediate-temperature CH₄-SOFCs (IT-CH₄-

SOFCs) has been a long-standing challenge^{255,257}. CH₄ molecules are thermodynamically stable. Additionally, SMR is a highly endothermic reaction. Thus, SMR is thermodynamically and kinetically unfavorable at lowered operating temperatures, suggesting an active catalyst should be integrated with the SOFC anode to activate both CH₄ and H₂O molecules. Ni-based cermet is the state-of-the-art SOFC anode, which exhibits acceptable catalytic activities. Upon exposure to CH₄, the Ni-based anode can readily activate C-H bonds. On the other hand, its outstanding capability of breaking the C-H bond also results in a Ni surface saturated with carbon-containing species (CH_x), which cannot be quickly oxidized, leading to carbon formation on Ni (i.e., coking). Continuous coking will block the active sites for SMR and deteriorate CH₄-SOFC performance. Several strategies have been established and validated to overcome these challenges, which include developing alloyed anodes²⁶¹, applying the internal anode catalytic reforming layer²⁶², and employing Ni-free oxide-based anodes²⁶³. Although the performance has been improved, the majority of these CH₄-SOFCs still require high operating temperatures or exhibit poor performance. For example, an oxide-based anode catalytic layer, La_{0.7}Sr_{0.3}Fe_{0.8}Ni_{0.2}O_{3-δ}, has been coated on the YSZ-Ni anode to enhance SOFC performance under CH₄²⁶⁴. At 850 °C, the peak power density has been improved from 0.433 W cm⁻² to 0.539 W cm⁻². Unfortunately, at 750 °C, the peak power density is relatively low (0.237 W cm⁻²). A high-entropy alloyed anode consisting of Cu-Ni-Co-Fe-Mn has been engineered to enhance coking resistance²⁶⁵. However, the CH₄ conversion achieved on this anode is poor, leading to a low current density of ~100 mA cm⁻² at 0.6 V and 750 °C. These representative anodes underscore the intricacies of developing a SMR catalyst that concurrently exhibits high catalytic activity, improved coking tolerance, and reduced operating temperature.

SMR requires the simultaneous activation of both CH₄ and H₂O molecules. Typically, the monometallic catalysts could favor the activation of either CH₄ or H₂O molecules. Therefore, leveraging the synergistic effects of two metals could create a bimetallic catalyst that reduces the activation energies of multiple catalytic processes, dramatically enhancing the catalytic activity, especially at a reduced operating temperature^{15,164}. Our prior work has validated that the synergistic effects between Ni and Ru can improve the dry reforming of methane (DRM)¹⁰⁰. Additionally, to achieve high-performance IT-CH₄-SOFCs, the catalyst support should also be rationally designed. It has been recognized that the oxide-based catalyst support with a high oxygen vacancy concentration could promote the dissociative adsorption of H₂O²⁶⁶. The characteristic redox couple Ce⁴⁺/Ce³⁺ in CeO₂ enables a high oxygen storage capacity; thus, it has been widely employed as the support of various catalysts for CO₂ hydrogenation¹⁵³, SMR²⁶², and DRM^{140,182}. Therefore, engineering CeO₂ to further increase the oxygen vacancy concentration could potentially promote SMR. Sm-doped CeO₂ (SDC) displays the smallest enthalpy of association between the dopant cations and oxygen vacancies in the fluorite lattice¹⁶¹. Thus, SDC exhibits enhanced oxygen vacancy concentration. Therefore, we hypothesized that a Ni-Ru bimetallic catalyst that is supported on an oxide with abundant oxygen vacancies, such as SDC, could concomitantly promote the activation of H₂O and CH₄ while facilitating the subsequent oxidation of CH*, attaining improved catalytic performance and enhanced coking tolerance.

In this work, density functional theory (DFT) was first employed to understand the synergistic impacts of Ni and Ru, and the Sm doping on SMR. We have identified that the Ni-Ru dual metal sites could effectively reduce the energy barrier required for the initial activation of carbon-hydrogen (C-H) bonds, facilitating the continuous release of carbon—an essential step in the SMR process. Additionally, the choice of SDC as a catalyst support with an abundance of

oxygen vacancies (O_v) exhibits a strong affinity for binding and activating water (H_2O) molecules, which enhances oxygen supply and accelerates critical reactions within the SMR process. Subsequently, a series of carefully designed experiments were conducted to validate and corroborate the insights derived from our DFT modeling. The $Sm_{0.2}Ce_{0.7}Ni_{0.1}Ru_{0.05}O_{2-\delta}$ (SCNR) catalyst was rationally synthesized to achieve in-situ exsolved Ni-Ru supported on SDC. With applying SCNR as the internal SMR catalytic layer, the operating temperatures of CH_4 -SOFC have been lowered to 600-700 °C, achieving a groundbreaking power density of $\sim 1159\text{ mW cm}^{-2}$ at 700 °C and 361 mW cm^{-2} at 600 °C. Additionally, the steam concentration can be lowered to 5%, implying almost dry CH_4 can be directly fed to the SOFC anode. More than 2000 h stability testing has been conducted under almost dry CH_4 concentration (5% H_2O), validating the long-term durability and coking resistance of SCNR. These results have highlighted the promising future of employing CH_4 -SOFC to power vehicles.

5.2.3 Methods and materials

5.2.3.1 Density functional theory (DFT)

All spin-polarized density functional theory (DFT) calculations were performed using the Vienna *Ab Initio* Simulation Package (VASP)^{166,267}. The projector augmented wave (PAW) pseudopotentials²⁶⁸, and the GGA-PBE functional²⁶⁹ were used to account for the core electrons and the electron exchange-correlation effects. The plane-wave basis set was expanded with a cutoff energy of 400 eV. Gaussian smearing ($\sigma = 0.05\text{ eV}$) was employed for CeO_2 and SDC models, and the first-order Methfessel-Paxton method of smearing ($\sigma = 0.2\text{ eV}$) was used for Ni (111) and Ru (0001) models. The reciprocal first Brillouin zone was sampled using a $2 \times 2 \times 1$ mesh k -point mesh automatically generated from the Monkhorst-Pack scheme²⁷⁰. The Hubbard U method¹⁷¹, with (U -

$J_{\text{Ce}} = 4.5$ eV, was adopted to correct the self-interaction effects of the f -electrons in Ce^{15,194}. The 4f electrons of Sm were treated as the core and, thus, were not corrected with the U values¹⁷². Molecular adsorptions on CeO₂ and SDC models were corrected using the DFT-D3 method with the Becke-Johnson damping function²⁷¹. The structures and energies of all transition states were obtained from the climbing image-nudged elastic band (CI-NEB) method²⁷² and the dimer method²⁷³.

Both metallic Ni (and Ru) and lattice oxygen vacancy (O_v) sites play vital roles during SMR. Specifically, water dissociation favors the O_v site²⁷⁴, whereas methane activation predominantly occurs on the metal sites¹⁵. To fully account for these critical chemistries, we built 3-layer p (3×3) Ni (111) (Figure S1A), Ru (0001) (Figure S1B), and Ni₃-in-Ru (0001) (Figure S1C) slab models to represent pure Ni, Ru, and Ni-Ru dual metal systems for methane activation, respectively. In Ni₃-in-Ru (0001), three Ru atoms in the top layer were replaced by Ni atoms. To model water dissociations, four systems, i.e., CeO₂-Ni₄ (Figure S1D), CeO₂-Ru₄ (Figure S1E), SDC-Ni₄ (Figure S1F), SDC-Ru₄ (Figure S1G) with O_v were employed. In this study, CeO₂-Ni₄, CeO₂-Ru₄, SDC-Ni₄, and SDC-Ru₄ will represent different chemical environments for O_v. The CeO₂-Ni₄ and CeO₂-Ru₄ were obtained by relaxing respective Ni₄ and Ru₄ clusters on 3-layer p (2×4) CeO₂ (111). The SDC-Ni₄ and SDC-Ru₄ systems were adopted from our previous work on dry reforming of methane¹⁰⁰. The O_v site with the lowest formation energy was selected in each model. All optimized structures mentioned above are shown in Figure S1, visualized using the VESTA software¹⁷⁴.

5.2.3.2 Materials and catalysts preparation

$\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (SCNR) was synthesized via a wet-chemistry method using a stoichiometric amount of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{HN}_4\text{O}_{10}\text{Ru}$ as the precursors. Briefly, the calculated amounts of corresponding salts were dissolved and mixed in DI water. After approximately 30 min of agitation, citric acid (CA) and ethylenediaminetetraacetic acid (EDTA) were introduced into the mixture with the ratio of 1 (total metal ions) : 2 (CA) : 2 (EDTA). To ensure comprehensive complexation, the mixture was continuously stirred for an additional 30 min. Subsequently, the *pH* of the mixture was adjusted to approximately 9 by gradual addition of the aqueous NH_4OH solution. The solution was then subjected to continuous stirring and heated at 250 °C. Upon the formation of a gel-like substance, the material underwent drying at 175 °C for 24 h in a drying oven, followed by calcining the powder at 600 °C for 5 h to obtain the SCNR powder. The $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$ (SCN), $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$ (SCR), and $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (CNR) were synthesized using the same wet-chemistry method.

5.2.3.3 Catalyst characterizations

X-ray diffraction (XRD) patterns were acquired employing a Rigaku MiniFlex diffractometer, employing Cu K α radiation source operating at 30 kV and 15 mA. The range of 2θ was 20-80°, and the scanning speed was set at 1°/min. X-ray photoelectron spectroscopy (XPS) analyses were conducted utilizing a Phi 5000 VersaProbe II X-ray Photoelectron Spectrometer. The microstructure of SOFCs was observed using a scanning electron microscope (JEOL JSM-6060LV). The morphological characteristics of the reduced SCNR powder were investigated via transmission electron microscopy (FEI Tecnai Osiris). Temperature-programmed reduction (TPR) was conducted using a ChemBET Pulsar. In-situ Raman spectroscopy was performed utilizing the

Bruker Senterra. In situ High temperature XRD (HT-XRD) data were collected on a STOE-STADI-MP powder diffractometer equipped with an asymmetric curved Germanium monochromator (AgK α 1 radiation, $\lambda = 0.559407$ Å) and one-dimensional silicon strip detector (MYTHEN2 1K from DECTRIS). In situ diffused reflectance infrared fourier transform spectroscopy (DRIFTS) was performed using a Thermo Fisher iS50 FTIR spectrometer equipped with the Praying Mantis high-temperature reaction chamber.

5.2.3.4 Catalytic performance testing

The SMR catalytic activities were assessed by using a continuous flow fixed-bed quartz tubular reactor (ID: ~7.0mm) at 1 atm. 120 mg of each catalyst was loaded into the reactor for the performance evaluation. To monitor the temperature, a thermocouple was inserted proximate to the catalyst within the tubular reactor. The catalyst was first reduced under 20% H₂ balanced with Ar (50 sccm) at 600 °C for 30 mins. Upon reduction, the reactor temperature was elevated to 700 °C, subsequently introducing a flow of 15 sccm CH₄ gas through a heated water bubbler, with a steam-to-carbon (S:C) ratio of 1:1 or 1:2, directed into the reactor. The composition of the outlet gas was determined utilizing an online gas chromatography (INFICON 3000 Micro GC). Prior to measurement, the reactor was maintained at each temperature for approximately 30 min to attain equilibrium. The CH₄ conversion (X_{CH_4}) is calculated as follows:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\%$$

Where $F_{CH_4,in}$ or $F_{CH_4,out}$ represent the inlet and outlet methane flow rate, respectively.

5.2.3.5 CH₄-SOFCs performance testing

All SOFCs tested in this work were anode-supported SOFCs. A porous Fe-Cr alloy is used as the metallic anode support. The anode functional layer consisted of a composite material comprising scandia and yttria co-stabilized zirconia (ScYSZ) and nickel oxide (40 wt% ScYSZ + 60 wt% NiO). ScYSZ was employed as the electrolyte, with a thickness of approximately 8 μm . An additional gadolinia doped ceria (GDC) barrier layer ($\sim 1\ \mu\text{m}$ in thickness), was applied on the electrolyte by physical vapor deposition (PVD). Button cell and GDC target were placed 85 mm apart. The sputtering pressure was 0.45 Pa, and the substrate was heated at 300°C. The diameter of all SOFCs was standardized at 2.5 cm. A composite PBSCF²⁵⁹ cathode prepared using a wet-chemistry method was subsequently brush-painted onto the electrolyte and fired at 765 °C for 5 min. To enhance the internal SMR activity, the SCNR catalyst ink was coated on the entire surface area of the anode, covering a total area of $\sim 4.9\ \text{cm}^2$. The CH₄-SOFC configuration is illustrated in Figure S2.

Subsequently, the cell was sealed on an alumina tube using a glass sealant (MO·SCI: 1709P/-45). A gold paste was employed as the current collector. During the sealing process, the anode was exposed to 20 vol.% H₂ (20 sccm H₂ + 80 sccm Ar) to prevent the oxidation of the metallic support in the anode during the heating process. Throughout this process, a heating rate of 10 °C/min was used. The CH₄-SOFC performance was assessed at 700 °C, 650 °C, and 600 °C. Prior to electrochemical measurements, the CH₄-SOFCs were stabilized at each temperature for approximately 20 minutes. Electrochemical performance was evaluated using a Gamry 3000 Potentiostat. Ambient air served as the oxidant for all examined cells. Different steam-to-carbon ratios (S:C) were employed to assess the performance of CH₄-SOFCs. A CH₄ flow rate of 10 sccm was maintained, and the steam concentration was regulated through a customized bubbler. The effective cathode area of all CH₄-SOFCs is 0.7 cm².

5.2.4 Results and discussion

5.2.4.1 CH₄-SOFC performance and durability

Simultaneously achieving high CH₄-SOFC power density and durability, particularly at < 650°C, is challenging, which primarily stems from the absence of a rationally designed SMR catalyst that is compatible with SOFCs. Despite extensive SMR catalysts have been developed for packed bed reactors (PBRs), these catalysts might not work for SOFCs. The SOFC-compatible SMR catalysts should exhibit (1) high electronic conductivity to minimize ohmic resistance; (2) high physical and chemical compatibility with SOFC anode; and 3) excellent SMR activity and coking tolerance at <650 °C under a relatively low steam concentration.

As shown in Figure 5.6A, a limited number of CH₄-SOFCs that capable of delivering practically valuable power density and durable operation. Persson et al.²¹³ demonstrated that a lanthanum strontium iron nickel titanate internal reforming layer can help achieve a power density of ~200 mW cm⁻² at 650 °C with a short-term stable operation (~120 h). However, a high steam concentration of 67% is required to mitigate coking. Nevertheless, a high steam concentration can cause high-temperature corrosion of FeCr-based anode, leading to rapid degradation. Liu et al.²⁷⁵ reported a Ni-Cu-Fe alloyed anode for internal SMR. Although enhanced SOFC performance was demonstrated at low temperatures (e.g., 287 mW cm⁻² at 600 °C), the stability assessment was very short (~48 h). Further investigations should be conducted to validate its long-term coking tolerance.

In this work, we rationally designed a Ni-Ru bimetallic catalyst supported on SDC (SCNR), serving as a highly active and coking tolerant internal reforming layer. Compared to the literature results, excellent fuel cell performance for power generation was obtained (Figure 5.6A and Table S1). Moreover, the long-term durable operation of CH₄-SOFC has been a long-standing challenge.

Most of the durability testing reported in literature is less than 200 h (Figure 5.6B). Herein, with using SCNR as the internal SMR layer, we have demonstrated >2200 h long-term stability testing under nearly dry CH₄ (5% steam) (Figure 5.6B). This remarkable long-term durable operation highlights the promising coking tolerance of this newly developed catalyst for CH₄-SOFCs.

As shown in Figure 5.6C, without applying the SMR catalyst, the pristine CH₄-SOFC performance was poor. The SCNR catalyst developed in this work leads to an approximate 52% performance enhancement in terms of the peak power density (PPD) at 700 °C. Notably, the performance enhancement tends to be more significant with lowering the operating temperatures. For example, the PPD has been significantly improved from 190 W cm⁻² to 361 W cm⁻² at 600 °C, representing an increase of ~89%. Therefore, the SCNR catalyst plays a critical role in enhancing CH₄-SOFC power density and durability, which addresses the two main challenges of Ni-based anodes. As illustrated in Figure 5.6D, the enhanced catalytic activity and improved durability achieved on SCNR can be attributed to the synergistic effects of in-situ exsolved Ni-Ru bimetallic catalyst and the abundant oxygen vacancies (O_v) in SDC. The SDC-supported Ni-Ru bimetallic catalyst creates a kinetically and thermodynamically favorable pathway for the activation of both CH₄ and H₂O molecules, while accelerating the oxidation of CH* and consequently improving the coking tolerance.

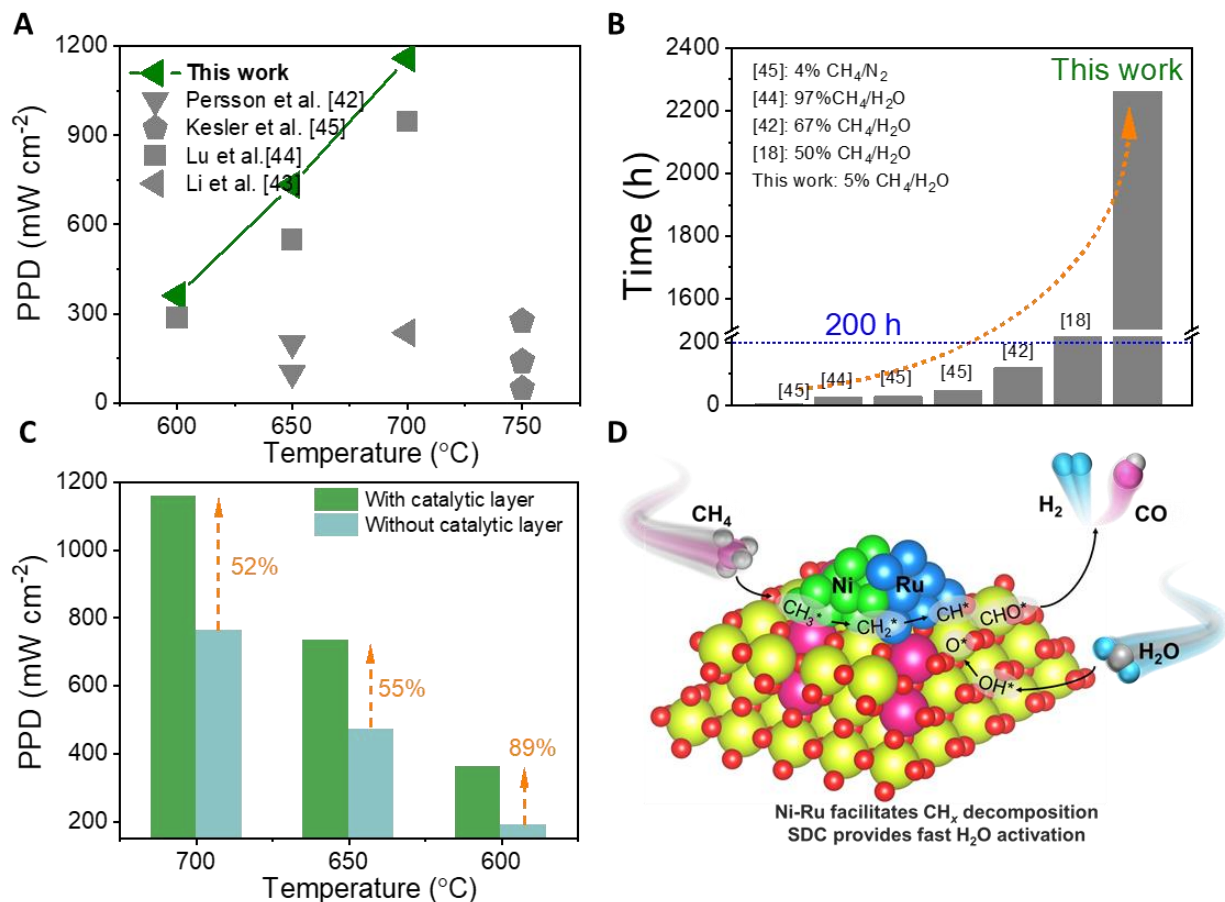


Figure 5.6. The performance and durability of CH₄-SOFCs. (A) Comparison of peak power densities (PPDs) of CH₄-SOFCs (this work) with the literature results^{213,227,275,276}. (B) Comparison of stability of CH₄-SOFCs (this work) with the literature results. (C) The PPDs of CH₄-SOFCs with and without SCNR catalytic layer. (D) Schematic illustration of the synergistic effects of Ni and Ru, and Sm doping on steam methane reforming. For SMR catalyst developed in this work, i.e. SCRn, Ce, O, Sm, Ni, and Ru atoms are displayed in yellow, red, wine, green and blue, respectively.

5.2.4.2 The synergistic effects of Ni and Ru and SDC support

DFT serves as a powerful tool for conducting computational studies to guide our SMR catalyst design. The specific goal is to investigate and validate three hypotheses, including (1) Sm doping could increase oxygen vacancy concentration and consequently promotes the H₂O adsorption and dissociation; (2) the synergy of Ni-Ru bi-metallic system could promote the initial CH₄ activation and subsequent decomposition of CH_x; and (3) SDC-supported Ni-Ru could

simultaneously activate both H₂O and CH₄ molecules, while facilitating the oxidation of CH* and improving coking tolerance.

The dissociation of water is related to the availability of the O_v site, and the binding energy^{277,278}. The vacancy formation energies (ΔE_{O_v}) and the binding energies of H₂O (BE_{H_2O}) were computed according to Equations 1 and 2, respectively.

$$\Delta E_{O_v} = E_{O_v} + \frac{1}{2} E_{O_2(g)} - E_{surf} \quad (1)$$

$$BE_{H_2O} = E_{H_2O*} - E_{O_v} - E_{H_2O(g)} \quad (2)$$

where E_{O_v} is the total energy of the oxide support with a single O_v site, $E_{O_2(g)}$ is the total energy of the gas-phase O₂ molecule, E_{surf} is the total energy of vacancy-free oxide, E_{H_2O*} is the total energy of the slab with the water adsorbate, and $E_{H_2O(g)}$ is the energy of the gas-phase water molecule.

Pristine CeO₂ (111) and SDC (111) surfaces were used as reference systems. The formation energy of O_v site in clean CeO₂(111) is 2.84 eV (Figure 5.7A), which compares well with the values reported in the literature²⁷⁴. The addition of Ni₄ and Ru₄ clusters does not significantly affect ΔE_{O_v} , which are 2.70 eV and 2.73 eV, respectively. In SDC (111), however, O_v formation is much more energetically favorable. The ΔE_{O_v} for removing one lattice oxygen near the Sm dopant in SDC (111) is -0.79 eV, suggesting that O_v formation in stoichiometric SDC could be spontaneous. As shown in Figure 5.7A, ΔE_{O_v} becomes positive (endothermic) upon the addition of Ni₄ and Ru₄ clusters, at 0.27 eV and 1.16 eV, respectively. The calculated ΔE_{O_v} reflects the O_v concentration follow the trend of SDC-Ni₄ > SDC-Ru₄ > CeO₂-Ni₄ ≈ CeO₂-Ru₄.

To gain a deeper understanding of the metal-support interactions, Bader charge analyses were performed to investigate the charge transfer between metal clusters and supports. As shown in Figure 5.7C, on both CeO₂ (111) and SDC (111) surfaces, the additions of both Ni₄ and Ru₄

clusters result in charge accumulations on the oxygen atoms involved in vacancy formation, which means the binding between oxygen and support is stronger. On SDC (111), the Ru₄ cluster contributes to a higher charge accumulation than Ni₄ (0.09 e versus 0.06 e), which explains why the ΔE_{O_v} become more positive for SDC-Ru₄ than SDC-Ni₄. However, in CeO₂-Ni₄ and CeO₂-Ru₄, the charge accumulation occurs mainly at the neighboring Ce sites (dashed black circles), effectively shielding the O_v site (dashed red circles). Therefore, adding clusters has not significantly affected ΔE_{O_v} on the CeO₂ surface. These results indicate that concentrations of O_v in CeO₂ near Ni and Ru clusters will remain relatively unchanged. Nevertheless, the concentration of O_v will always be higher in SDC than in CeO₂, even in the presence of Ni₄ and Ru₄.

Next, the adsorptions of H₂O at different O_v sites were considered, as illustrated in Figure 5.7B. On CeO₂ (111), the BE_{H_2O} is -1.18 eV. BE_{H_2O} slightly increases on CeO₂-Ni₄ and CeO₂-Ru₄ at -1.10 and -1.07 eV, respectively. Compared to the metal sites, it becomes clear that water molecules favor the O_v site, where the dissociation will most likely occur. On SDC (111), the corresponding BE_{H_2O} is -0.98 eV, weaker than on CeO₂ (111) due to the less oxyphilic Sm dopant. However, interestingly, the binding of water molecules on O_v increases in the presence of Ni₄ and Ru₄ clusters, which remain stronger than at the metal site. In particular, the BE_{H_2O} on SDC-Ru₄ is 0.33 eV stronger compared to the cluster-free SDC. The trend of BE_{H_2O} on four employed models is SDC-Ru₄ > CeO₂-Ni₄ $\approx$ CeO₂-Ru₄ > SDC-Ni₄. Bader charge analysis of water adsorption on four models also shows that the oxygen atom in the H₂O molecule acquires the highest charge accumulation on SDC-Ru₄ (Figure S3), corresponding to the strongest binding of H₂O oxygen at the vacancy site.

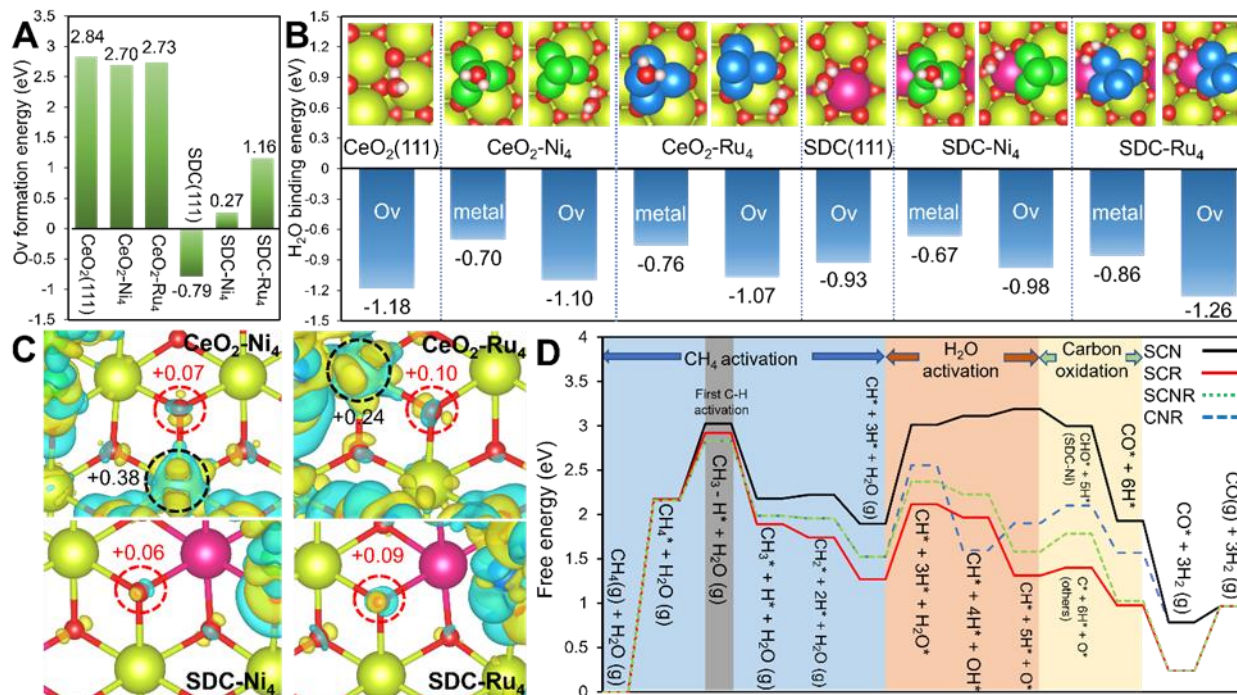


Figure 5.7. Computational study of the SMR catalysts. (A) Oxygen vacancy formation energy (ΔE_{O_v}) and (B) H₂O binding energy (BE_{H_2O}) on CeO₂(111), CeO₂-Ni₄, CeO₂-Ru₄, SDC (111), SDC-Ni₄, and SDC-Ru₄ with optimized water adsorption configurations. H, Ce, O, Sm, Ni, and Ru atoms are displayed in white, yellow, red, wine, green and blue, respectively. (C) Charge density differences of pristine CeO₂-Ni₄, CeO₂-Ru₄, SDC-Ni₄, and SDC-Ru₄ due to the presence of Ni₄ and Ru₄ clusters. Isosurfaces (0.003 e/bohr³ of value) in yellow represent charge accumulation and cyan represents depletion. The O_v sites are indicated with dashed red circles and the neighboring atoms with notable charge density change are marked with dashed black circles. The numerical charge variations are also indicated. (D) Free energy diagram of SMR process on SCN, SCR, SCNR, and CNR under 600 °C and 1 bar.

The full SMR mechanism on the SDC-supported Ni-Ru dual-metal system was investigated, as summarized in Figure 5.7D. DFT-calculated binding energies and the preferred sites of SMR intermediates are reported in Table S2, with the configurations of these species illustrated in Figures S4 and S5. DFT calculations revealed that Ni₃-in-Ru (0001) yields an energy barrier of 0.67 eV for the first C–H bond activation, slightly lower than on Ru (0001) (0.75 eV), but notably lower than on Ni (111) (0.86 eV). These results indicate that the Ni-Ru dual-metal system does promote initial methane conversion. Subsequent stepwise CH_x ($x = 1,2,3$)

decompositions are also compared in Figure 5.7D. It can be noted that the dual-metal systems remain more competitive than either the single Ni or Ru catalysts.

To match facile methane decomposition, an ideal catalyst should also support facile water dissociation in parallel. As discussed earlier, H₂O binding is the strongest on SDC-Ru₄ at the O_v site, which is employed in SCR and SCNR catalysts. H₂O dissociations on SCR and SCNR catalysts are exothermic, whereas on SCN, H₂O dissociation is endothermic due to weaker bindings of H* and OH*. On CNR, the dissociation of H₂O is also exothermic, but the decomposition of OH becomes endothermic. Therefore, the overall water dissociation on SCNR is thermodynamically favorable. For carbon oxidation, two routes were considered, i.e., CH* → C* → CO* and CH* → CHO* → CO*. Figure 5.7D shows that the CH* → CHO* → CO* pathway is thermodynamically favored only on SCN, while CH* → C* → CO* is the dominant pathway on the other surfaces. The decomposition of CH* to C* is an endothermic process, but exothermic when C* is oxidized to CO*.

In conclusion, the high performance of SCNR can be attributed to the synergy between the enhanced CH₄ and H₂O activation. The Ni-Ru dual metal site lowers the activation energy of the first C-H bond activation and creates a thermodynamically favorable pathway for CH_x decomposition. Meanwhile, the SDC support provides abundant O_v sites, which bind H₂O strongly and enable exothermic H₂O decomposition. The elevated O_v concentration and H₂O activation both contribute to enhanced oxygen supply.

5.2.4.3 In-situ exsolved Ni-Ru bimetallic catalyst

The computational studies have suggested that SCNR could lead to improved SMR performance and coking tolerance. To elucidate the synergy between Ni and Ru, we also

synthesized another two reference catalysts, including $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ni}_{0.15}\text{O}_{2-\delta}$ (SCN) and $\text{Sm}_{0.2}\text{Ce}_{0.7}\text{Ru}_{0.15}\text{O}_{2-\delta}$ (SCR), for comparison. Additionally, the CeO_2 -supported Ni-Ru bimetallic catalysts, $\text{Ce}_{0.9}\text{Ni}_{0.1}\text{Ru}_{0.05}\text{O}_{2-\delta}$ (CNR), was prepared to assess the impacts of Sm doping on SMR.

In this work, we have intentionally chosen to leverage the in-situ exsolution method to create SCNR, SCR, SCN, and CNR catalysts. In-situ exsolution allows us to precisely engineer the catalysts' architecture at the nanoscale, facilitating controlled dispersion of catalytically active species within the support matrix, as the exsolved clusters remain firmly anchored within the support²⁷⁹. In-situ exsolution of bimetallic catalysts first requires synthesizing oxides doped with both Ni and Ru. The wet-chemistry method we employed can mix the ions at an atomic level, obtaining a single-phase oxide with a high concentration of Ni and Ru. Upon reduction, the Ni and Ru will exsolve and form nanoparticles or clusters on the oxide surface.

Figure 5.8A and Figure S6 illustrate the X-ray diffraction (XRD) patterns of the as-synthesized catalysts, which show that Sm-doped CeO_2 or CeO_2 is the domain phase. Neither NiO nor RuO_2 was observed on as-synthesized SCNR, indicating both Ni and Ru are mainly dissolved into the SDC lattice, which is essential for the subsequent in-situ exsolution under a reducing atmosphere. On the other hand, small peaks at $\sim 35.0^\circ$ and 54.3° , which correspond to RuO_2 , were observed on SCR catalyst, implying the Ru is partially dissolved into SDC lattice. However, the Ni could be fully doped into SDC. As shown in Figure 5.8B, upon reduction, considerable amounts of a metallic phase, either Ni or Ru, presents on SCN or SCR. However, SCNR does not contain any visible metallic phase, suggesting the Ni and Ru might form clusters that have strong interactions with the oxide support.

H_2 -temperature programmed reduction (H_2 -TPR) was then performed to better understand the in-situ exsolution (Figure 5.8C). H_2 -TPR profiles can divulge insights of the metallic Ni and

Ru nature and their interactions with the oxide support¹⁷⁶. The reduction temperature, at which the H₂-TPR profile peaks, indicates the degree of interaction of the metallic phase with the oxide support. A relatively high reduction temperature suggests that the metallic phase strongly interacts with the oxide support¹⁷⁷. Typically, the in-situ exsolution of Ni from the oxide support requires a higher reduction temperature than that needed to reduce bulk NiO particles, suggesting that in-situ exsolved Ni has stronger interactions with the oxide support than interactions between bulk Ni particles and the oxide support. Specifically, the H₂-TPR profile of SCN exhibits two overlapped peaks at ~260 °C and ~365 °C, corresponding to the reduction of bulk NiO particles (area c) and the in-situ exsolved Ni (area d). The TPR profile of SCR also presents two overlapped two peaks at ~100 °C and 163 °C, which correspond to the reduced RuO₂ particles (area a) and in-situ exsolved Ru (area b).

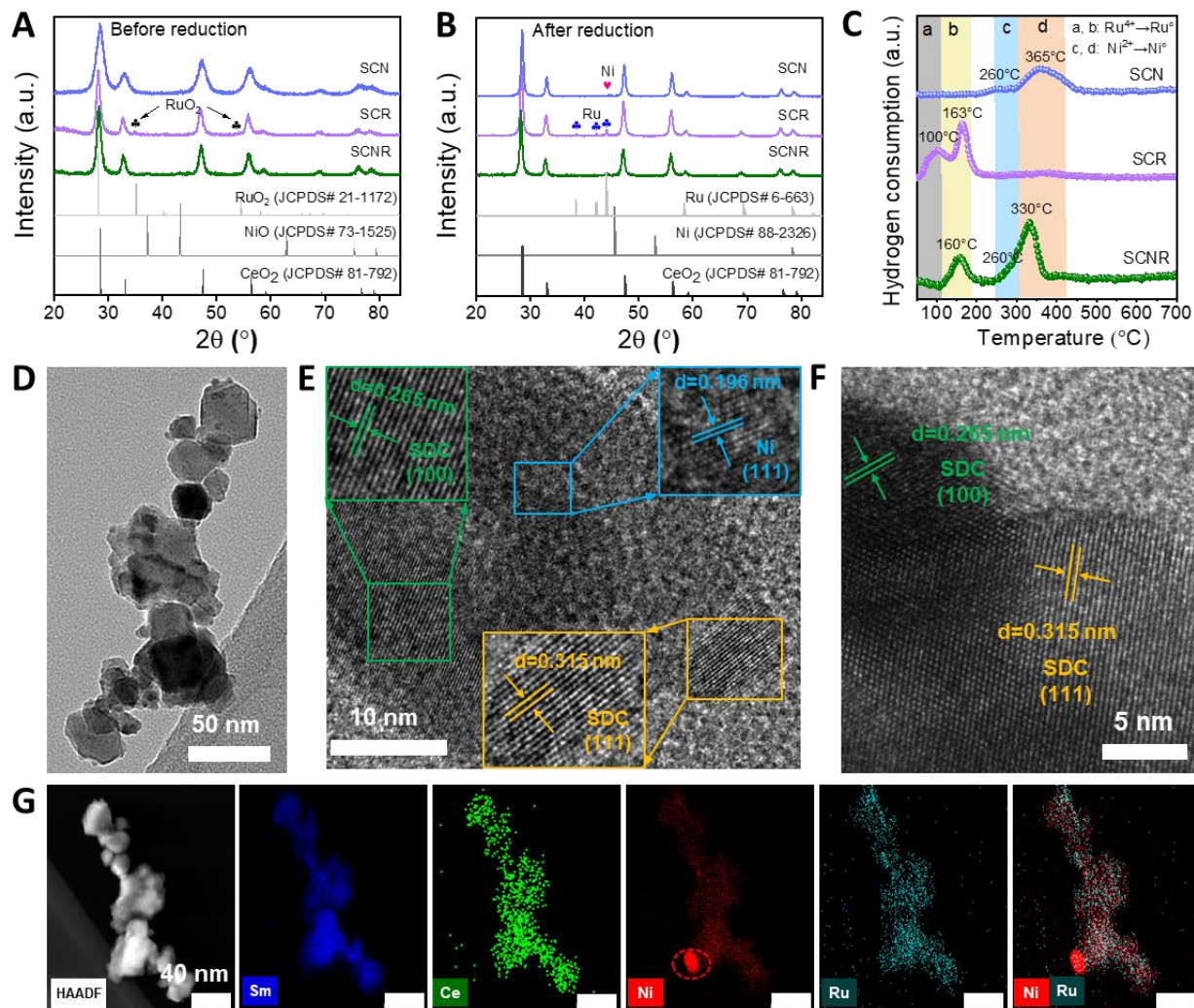


Figure 5.8. The crystal structure and morphology of SMR catalysts. (A) X-ray diffraction (XRD) patterns of as-synthesized SCN, SCR, and SCNR before reduction. (B) XRD patterns of SCN, SCR, and SCNR after reduction. (C) H_2 -temperature programmed reduction (H_2 -TPR) profiles of SCN, SCR, and SCNR. (D) Bright field transmission electron microscopy image of reduced SCNR. (E-F) High-resolution transmission electron microscopy (HR-TEM) images of reduced SCNR. (G) High-angle annular dark-field (HAADF) and Energy-dispersive X-ray spectroscopy (EDS) mapping images of reduced SCNR.

Prior to the peak assigned to the exsolution of Ni (330 $^\circ\text{C}$), the H_2 -TPR profile of SCNR shows the reduction of small amounts of bulk NiO particles, which is associated with the peak at 260 $^\circ\text{C}$, implying that NiO is not fully dissolved in the SDC lattice and a minor amount of NiO exhibits as bulk NiO particles, which is under resolution of XRD. Additionally, the peak

corresponding to the Ni nanoparticles or clusters on SCNR shifts to a lower temperature compared to that of SCN (365 °C for SCN and 330 °C for SCNR), indicating that the active H species adsorbed on the pre-reduced Ru sites could readily spillover to the neighboring Ni species in SDC lattice, and consequently promoting the exsolution of Ni from SDC bulk¹⁷⁸. Therefore, the reducibility of the SCNR catalyst is enhanced, compared to the Ru-free SCN catalyst. Moreover, the presence of Ru can closely interact with NiO species, resulting in a high dispersion on the SNR, which might also lead to the Ni exsolution at a relatively low temperature¹⁸⁰. The peak associated with the reduction of bulk RuO₂ is not observable, indicating that Ru is fully dissolved into the support lattice, which is also consistent with the XRD results.

TEM images and energy-dispersive X-ray spectroscopy (EDS) mapping images of reduced SCNR shown in Figures 5.8D-5.8G reveal the nature of in-situ exsolved Ni and Ru. As displayed in Figure 5.8D, SCNR exhibits a particle size of ~20-30 nm. The high-resolution TEM images (Figures 5.8E-5.8F) show that Sm-doped CeO₂ (SDC) and metallic Ni have two distinctive d-spacings, 0.315 nm and 0.265 nm, which correspond to the SDC (111) and SDC (100) planes, respectively. As shown in Figure 5.8G, Sm and Ce are uniformly distributed on SCNR. However, Ni manifests in two distinct structures, encompassing minor Ni particles (as circled in red) and exsolved Ni clusters that are uniformly dispersed on the whole catalyst surface. The minor Ni particle originates from the reduction of relatively large bulk NiO particles, while the Ni clusters exsolve from the SDC lattice. The EDS mapping images also display a uniform distribution of Ru, with no Ru nanoparticles observed, indicating the presence of metallic Ru exclusively in the form of Ru clusters. These EDS mapping images are in alignment with XRD and H₂-TPR findings, identifying that Ni and Ru primarily exhibit as clusters. Although the XRD pattern for reduced SCNR does not clearly display the peaks corresponding to Ru and Ni, the H₂-TPR profile and

TEM results suggest that Ru and Ni clusters can be created on catalysts support via in-situ exsolution.

The surface electronic structure of reduced SMR catalysts was investigated using X-ray photoelectron spectroscopy (XPS), which is depicted in Figures 5.9A-5.9D and Table S3. The Ni 2p_{1/2} photoemission feature is displayed in Figure 5.9A. The XPS spectra distinctly reveal the existence of Ni in both oxidative (Ni²⁺) and metallic (Ni⁰) states. The Ni 2p_{1/2} of SCR is flat and linear line, indicating there is no Ni detected in SCR. The presence of metallic Ni is relatively low, constituting 21.4 mol%, 15.8 mol% and 11.3 mol% for SCN, SCNR, and CNR, respectively, which could be attributed to the facile oxidation of surface Ni clusters. Similar phenomena were observed on the Ru 3p_{3/2} spectra (Figure 5.9B). The inherent tendency of surface Ru clusters to be oxidized upon air exposure leads to the formation of Ru⁴⁺. Notably, the Ni⁰/Ni²⁺ and Ru⁰/Ru⁴⁺ ratios for SCNR have been found to be lower compared to those of SCN and SCR, respectively. This finding indicates that Ni and Ru tend to exsolve as clusters that exhibit strong interactions with the oxide support, which is consistent with the H₂-TPR profiles. Therefore, both the XPS and H₂-TPR results consolidate the conclusion that both Ni and Ru predominantly exist as clusters on SDC.

The cataloging of oxygen species unveils the presence of four distinct types of oxygen (Figure 5.9C), including lattice oxygen (O_L), oxygen vacancy (O_V), hydroxyl species (O_{OH}), and chemisorbed H₂O (O_W). With the introduction of Ru, there is a noticeable increase in the O_W concentration, ranging from ~8 mol % (SCN) to ~21.4 mol %, 17.6 mol % and 18.9 mol % for SCR, SCNR and CNR, respectively. This is also in good agreement with concentrations of the oxygen atoms in water molecules observed from BE_{H_2O} calculation (Figure 5.7B). The increased O_W concentration indicated the water uptake capability can be enhanced with adding Ru, suggesting Ru can improve coking tolerance. Nevertheless, the trend of O_V concentration is

opposite to that of O_w , which follows the sequence of $SCN > SCNR > CNR > SCR$, which is also consistent with the DFT modeling results (Figure 5.7A). This suggests that introducing Ni could promote the formation of oxygen vacancies. This might be attributed to the charge balance since Ni exists in the oxidation state of Ni^{2+} and replaces one Ce^{4+} with one Ni^{2+} ($CeO_2 \xrightarrow{NiO} Ce''_{Ni} + O^x_O + V^{\bullet\bullet}_O$), leading to the generation of one oxygen vacancy. Furthermore, the addition of Sm also promotes the formation of oxygen vacancies, as supported by the higher concentration of oxygen vacancies in SCNR ($O_v=23.3$ mol %) compared to CNR ($O_v=19.6$ mol %). This observation aligns well with the fact that CNR exhibits a lower concentration of Ce^{3+} necessary to maintain electrostatic neutrality (Figure 5.9D). Consequently, all the characterizations indicate that SCNR has the potential to achieve improved SMR performance and enhanced coking tolerance.

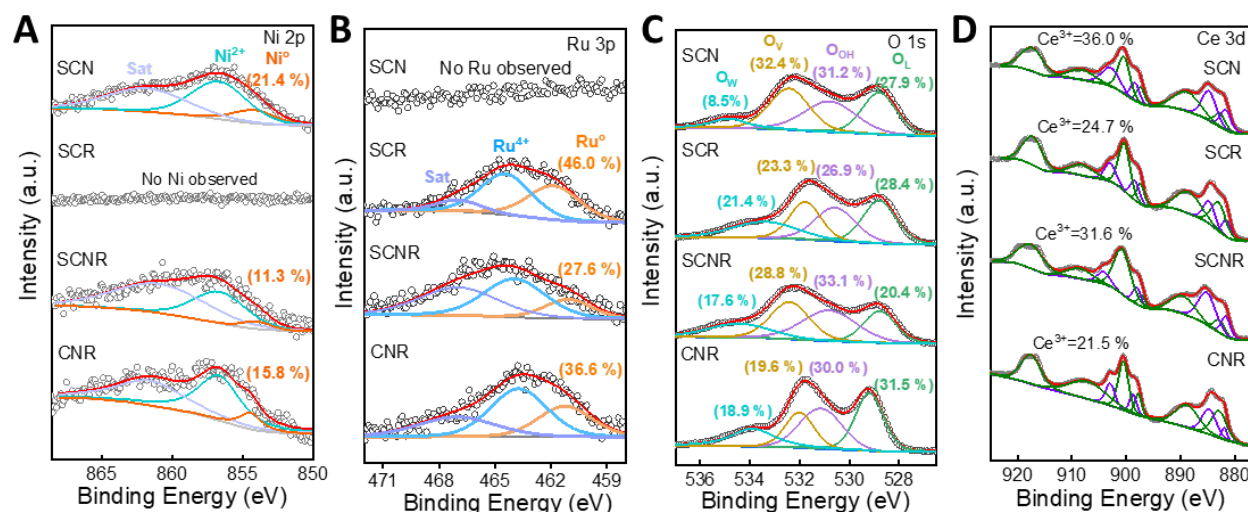


Figure 5.9. X-ray photoelectron spectroscopy (XPS) of (A) Ni 2p, (B) Ru 3p, (C) O 1s, and (D) Ce 3d for reduced SCN, SCR, SCNR, and CNR catalysts. The unit for the element concentration is mol %.

5.2.4.4 Enhanced catalytic activity and improved coking tolerance

To assess the catalytic activities of newly developed SMR catalysts, catalytic performance was evaluated in a packed bed reactor (PBR) under a relatively low S:C ratio of 1:2. The SCNR

catalyst achieves the highest CH₄ conversion (Figure 5.10A) and H₂ production rate (Figure S7) in the temperature range of 550-700 °C. Particularly, at 700 °C, the CH₄ conversion of SCNR reaches 36.4%, which is higher than that attained on SCN or SCR. These findings substantiate the synergy between Ni and Ru, which enhances the SMR activity. This synergy tends to be more significant with reducing the operating temperature. At 500 °C, a CH₄ conversion of 21.6% is achieved on SCNR, representing a substantial improvement as compared to SCN (9.4%) and SCR (15.2%). These results underscore the highlighted significance of the synergistic effects at a low operating temperature.

The computational studies have suggested Sm doping can further promote SMR performance. To validate it, the influence of Sm doping on CeO₂ support was investigated. As illustrated in Figure 5.10B and Figure S8, compared to the CeO₂-supported Ni-Ru, Sm doping can enhance the overall catalytic activity. For example, the SCNR catalyst leads to a CH₄ conversion increasement of 24.7%, 23.5%, 19.2% and 26.3% at 700, 650, 600 and 550 °C, respectively. The catalytic performance was also assessed under S:C=1:1 (Figure S9-S10), which further confirms that SCNR exhibits superior SMR performance under a wide range of operating conditions.

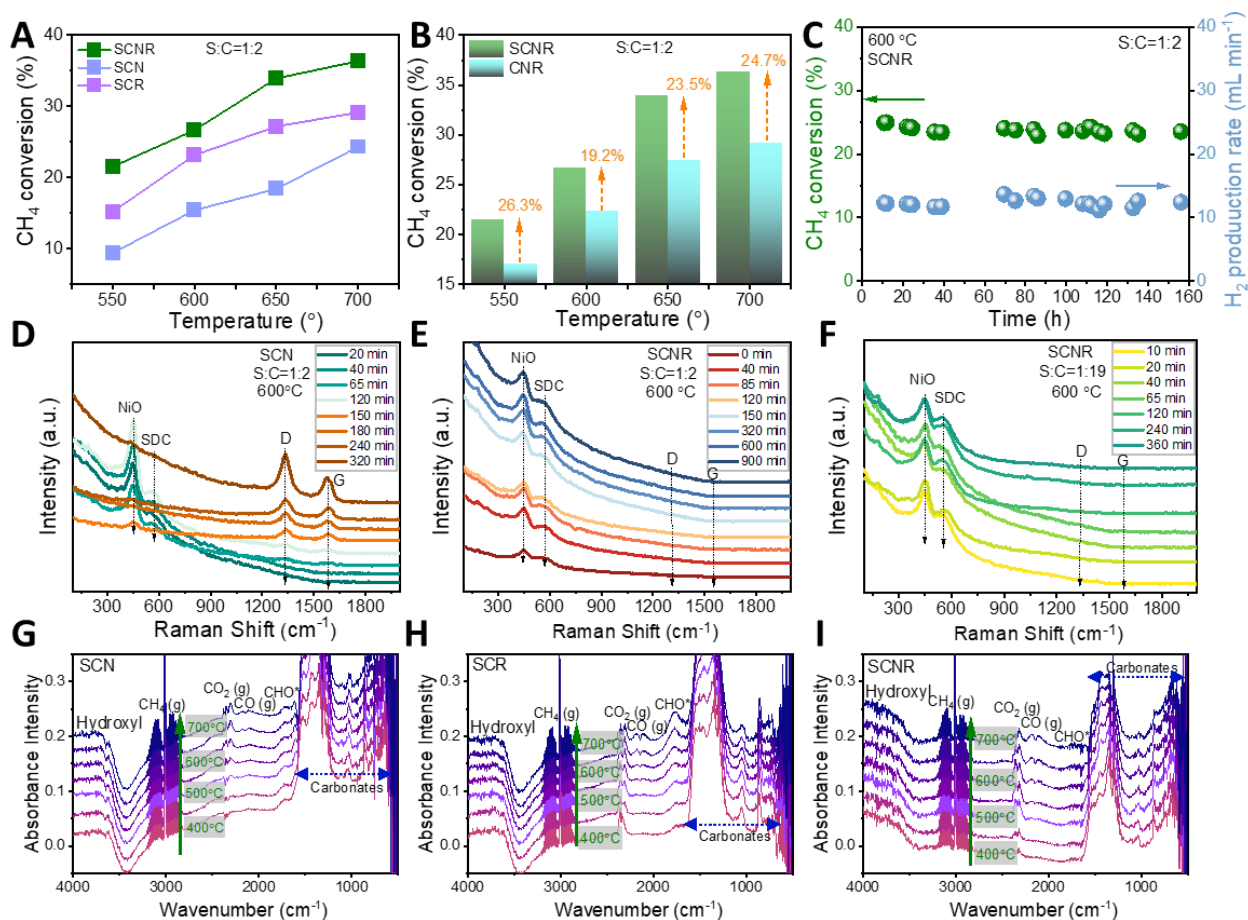


Figure 5.10. The CH₄ conversion and coking tolerance of rationally designed SMR catalysts. (A) The CH₄ conversion achieved on SCNR, SCN, and SCR in PBRs. (B) Comparison of the CH₄ conversion achieved on SCNR and CNR in PBRs. (C) The CH₄ conversion as a function of operation time obtained on SCNR in a PBR at 600 °C. In situ Raman spectroscopy of SMR on (D) SCN at 600 °C and under a S:C ratio of 1:2, (E) SCNR at 600 °C and under a S:C ratio of 1:2, and (F) SCNR at 600 °C and under a S:C ratio of 1:19. D band corresponds to the disordered or amorphous carbonaceous structures, and G band is related to the graphite or graphitic-like structures. In situ DRIFTS spectra of (G) SCN, (H) SCR and (I) SCNR to probe the intermediate species under a S:C ratio of 1:20.

Another challenge associated with SMR catalyst pertains to the propensity to coking, particularly at a low steam concentration. At 600 °C, we conducted a long-term stability testing of SCNR under a S:C ratio of 1:2 (Figure 5.10C). Remarkably, SCNR exhibits good stability over approximately 160 hours of operation, with a stable CH₄ conversion (~25%) and H₂ production rate (~12.5 mL min⁻¹) obtained. In situ HT-XRD patterns (Figure S11) show that no indications of structural decomposition or observable phase transitions were observed across the entire

temperature range, extending up to 750°C. These findings further corroborate the claim that SCNR demonstrates outstanding structural stability under SMR conditions. To gain an in-depth understanding of the coking tolerance, we employed in-situ Raman spectroscopy to explore the dynamic interactions between gaseous reactants and catalysts. The D ($\sim 1350\text{ cm}^{-1}$) and G ($\sim 1580\text{ cm}^{-1}$) bands, originating from the Raman scattering of carbonaceous materials, play a significant role in assessing coking features. The obtained Raman spectra, depicted in Figures 5.10D-5F, were acquired as a function of time following exposure to a $\text{CH}_4\text{-H}_2\text{O}$ mixture. Evidently, the appearance of the D-band and G-band, indicative of coking, manifested rapidly on SCN after approximately 65 minutes under a S:C ratio of 1:2 (Figure 5.10D), signifying its susceptibility to coking. With operational duration increasing, the intensity of these peaks grew concurrently. In contrast, SCNR displays negligible signs of coking after 900 min of operating, thereby corroborating its markedly improved coking tolerance relative to SCN (Figure 5.10E). These results emphasize the role of Ru in enhancing coking tolerance. Furthermore, the performance evaluation of the SCNR catalyst under more stringent conditions, for example, at a S:C of 1:19 (5 % steam), reveals an absence of coking, reinforcing the superior coking tolerance of the SCNR catalyst.

In-situ DRIFTS analyses were employed to probe the nature of active adsorbed species on the catalyst surface during the SMR process, aiming to better understand the SMR mechanisms. Figures 5.10G-H show steady-state spectra recorded under simulated SMR operating conditions on SCN, SCR, and SCNR at an operating temperature ranging from 400°C to 700°C. The DRIFTS spectra reveal distinctive bands in two primary regions, with one set emerging between 4000 and 2500 cm^{-1} and another set between 2500 and 500 cm^{-1} ²⁸⁰. The bands in the first region correspond to hydroxyl groups (4000-3700 cm^{-1}) and CH_4 (g) ($\sim 3016\text{ cm}^{-1}$). Bands in the second region

correspond to CO_2 (g) ($2380\text{--}2260\text{ cm}^{-1}$) and CO(g) (~ 2183 and 2108 cm^{-1}), CHO^* ($\sim 1725\text{ cm}^{-1}$), and associated carbonate species ($500\text{--}1490\text{ cm}^{-1}$). It is evident that SCNR exhibits a greater propensity to forming CO(g) compared to SCR and SCN, which is consistent with the catalytic activity trend obtained from PBR experiments ($\text{SCNR} > \text{SCR} > \text{SCN}$). Notably, the introduction of Ru proves advantageous for the formation of CHO^* . This suggests that the introduction of Ru boosts CO production through this carbon self-cleaning pathway²⁸¹. This finding is consistent with enhanced coking tolerance for Ru-containing catalysts and SMR mechanisms illustrated in Figure 5.6D.

5.2.4.5 CH_4 -SOFC equipped with SCNR achieves unprecedented performance and durability

The high-performance and coking-tolerant CH_4 -SOFCs were constructed by coating an SCNR anode catalytic layer. The performance of CH_4 -SOFCs was evaluated at $700\text{--}600\text{ }^\circ\text{C}$ and under a S:C of 1:2. Figures 5.11A and 5.11B show the current-voltage-power (I-V-P) curves of CH_4 -SOFCs equipped with SCNR catalyst and pristine CH_4 -SOFCs. The CH_4 -SOFC with SCNR catalytic layer significantly enhances power densities. For example, at $700\text{ }^\circ\text{C}$, SCNR-decorated CH_4 -SOFC exhibits a peak power density of 1159 mW cm^{-2} , outperforming CH_4 -SOFCs previously reported in the literature (Figure 5.6A). Additionally, the SCNR-decorated CH_4 -SOFC leads to more substantial improvements at low operating temperatures, which could be ascribed to the lower activation energy of the SCNR in terms of the SMR activity, compared to the bare anode of SOFCs. These results highlight that the SCNR catalytic layer effectively converts CH_4 to H_2 , consistent with the SMR performance demonstrated in PBRs (Figures 5.10A and 5.10B).

The corresponding EIS spectra (Figures 5.11C and 5.11D) show that area specific polarization resistance ($ASRp$) is substantially reduced on SCNR-decorated CH₄-SOFCs, indicating the SCNR catalytic layer facilitates electrochemical processes that occur on the anode. To better visualize this, a comparison of the $ASRp$ was shown in Figure 5.11E at a terminal voltage of 0.95 V and 0.85 V. This improvement is particularly noticeable at lower temperature and smaller terminal voltage. For example, at 600 °C and 0.85 V, the $ASRp$ of the SCNR-decorated CH₄-SOFC is 0.64 Ω cm², which is only 56% of the value for the cell with a bare anode (1.14 Ω cm²).

To gain deeper insights into the processes occurring in CH₄-SOFCs, distribution of relaxation time (DRT) analyses of EIS spectra at 600 °C and 0.85 V were conducted and presented in Figure 5.11F. The DRT plots are divided into three main regions, the low frequency (LF, 100-1000 Hz), intermediate frequency (MF, 1000-50000 Hz), and high frequency (HF, >50000 Hz) regions, corresponding to mass transport, surface exchange kinetics, and the charge transfer process, respectively^{50,127}. First, the LF peak substantially decreases with using SCNR as the internal SMR catalyst, indicating that the gas diffusion process is significantly accelerated, which is attributed to the fact that SCNR enhances CH₄ conversion and produces more H₂. Second, the CH₄-SOFC with SCNR also exhibits smaller MF peaks, indicating that surface exchange processes could also be promoted by SCNR. Additionally, the catalytic layer shows a slightly small value for the HF peak, indicating that charge transfer step is not the rate limiting step for the CH₄-SOFCs.

The electrochemical stability of CH₄-SOFCs were then examined at 600 °C and under 5 % steam. Figure 5.11G shows that the pristine CH₄-SOFC shows severe degradation, with the terminal voltage decreasing from 400 mV to nearly 0 mV within 6 hours. The severe degradation could be ascribed to coking (Figure S12), which blocks active sites for SMR (Figure S13). The SCNR-decorated CH₄-SOFC attains a terminal voltage that stabilized at ~ 0.5 V for a continuous

operation of >2250 h (Figure 5.11H). The SEM images (Figure S14) and Raman spectroscopy (Figure S12) of CH₄-SOFC do not show noticeable microstructural changes or carbon deposits indicating that SCNR improves the coking tolerance of the SOFC anode. The slight degradation shown in Figure 5.11H could be attributed to the coarsening of the SCNR catalyst. Prolonged exposure to SMR conditions has resulted in the agglomeration of SCNR particles (Figure S15), lowering the catalytically active surface area, which leads to the minor degradation.

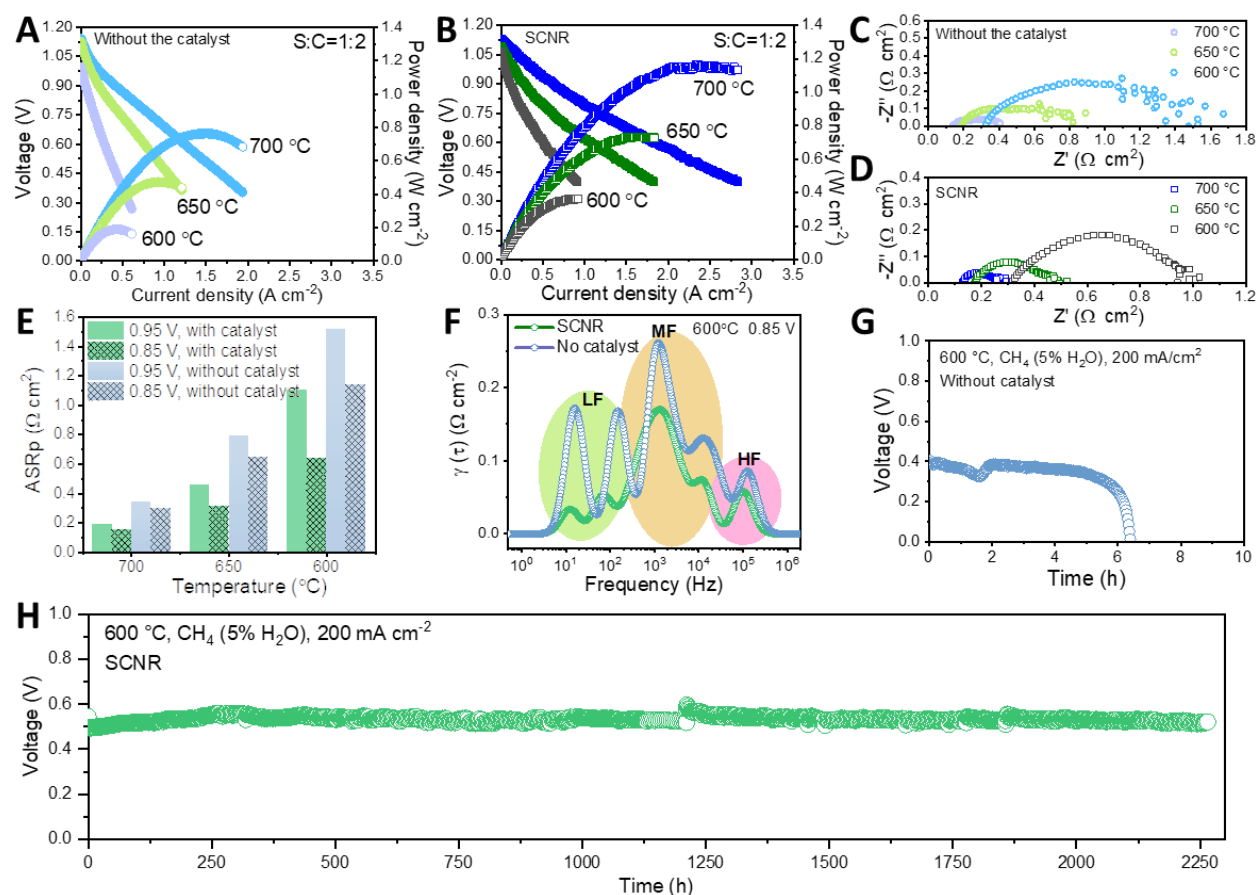


Figure 5.11. Electrochemical performance of CH₄-SOFCs. (A) I-V and I-P curves of a CH₄-SOFC without the anode catalytic layer. (B) I-V and I-P curves of a CH₄-SOFC with SCNR as the anode catalytic layer. (C) EIS spectra corresponding to the cell tested in (A). (D) EIS spectra corresponding to the cell tested in (B). (E) ASRp comparison of CH₄-SOFCs with and without the anode catalytic layer. (F) Distribution of relaxation time (DRT) analyses of EIS tested at 600 °C and 0.8 V. The electrochemical stability testing of CH₄-SOFC (G) without and (H) with the anode catalytic layer at 600 °C and 5% H₂O.

5.2.5 Conclusions

In this study, detailed DFT modeling was conducted to study the synergy between Ni and Ru and the impacts of Sm doping on SMR. We have determined that synergistic effects of Ni-Ru can significantly reduce the energy barrier of the first C-H bond activation in CH₄ molecules and favor the following CH_x decomposition. Moreover, the SDC support exhibits a high oxygen vacancy concentration, accelerating the H₂O adsorption and dissociation. Therefore, SDC-supported Ni-Ru (SCNR) can achieve enhanced SMR activity and improved coking tolerance. We have demonstrated the high-performance and durable CH₄-SOFCs by applying SCNR as the anode catalytic layer, resulting in exceptional peak power densities and stability, with continuous operation exceeding 2000 h. For example, employing the SCNR as an internal reforming catalytic layer has significantly increased the PPDs of CH₄-SOFC, with improvements from 762, 473, 190 mW cm⁻² to 1159, 733, and 361 mW cm⁻² at 700 °C, 650 °C, and 600 °C, respectively. These advancements underscore the catalytic activity and coking tolerance inherent to the newly developed SCNR, which also emphasize the critical role of SCNR decorated CH₄-SOFCs in achieving high-efficiency and durable power generation.

5.2.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1021/jacs.3c12121>.

Chapter 6 – Electrochemical CO₂ hydrogenation in PCECs for syngas production

6.1 Enhanced CO₂ methanation activity of Sm_{0.25}Ce_{0.75}O_{2-δ}-Ni by modulating the chelating agents-to-metal cation ratio and tuning metal–support interactions

6.1.1 Abstract

Highly active and selective CO₂ methanation catalysts are critical to CO₂ upgrading, synthetic natural gas production, and CO₂ emission reduction. Wet impregnation is widely used to synthesize oxide-supported metallic nanoparticles as the catalyst for CO₂ methanation. However, as the reagents cannot be homogeneously mixed at an atomic level, it is challenging to modulate the microstructure, crystal structure, chemical composition, and electronic structure of catalysts via wet impregnation. Herein, a scalable and straightforward catalyst fabrication approach has been designed and validated to produce Sm_{0.25}Ce_{0.75}O_{2-δ}-supported Ni (SDC-Ni) as the CO₂ methanation catalyst. By varying the chelating agents-to-total metal cations ratio (C/I ratio) during the catalyst synthesis, we can readily and simultaneously modulate the microstructure, metallic surface area, crystal structure, chemical composition, and electronic structure of SDC-Ni, consequently fine-tuning the oxide-support interactions and CO₂ methanation activity. The optimal C/I ratio (0.1) leads to an SDC-Ni catalyst that facilitates C-O bond cleavage and significantly improves CO₂ conversion at 250 °C. A CO₂-to-CH₄ yield of >73% has been achieved at 250 °C. Furthermore, a stable operation of >1500 hours has been demonstrated, and no degradation is observed. Extensive characterizations were performed to fundamentally understand how to tune and enhance CO₂ methanation activity of SDC-Ni by modulating the C/I ratio. The correlation of physical, chemical, and catalytic properties of SDC-Ni with the C/I ratio is established and thoroughly elaborated in this work. This study could be applied to tune the oxide-support interactions of various catalysts for enhancing the catalytic activity.

6.1.2 Introduction

Converting CO₂ and renewable H₂ to CH₄ can produce sustainable natural gas, reduce the reliance on fossil fuels, and decrease greenhouse gases emissions, leading to substantial economic and environmental benefits²⁸²⁻²⁸⁵. CO₂ methanation is thermodynamically favorable at 200-300 °C. However, CO₂ molecules are very stable, and accordingly, high operating temperatures (>300 °C) are required to activate CO₂ molecules and achieve practically valuable CH₄ yield, necessitating the development of highly active catalysts for CO₂ conversion at <300 °C^{286 287}. However, CO₂ methanation at high operating temperatures consumes extensive energy and inevitably favors CO₂-to-CO conversion, reduce the equilibrium CO₂ conversion, and decrease CH₄ yield and purity. Therefore, a CO₂ methanation catalyst that can attain a CH₄ selectivity of >99%, a CH₄ yield of >70% and a long operation stability at 250 °C is essential for economic renewable natural gas production. Despite enormous efforts that have been devoted to designing and synthesizing advanced CO₂ methanation catalysts via novel approaches, such as noble metal-based catalysts^{190,288-290}, metal-organic frameworks (MOFs)-supported metallic nanoparticles^{291,292}, and plasma treatment²⁹³, there are limited facial and scalable fabrication methods which can readily fine-tune metal-support interactions to realize a CO₂-to-CH₄ yield of >70% with a long-term stable operation (>1000 hours) at 250 °C.

It has been recognized for a long time that synergistic interactions are exhibited between oxide support and metallic nanoparticles. These interactions typically relate to the microstructure of metallic nanoparticles and oxide support, chemical compositions and electronic structure of both oxides and metallic nanoparticles, charge transfer between oxide and metal, and interfacial active area, which plays essential roles in activating and converting CO₂^{244,294-303}. Modulating these metal-support interactions is therefore a promising approach to improving CO₂ conversion

and tuning the CO₂ methanation selectivity³⁰⁴. It has been demonstrated that this approach can result in fifteen times higher productivity than conventional catalysts²⁴⁴. Despite that, the metal-support interactions should be deliberately designed and controlled for different sets of catalysts and chemical reactions; Otherwise, these interactions could be detrimental to catalytic performances and stability^{305,306}. For instance, reducing the particle size of oxide or metallic nanoparticles cannot continuously improve the catalytic performances³⁰⁷. Therefore, an approach that could straightforwardly and carefully tune metal-support interactions should be established to enhance CO₂-to-CH₄ yield at 250 °C.

CeO₂ has been widely used as the support for several catalytic reactions, including CO₂ methanation^{157-160,245,308}. This is attributed to the characteristic of CeO₂ that exhibits high oxygen storage capacity, which is ascribed to the redox couple of Ce⁴⁺/Ce³⁺³⁰⁹⁻³¹¹. Additionally, it is found that the oxygen vacancy is one of the most active sites as it functions as the basic site for CO₂ adsorption and the consequent formation of carbonate, formate, or CO intermediates. A higher oxygen vacancy concentration and enhanced lattice oxygen mobility can improve the catalytic activity of CeO₂-supported Ni^{153,312}. As Sm-doped CeO₂ displays the smallest enthalpy of association between the dopant cations and oxygen vacancies in the fluorite lattice¹⁶¹, we doped CeO₂ with Sm to further increase the oxygen vacancy concentration and simultaneously enhance the mobility of lattice oxygen. A CO₂-to-CH₄ yield of 73.3 % is achieved over SDC-Ni catalyst at 250 °C, which doubles the performances of CeO₂-supported Ni synthesized via the same approach (the CO₂-to-CH₄ yield is 39.0%), implying Sm doping can dramatically improve CO₂ methanation activities. Therefore, in this work, we focus on studying SDC-Ni as CO₂ methanation catalysts.

Wet impregnation is widely used to synthesize oxide-supported metallic nanoparticles, including CeO₂-supported Ni. However, this approach results in poor metal-support interactions

while the fabrication process is slightly complicated and time-consuming. Herein we demonstrated a straightforward approach to synthesizing CO₂ methanation catalysts. Unlike the impregnation process, the wet-chemistry method allows mixing Sm, Ce, and Ni ions at an atomic level, subsequently offering opportunities to control the compositions, morphology, and particle size of both SDC and Ni, and modulate the electronic structures of SDC and Ni, as well as tune the metal-support interactions. We recognize these objectives could be achieved by appropriately varying the ratios of chelating agents (i.e., citric acid and ethylene glycol) to total metal cations (C/I ratios). A C/I ratio of 0.1 results in the SDC-Ni catalyst with strong metal-support interactions, largest metallic Ni surface areas, and highest Ni dispersion, which delivers a single-pass CO₂ conversion of 73.6% and CH₄ selectivity of 99.5% at 250 °C. Compared with the traditional wet impregnation, a more than six times improvement of CH₄ yield has been achieved. According to the in-situ operando DRIFT spectra, we noted that an intermediate C/I ratio result in a catalyst (i.e., SDC-Ni-0.1), which significantly facilitates the C-O bond cleavage. Formate species could therefore quickly decompose to formyl, which can be subsequently hydrogenated to methane, leading to the enhanced CO₂-to-CH₄ yield, specially at 250 °C.

6.1.3 Methods and materials

6.1.3.1 Material and catalyst preparation

Sm_{0.25}Ce_{0.75}O_{2-δ}-supported Ni catalysts (SDC-Ni-*x*, *x* denotes C/I ratios, *x* = 0, 0.01, 0.05, 0.1, 0.5, and 2.0) were synthesized via one-pot wet chemistry method. The originally designed Ni loading of all these catalysts is 20 wt. %. A stoichiometry amount of samarium nitrate hexahydrate (Sm(NO₃)₃·6H₂O), cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O), and nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O) was firstly dissolved in distilled water. To tune the properties of

metal-support interactions, SDC-Ni-x were synthesized by adding chelating agents (i.e., citric acid and ethylene glycol) with C/I ratios of 0, 0.01, 0.05, 0.1, 0.5, and 2.0. The molar ratio of citric acid and ethylene glycol is 1:1. The above solution was subsequently stirred at 250 °C until a gel was formed. The gel was immediately moved to a drying oven at 175 °C for 24 h, followed by calcination under air at 600 °C for five hours to obtain the as-fired catalysts. CeO₂-Ni-0.1 and CeO₂-Ni-2.0 were synthesized via the same approach with the same Ni loading.

SDC-Ni-0.1-IM (IM means impregnation) was also prepared by using the conventional wet impregnation method. The catalyst support (SDC-0.1) was prepared by following the same approach with that of SDC-Ni-0.1 and using the same C/I ratio. The SDC-0.1 support was obtained after the same drying and calcination processes. Wet impregnation was then performed by mixing SDC-0.1 with DI water and nickel (II) nitrate hexahydrate (Ni loading is 20 wt. %). After stirring for four hours and evaporating the water on a hot plate at 250 °C, the powder was calcined in air at 600 °C for five hours to prepare SDC-Ni-0.1-IM catalyst.

6.1.3.2 Catalyst characterization

The as-fired catalysts were reduced under 20% H₂ balanced with Ar (20 sccm H₂ + 80 sccm Ar) at 600 °C for two hours. The X-ray diffraction (XRD) patterns were collected using a Rigaku MiniFlex diffractometer with a Cu K α radiation source operated at 30 kV and 15 mA (2 θ : 10-90°, scanning speed: 0.5°/min). The Rietveld refinements were performed using the open source GSAS software¹⁷⁵. The grain size of Ni (111) ($d_{Ni(111)}$) was estimated by Scherrer's equation:

$$d_{Ni(111)}(\text{nm}) = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where K is the shape factor (0.98), λ is the X-ray wavelength (0.154 nm), β is the full width at half-maximum in radians, and θ is the Bragg angle.

The turnover frequency of CO₂ methanation (TOF_{CH₄}) is calculated as the ratio of CH₄ production rate (r_{CH_4} , mol g cat⁻¹ min⁻¹) to the number of active Ni sites on the Ni surface ($N_{surface}$)³¹³, which was determined by H₂ pulse chemisorption experiments.

$$TOF_{CH_4} = \frac{r_{CH_4}}{N_{surface}} \quad (2)$$

X-ray photoelectron spectroscopy (XPS) was performed by using Phi 5000 VersaProbe II X-ray Photoelectron Spectrometer. Transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) were performed with a FEI Talos F200X TEM/STEM using a 200 keV accelerating voltage.

BET (nitrogen Brunauer-EmmettTeller) surface area analysis was performed using a ChemBET Pulsar to determine the surface area of SDC-Ni catalysts before reduction. Samples were firstly degassed at 250 °C for 2 hours and subsequently purge with N₂. The surface area was analyzed by using Quantachrome TPRwin v4.1.

Temperature-programmed reduction (TPR) was conducted using a ChemBET Pulsar. 0.1 g of the catalyst was pretreated in a U-shaped quartz tube at 140 °C for half an hour under flowing of N₂ (100 sccm) to remove any moisture and impurities. After cooling down to 25 °C, the gas was switched from N₂ to 15 % H₂ balanced with Ar under a flow rate of 100 sccm. The TPR analysis was then performed with a heating rate of 10 °C/min.

The metallic Ni surface area and Ni dispersion were measured by performing H₂ pulse chemisorption. H₂ pulse chemisorption was also conducted using a ChemBET Pulsar. 0.1 g of the catalyst was loaded in a U-shaped quartz tube and reduced at 600 °C for two hours under 20% H₂ balanced with N₂ (the same reduction procedure with catalyst testing in a fixed bed reactor). At 600 °C, the atmosphere was then changed to ultra-high purity (UHP) nitrogen for 2 hours to remove the gaseous and adsorbed hydrogen. After cooling the temperature to 25 °C under UHP nitrogen,

50 μL H_2 was repeatedly injected to the reactor until the H_2 chemisorption on Ni reaches equilibrium. The metallic Ni surface area and dispersion were analyzed by using Quantachrome TPRwin v4.1.

In-situ operando DRIFTS were performed with Thermo Fisher iS50 FTIR spectrometer equipped with the Praying Mantis™ high-temperature reaction chamber. The chamber temperature was controlled by the temperature controller while the catalyst temperature loaded into the reaction chamber was calibrated by the second thermocouple. The atmosphere of the reaction chamber was controlled by the mass flow controllers. In-situ operando DRIFTS of CO_2 methanation over SDC-Ni-0.1 and SDC-Ni-2.0 were performed when the chamber atmosphere was switched from 100 sccm UHP Ar to 11 sccm CO_2 , 44 sccm H_2 , and 45 sccm UHP Ar at 250 °C. To probe the CO_2 methanation pathway, formic acid was used as the reactant. At 250 °C, the spectra were first collected over 40 minutes when the chamber atmosphere was changed from UHP Ar to a mixture of Ar and formic acid (Ar bubbles through formic acid at room temperature). The chamber atmosphere was subsequently changed from a mixture of Ar and formic acid to Ar to degas the chamber. The spectra were simultaneously collected. Finally, the spectra were collected upon changing the chamber atmosphere from Ar to 20% H_2 balanced with Ar to reduce the intermediate species adsorbed on SDC-Ni. The total gas flow rate for these steps is 100 sccm.

6.1.3.3 Catalyst testing

The CO_2 methanation measurements were carried out in a continuous flow fixed bed (quartz) tubular reactor (0.28-inch i.d.) at 0.1MPa. 100 mg of each catalyst was loaded into the reactor. A thermocouple was inserted into the tube reactor close to the catalyst to measure the temperature. The catalyst was first reduced under 20% H_2 balanced with Ar (100 sccm) at 600 °C

for two hours. After reduction, the reactor temperature was decreased to 300 °C and the feedstock, a mixture of CO₂ and H₂ with a H₂/CO₂ ratio of 4 or 1 at a flow rate of 20 sccm, is introduced to the reactor (GHSV=12000 ml h⁻¹g⁻¹). The outlet gas compositions were determined using an online gas chromatography (INFICON 3000 Micro GC) at 300 °C and 250 °C. The reactor was hold at each temperature for 40 mins before measuring the outlet gas compositions. The CO₂ conversion (X_{CO_2}), CH₄ selectivity (S_{CH_4}), CH₄ yield (Y_{CH_4}) are calculated as follows:

$$X_{CO_2}(\%) = \frac{F_{CO_2,in} - F_{CO_2,out}}{F_{CO_2,in}} \times 100\% \quad (3)$$

$$S_{CH_4}(\%) = \frac{F_{CH_4,out}}{F_{CH_4,out} + F_{CO,out}} \times 100\% \quad (4)$$

$$Y_{CH_4}(\%) = X_{CO_2} \times S_{CH_4} \times 100\% \quad (5)$$

Where F_{in} or F_{out} represents the flow rate of inlet gas or outlet gas, respectively.

6.1.4 Results and discussion

6.1.4.1 The C/I ratio – catalytic performances relationship

SDC-Ni-x (x=0, 0.01, 0.05, 0.1, 0.5 and 2.0) catalysts are synthesized via one-pot wet-chemistry method illustrated in Figure S1. A stoichiometric amount of samarium nitrate, cerium nitrate, and nickel nitrate is mixed with a certain amount of citric acid (CA) and ethylene glycol (EG). Metal citrates are first formed, reacting with the ethylene glycol, namely polyesterification, to generate a covalent network with trapped Sm, Ce, and Ni ions. The produced gel will be subsequently dried and fired in air to synthesize CO₂ methanation catalysts. The C/I ratios can therefore determine the amount of polyesterified network and consequent homogeneity of metal ions dispersed throughout the network.

This facile one-pot approach can readily fabricate a composite of SDC and NiO under a wide range of C/I ratios (Figure S2 and Table S1). After reduction, the catalysts can then be reduced to SDC-supported Ni (Figure S3 and Table S2). No impurity phase is observed, validating that this approach could be applied for synthesizing SDC-Ni-x catalysts. The impact of C/I ratio on the surface area is shown Table S3. A surface area of 16.11, 24.96, and 30.57 cm²/g is obtained under a C/I ratio of 0.01, 0.1, and 2.0, respectively. Increasing the C/I ratio causes a higher polyesterification rate, resulting in more covalent networks and consequently leading to higher porosity.

To understand the impact of Sm doping, CeO₂-supported Ni with 20 wt.% Ni (CeO₂-Ni-0.1) was synthesized via the same approach as SDC-Ni-0.1. The CH₄ yield over SDC-Ni-0.1 almost doubles the performance of CeO₂-Ni-0.1 (Figure S4A) at 250 °C, indicative of the beneficial impacts of Sm doping. We also compare the performances of SDC-Ni-0.1 with SDC-supported impregnated Ni (SDC-Ni-0.1-IM) and noted that the CH₄ yield of SDC-Ni-0.1 is more than six times higher than that of SDC-Ni-0.1-IM at 250 °C (Figure S4B). By employing this wet-chemistry catalyst synthesis approach, the CH₄ yield at 250 °C has been improved from ~11.2% to 73.3%, suggesting this method leads to enhanced metal-support interactions than wet impregnation.

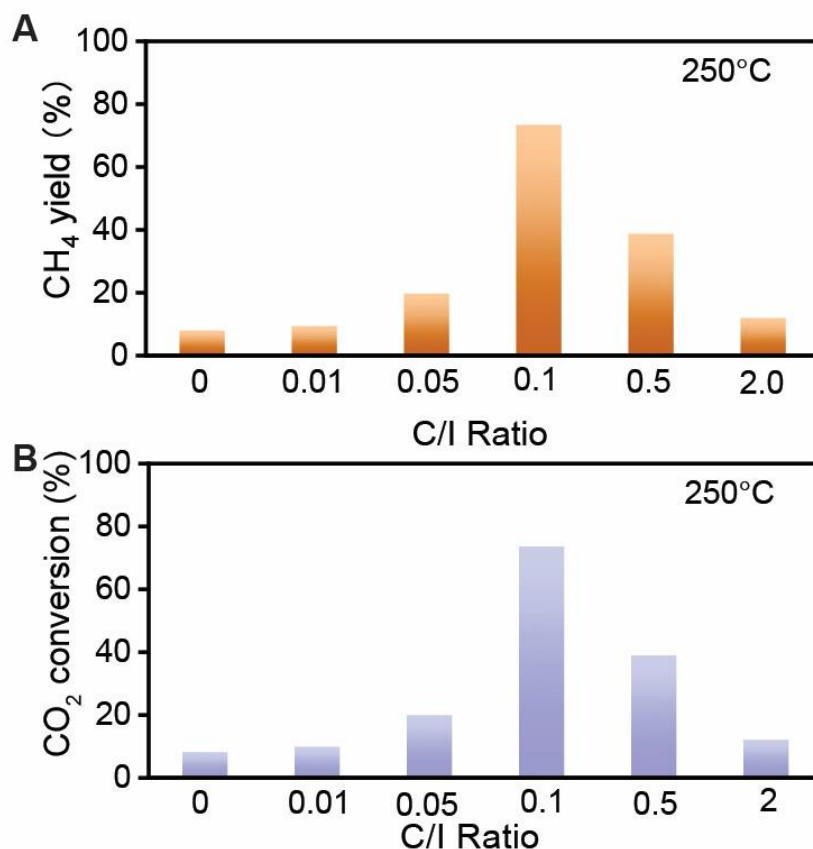


Figure 6.1. Catalytic performances of SDC-Ni- x (C/I ratio $x = 0, 0.01, 0.05, 0.1, 0.5$ and 2.0). (A) CO₂-to-CH₄ yield over SDC-Ni catalysts synthesized under various C/I ratios. (B) CO₂ conversion as a function of the C/I ratio.

We then studied how to further tune the metal-support interactions by modulating the C/I ratio. The CH₄ yield as a function of the C/I ratio displays a volcano-like trend at 250 °C (Figure 6.1A). SDC-Ni synthesized with a C/I ratio of 0.1 (i.e., SDC-Ni-0.1) exhibits the highest CH₄ yield (73.6%), which represents outstanding CO₂ methanation performances at 250 °C (Table S4). The CH₄ yield over SDC-Ni-0.1 is more than seven times and six times higher than SDC-Ni-0.01 and SDC-Ni-2.0, respectively. As shown in Figure S5 turnover frequency (TOF) of SDC-Ni as a function of the C/I ratio also shows the same trend, which implies modulating the C/I ratio can significantly tune the catalytic properties. An excessive amount of chelating agents, for instance, a C/I ratio of 2.0, is generally used to synthesize catalysts with small particle size and high surface

areas. However, a C/I ratio of 2.0 does not give rise to the best catalytic performances. It has been recognized that the C/I ratio can substantially affect the CO₂ conversion while its impacts on CH₄ selectivity is not obvious (Figure 6.1B and Figure S6). For example, at 250 °C, SDC-Ni-0.1 shows a CO₂ conversion of 73.6%, which is 7.5 time of SDC-Ni-0.01 and 6.1 time of SDC-Ni-2.0. Moreover, this approach is also applied for synthesizing CeO₂-Ni catalysts. At 250 °C, the CH₄ yield over CeO₂-Ni-0.1 is ~13 times higher than that of CeO₂-Ni-2.0 (Figure S7), which suggest altering the C/I ratio could be employed to modulate various catalysts. Additionally, SDC-Ni-0.1 achieves a CH₄ selectivity of >99.5% that is slightly higher than the other four catalysts (Figure S6). Even at a H₂/CO₂ ratio of 1:1, SDC-Ni-0.1 also enables highly selective CO₂ hydrogenation to CH₄, implying the created active sites favor a certain CO₂ methanation pathway, which is not greatly impacted by the H₂/CO₂ ratio (Figure S8).

Both CH₄ yield and long-term durability are essential for economic CO₂ methanation and large-scale commercialization. We therefore determine the long-term stability of SDC-Ni-0.1 at 300 °C and 250 °C (Figure S9). There is no observable degradation after 700 hours of operation at 300 °C and an additional 700 hours of testing at 250 °C. After 1400 hours of testing, the temperature was increased back to 300 °C, the CH₄ yield can be almost recovered back to its initial performances, revealing its better stability. Post-mortem characterizations of the catalyst show no apparent agglomeration or coking (Figure S10).

6.1.4.2 Impacts of the C/I ratio

The metal-support interactions could be evidenced by the H₂ temperature-programmed reduction (H₂-TPR) profiles. H₂-TPR was therefore performed on SDC-Ni-*x* (*x* = 0.01, 0.1 and 2.0, Figure 6.22A). There are three reduction peaks falling in the range of 365-410 °C (α), 430-

470 °C (β), and 460-505 °C (γ), which are attributed to the NiO species with different extent of interactions with the SDC support^{176,177}. With increasing the C/I ratio, the peaks slightly shift to higher temperatures, indicating a high C/I ratio tends to decrease the reducibility of Ni species. In other words, the shift of reduction peaks to higher temperatures implies the presence of stronger Ni-support interactions¹⁷⁷. Additionally, with increasing the C/I ratio, the α and γ peak area tends to increase while the β peak area decreases (Figure S11). Typically, the α peak is ascribed to NiO with a relatively small size while the β peak is attributed to NiO with a larger particle size^{245,246}. Increasing the C/I ratio tends to produce a higher amount of polyesterified network, which can give rise to a smaller grain/particle size (Figure 6.2B). For example, a C/I ratio of 0.01 leads to a Ni grain size of 26.9 nm and SDC grain size of 11.4 nm, while the grain size of Ni and SDC can be reduced to 7.6 nm and 7.4 nm at a C/I ratio of 2.0 (Figure 6.2B and Figure S12). This is consistent with the TPR result that the β peak area of SDC-Ni-2.0 is higher than that of SDC-Ni-0.01. It is also noted that the particle size of Ni is more sensitive to the C/I ratios while the particle size of SDC is relatively similar, suggesting altering the C/I ratio can significantly tune morphology of metallic phase. Figure 6.2A shows that an additional reduction peak (γ) presents in the TPR profile. The γ peak could be attributed to the exsolution of Ni nanoparticles from the SDC lattice, displaying the strongest metal-support interaction. As impregnation cannot dope SDC with Ni, H₂-TPR was also performed on SDC-Ni-0.1-IM, which does not display the γ peak (Figure S13), affirming the γ peak is related to the exsolution of Ni from SDC lattice. These results indicate this wet-chemistry approach can lead to stronger metal-support interactions than impregnation while modulating the C/I ratio could fine-tune the metal-support interactions. Additionally, the strong metal-support interactions could enhance the thermal stability of Ni nanoparticles and prevent its coarsening, which is essential for its long-term stability^{177,314}.

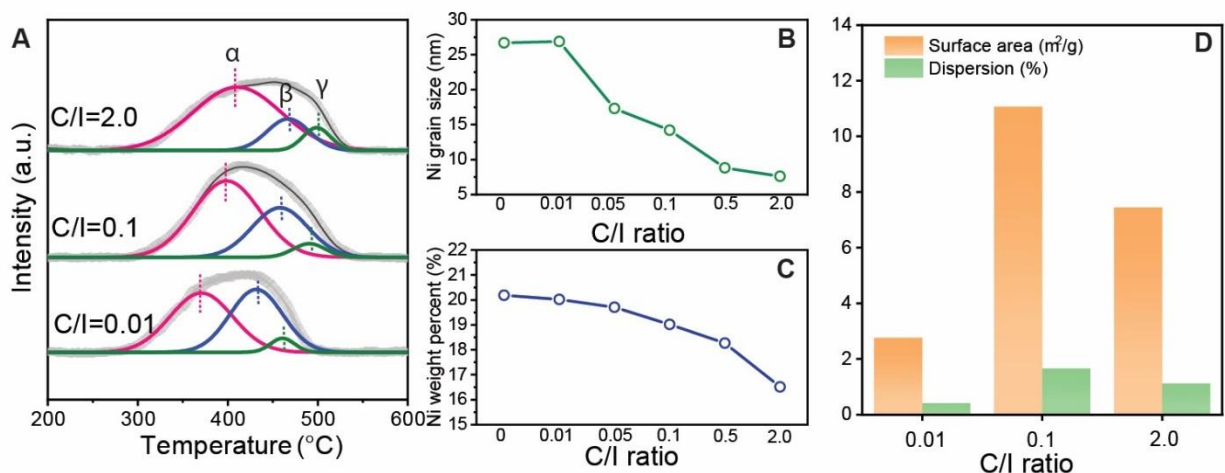


Figure 6.2. Impacts of the C/I ratio on structural properties of SDC-Ni-x. (A) H₂-TPR profiles of SDC-Ni-x (x = 0.01, 0.1 and 0.2). (B) The Ni grain size as a function of the C/I ratio. (C) The amount of metallic Ni as a function of the C/I ratio. (D) The metallic Ni surface area and dispersion of SDC-Ni-x (x = 0.01, 0.1, and 0.2).

Extensive efforts have been devoted to fabricating catalysts with increasingly smaller particles. However, simply reducing the particle size of Ni nanoparticles does not successively improve the catalytic activity³⁰⁷, while the intermediate Ni particle size potentially lead to the highest catalytic activity (Figure 6.1A and Figure 6.2B). Therefore, the particle size is not the only determination factor that affects the catalytic performance. Increasing the C/I ratios can also enhance the amount of Ni ions entangled in the polyesterified networks, thus, increasing the amount of Ni doped into the SDC lattice (Figure S14). Figure 6.2C shows the weight percent of Ni present in reduced SDC-Ni as a function of the C/I ratio. The Ni loading of these catalysts is initially designed as 20 wt.%. The weight percent of metallic Ni in SDC-Ni-0.01 is ~20.0 wt%, indicating the Ni doped into SDC is negligible. Increasing the C/I ratios enhances the amount of Ni incorporated into the SDC lattice (decreasing the amount of metallic Ni), leading to ~1.0 wt. % Ni doped in SDC at C/I=0.1 and ~3.5 wt.% Ni doped in SDC at C/I=2.0. As the ionic radius of Ni ions (55 pm) is smaller than Sm ions (95.8 pm) and Ce ions (87 pm)²⁴⁷, a high C/I ratio could

increase the Ni concentration in SDC and consequently decrease the lattice constant of SDC, while the C/I ratio does not impact the lattice parameters of NiO and Ni (Figure. S15). It should also be noted that the lattice constants of reduced SDC are bigger than as-fired SDC (Figure S15A), which could be ascribed to the exsolution of Ni nanoparticles from the SDC lattice or the reduction of Ce^{4+} to Ce^{3+} ions. The amount of exsolved Ni nanoparticles and the total metallic Ni surface area are key to the CO_2 methanation activity. H_2 pulse chemisorption was conducted to determine the metallic Ni surface area and its dispersity. There is a consensus in the existing studies that smaller metallic particles with high dispersion exhibit larger active metal surface area, giving higher H_2 uptake capacity³¹⁵. While SDC-Ni-0.1 catalyst, with the medium particle size, possesses the highest the Ni surface area and dispersity (Figure 6.2D). It should be noted that the metallic Ni surface area is determined by the amount of metallic Ni and its particle size. Increasing the C/I ratios is beneficial to obtaining smaller Ni particles (Figure 6.2B). However, it will also promote the Ni diffusion into SDC lattice, decreasing the amount of metallic Ni (Figure 6.2C). Thus, an intermediate C/I ratio (0.1) results in the highest metallic surface area and Ni dispersion, which consequently leads to the best catalytic performances.

X-ray photoelectron spectroscopy (XPS) was also performed to establish the C/I ratios – electronic structure relationships. Figure 6.3 and Table S5 summarize the XPS analysis results of reduced representative SDC-Ni-x ($x = 2.0, 0.1$, and 0.01). Figure 6.3A shows that increasing the C/I ratio tends to enhance the oxygen vacancy concentration, which is due to the higher amount of Ni doped into SDC (Figure S14). The essential role of oxygen vacancies in CO_2 methanation has been proven, showing higher oxygen vacancy concentration could improve CO_2 conversion²⁴⁵. However, as a C/I ratio of 2.0 increases the doping of Ni in SDC, the amount of metallic Ni is low at a C/I ratio of 2.0 (Figure 6.2C), which indicates SDC-Ni-2.0 cannot deliver the highest catalytic

performance. The signal of Ni^{3+} can be clearly distinguished from that of Ni^{2+} ions (Figure 6.3B). Distinctly, with increasing the C/I ratio, the amount of Ni^{3+} increases and SDC-Ni-2.0 exhibits the highest amount of Ni^{3+} . The exsolution of Ni nanoparticles creates Ni vacancies in the SDC, which oxidizes some Ni^{2+} ions to Ni^{3+} ions to maintain the charge neutrality^{316,317}. It has been recognized that the abundance of existing Ni vacancies and Ni^{3+} ions could also induce the stronger metal-support interactions and enhanced catalytic performance^{318,319}. Increasing the C/I ratio tends to increase the amount of Ni vacancies and Ni^{3+} ions, confirming the metal-support interactions could be enhanced at a higher C/I ratio, which is consistent with the TPR results. Figure 6.3C and Table S5 show the concentration of Ce^{3+} tends to increase at a higher C/I ratio, which is due to the Ni doping that could reduce the oxidation state of Ce from Ce^{4+} to Ce^{3+} . The XPS results imply the amount of Ni doped into SDC and the metallic Ni could be controlled by altering the C/I ratio, which can then modulate the metallic Ni surface area, oxygen vacancies, and metal-support interactions.

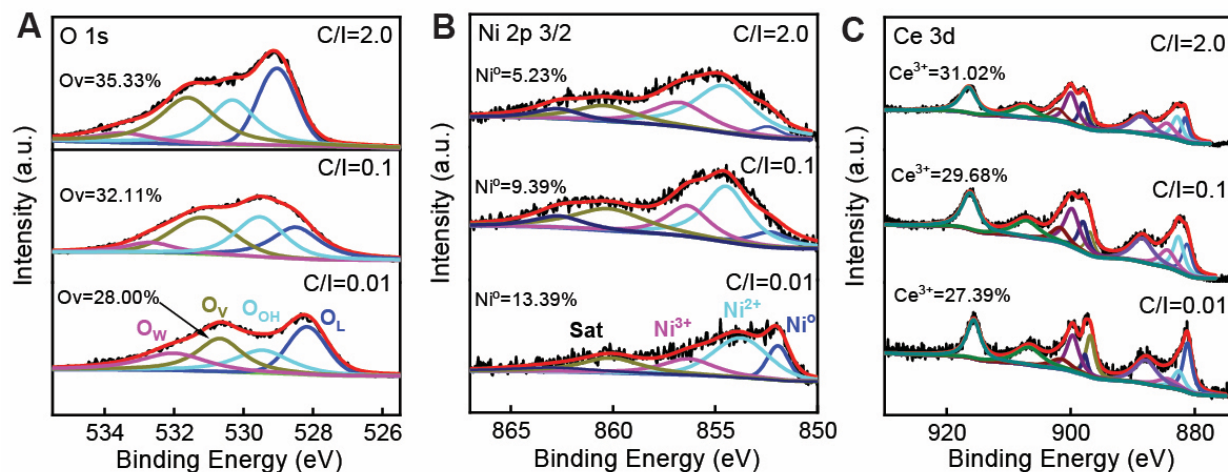


Figure 6.3. Impacts of the C/I ratio on the electronic structure of SDC-Ni- x ($x=0.01, 0.1$, and 2.0). XPS spectra of the reduced SDC-Ni- x synthesized with different C/I ratios ($0.01, 0.1$, and 2.0). (A) O 1s, (B) Ni 2p $_{3/2}$, (C) Ce 3d.

6.1.4.3 Metal-support interaction and Ni morphology

The metal-support interactions are of great significance to high CO₂ methanation activity, which is determined by the structure of both SDC and Ni. The TEM images and corresponding particle size distribution show a C/I ratio of 2.0 leads to a smaller particle size than a C/I ratio of 0.1 (Figures 6.4A and 6.4B). Complementing the bright-field TEM images, as shown in Figures 6.4C and 6.4D, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and corresponding energy dispersive X-ray spectroscopy (EDS) mapping show a C/I ratio of 0.1 leads to a bigger Ni particle/grain size than catalysts synthesized under a C/I ratio of 2.0 (Figures 6.4E-6.4H). This finding is in line with the XRD results (Figure 6.2B). The high-resolution TEM (HRTEM) images shown in Figure S16 show that a C/I ratio of 2.0 gives rise to SDC with a smaller interplanar spacing than that of SDC-Ni-0.1, further affirming the fact that a high C/I ratio enhances the Ni doped into SDC. It has been found that the SDC particle size is not significantly affected by the C/I ratio (Figure S12). Therefore, the amount of exsolved Ni nanoparticles, total metallic Ni surface area, and the metal-support interactions cooperatively determine the catalytic activities. As illustrated in Figure 6.4I, SDC-Ni-0.01 exhibits weak metal-support interaction and has a low metallic Ni surface area, leading to poor CO₂ methanation performance. SDC-Ni-2.0 exhibits strong metal-support interaction. However, a high amount of Ni is trapped by SDC lattice and the metallic Ni surface area is also relatively low, creating less active interface and consequently low CO₂ methanation activity. The intermediate amount of C/I ratio (C/I=0.1) gives rise to relatively strong metal-support interaction while simultaneously has the highest metallic Ni surface area and largest active interface area, which contributes to the exceptional CO₂ methanation performances.

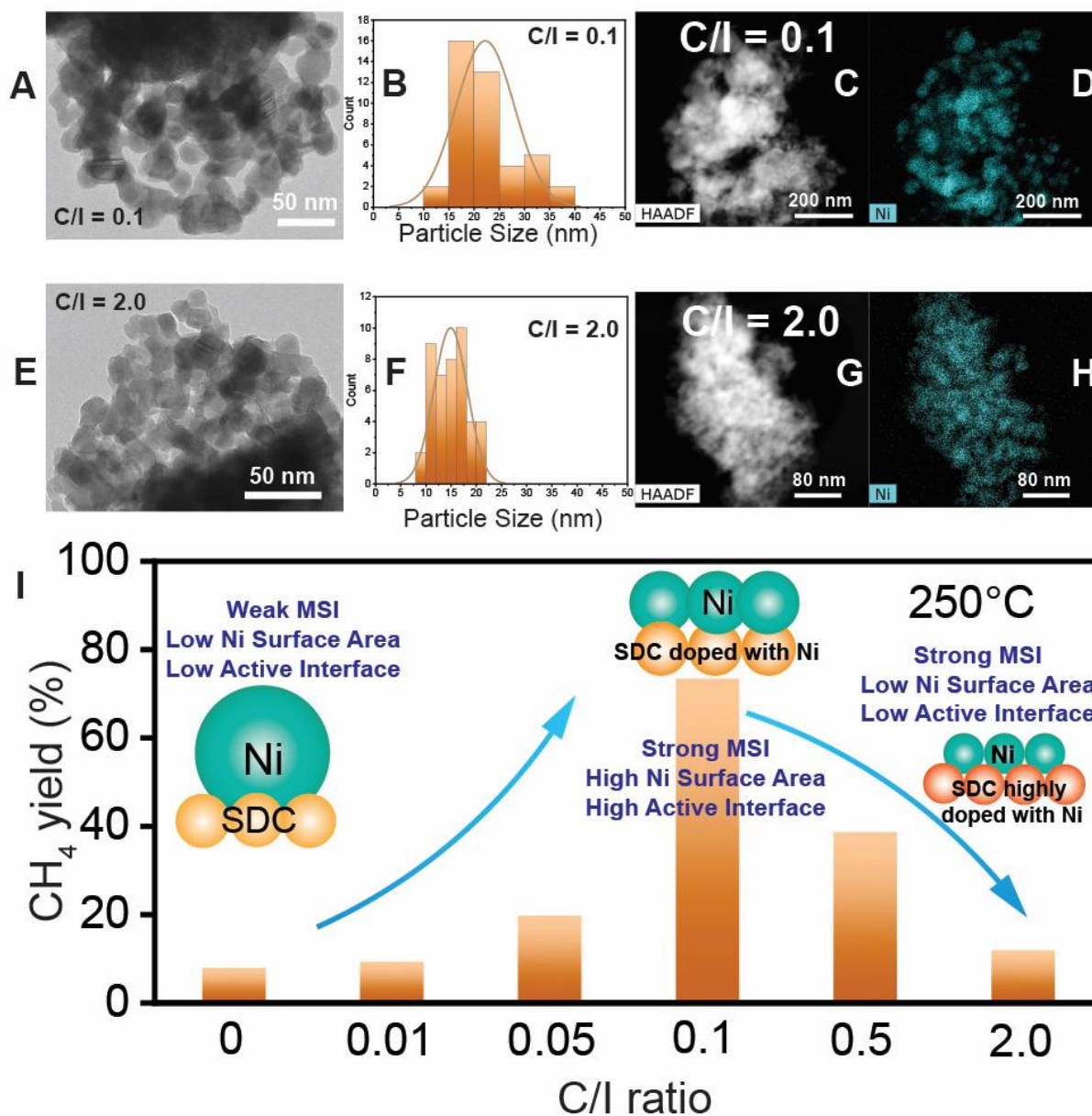


Figure 6.4. The relationship between the C/I ratio and catalyst morphology. (A-D) Bright-field TEM image, particle size distribution, and HAADF-STEM image with EDS mapping of reduced SDC-Ni synthesized under a C/I ratio of 0.1. (E-H) Bright-field TEM image, particle size distribution, and HAADF-STEM image with EDS mapping of reduced SDC-Ni synthesized under a C/I ratio of 2.0. (I) Schematic illustration of the impacts of C/I ratio on catalytic morphology and the interplay between the metal-support interaction and Ni particle size.

6.1.4.4 In-situ operando DRIFTS

To better understand how the C/I ratio could significantly impact the catalytic performances, comprehensive in-situ operando DRIFTS measurements were conducted to probe the intermediate species and identify the CO₂ methanation pathways. Time-resolved DRIFT spectra were recorded upon changing the atmosphere of the high-temperature reaction chamber, identifying the reactive-adsorbed species and their corresponding roles in catalytic reactions.

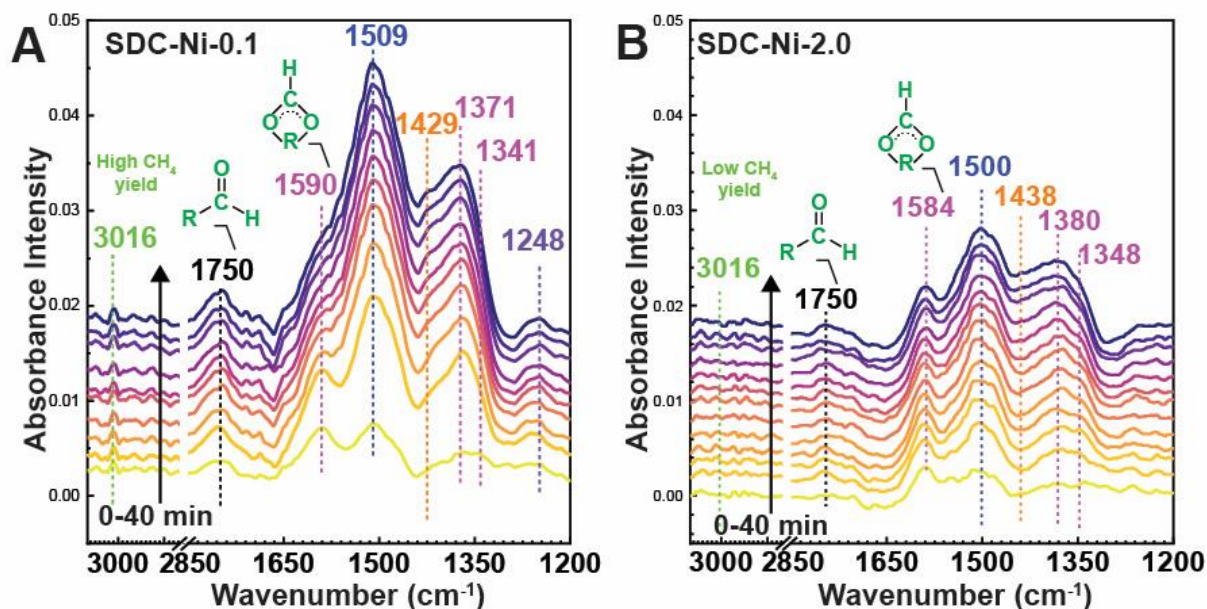


Figure 6.5. Time-resolved DRIFT spectra of CO₂ methanation over (A) SDC-Ni-0.1. (B) and SDC-Ni-2.0. The spectra were collected when the feed gas was switched from 100 sccm UHP Ar to 11 sccm CO₂, 44 sccm H₂, and 45 sccm UHP Ar at 250 °C.

Figure 6.5 presents the operando DRIFT spectra of CO₂ methanation over SDC-Ni-0.1 and Ni-SDC-2.0 at 250 °C. The evolution key species' infrared (IR) signals were recorded after switching the gas from ultra-high purity (UHP) Ar to 11 sccm CO₂, 44 sccm H₂ and 45 sccm Ar. Some IR bands gradually grow while some bands vanish, enabling probing of the active species involved in CO₂ methanation. The CH₄ (3016 cm⁻¹) detected over SDC-Ni-2.0 is not as obvious as the CH₄ formed over SDC-Ni-0.1, which is consistent with the packed bed reactor testing (Figure 6.1A). No detectable CO peaks were found from both catalysts (Figure S17), indicating

they are highly selective for CH₄ production. As shown in Figure 6.5, after switching the gas, the intensity of bands belonging to monodentate carbonate (~1500 cm⁻¹, ~1370 cm⁻¹), bidentate formate (~1590 cm⁻¹, 1300-1340 cm⁻¹), bicarbonate (~1430 cm⁻¹, ~1646 cm⁻¹), formyl (~1750 cm⁻¹), and carboxylate (~1248 cm⁻¹) tend to change, suggesting CO₂ methanation embraces those species^{190,191,320-322}. After ~40 minutes of treatment, the concentration of these species achieves equilibrium. At 250 °C, bidentate formate species (~1590 cm⁻¹) over Ni-SDC-0.1 quickly vanish while the concentration of formyl (~1750 cm⁻¹) simultaneously increases, suggesting that formate species could readily decompose to formyl. Formyl could then be hydrogenated to methoxy and subsequently CH₄³²³. Nevertheless, the IR signals of formyl over SDC-Ni-2.0 are not significant while the bands belonging to formate are strong. Therefore, the formate species are not prone to decompose over SDC-Ni-2.0 and the subsequent hydrogenation of formyl to CH₄ is ceased, leading to low CH₄ yield. C-O bond cleavage is the crucial step during the formate-to-formyl process, and thus activation energy of C-O bond cleavage over SDC-Ni-0.1 is lower than SDC-Ni-2.0. Moreover, upon changing the atmosphere, the IR signals of monodentate carbonate emerge and grow, suggesting the monodentate carbonate species could be one of the reactive-adsorbed species.

To confirm formate and formyl are the key species during CO₂ methanation and better understand the uniqueness of SDC-Ni-0.1, formic acid was used as the reactant³²⁴. Upon exposure to formic acid (Figure S18), multiple IR bands readily develop, which can be assigned as the gaseous formic acid and intermediate species on the catalyst. After changing the gas from diluted formic acid to Ar (Fig. 6.6A and 6.6B), we focus on studying the kinetic of formate decomposition. The formate can decompose or be converted over SDC-Ni-0.1 with a much faster speed than that over SDC-Ni-2.0. After treatment under Ar for 40 minutes, there are no obvious signs of formate

groups over SDC-Ni-0.1. However, the formate species remain on SDC-Ni-2.0 upon outgassing the sample. This observation is consistent with the conclusion made during CO₂ methanation, confirming that C-O bond cleavage and formate decomposition kinetics over SDC-Ni-0.1 is much faster than that over SDC-Ni-2.0. Therefore, SDC-Ni-0.1 leads to higher CO₂ methanation activity.

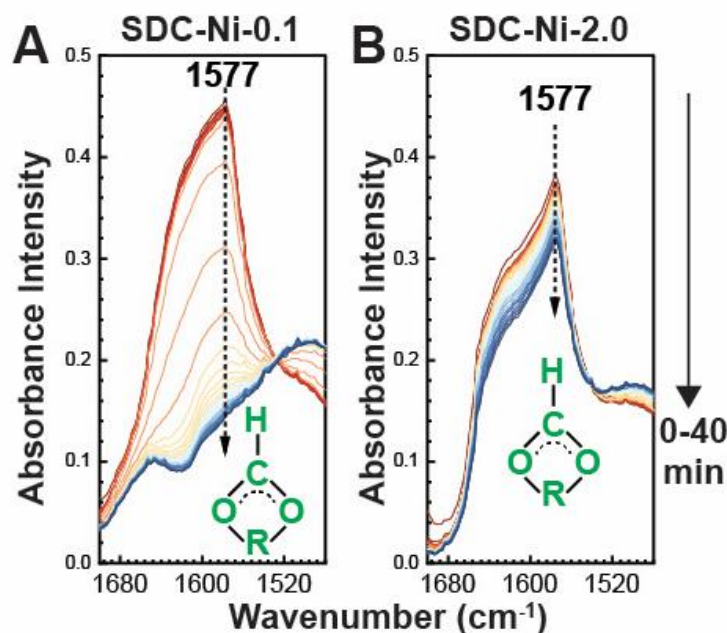


Figure 6.6. Evolution of DRIFT spectra collected at 250 °C over SDC-Ni-0.1(A) and SDC-Ni-2.0 (B). Both catalysts were pre-treated under a mixture of Ar with HCOOH for 1 hour. The spectra were collected after the atmosphere was changed from the mixture of Ar with HCOOH to UHP Ar.

To further strengthen the conclusion that CH₄ is produced via the formate pathway and better understand how SDC-Ni-0.1 leads to enhanced catalytic performances, the gas composition was then switched from Ar to 20% H₂ balanced with Ar, providing H₂ for hydrogenating adsorbed species on the catalysts. The resulting spectra over both catalysts are shown in Figures 6.7A–6.7D. As the hydrogenation is resumed, the intensity of carbonate, hydroxyl, and bicarbonate species gradually decreases (Figure S18). The residue and low-concentration formate species over SDC-Ni-0.1 can quickly decompose and form formyl species which are subsequently hydrogenated to

CH₄ (Figure 6.7B). CH₄ can be produced over SDC-Ni-0.1 that is originated from the formate species, reinforcing the formate pathway established in this work. Furthermore, no methoxy was observed while CH₄ could be produced, suggesting the second C-O cleavage and methoxy-to-methane process over SDC-Ni-0.1 are fast. After ~4 minutes of treatment under H₂, the formate species over SDC-Ni-0.1 are fully converted while the formate over SDC-Ni-2.0 is still evident after 40 minutes. Moreover, although methoxy (2920 cm⁻¹) is observed on SDC-Ni-2.0, methane is not produced, which indicates that C-O cleavage is sluggish during the hydrogenation of methoxy to methane over SDC-Ni-2.0.

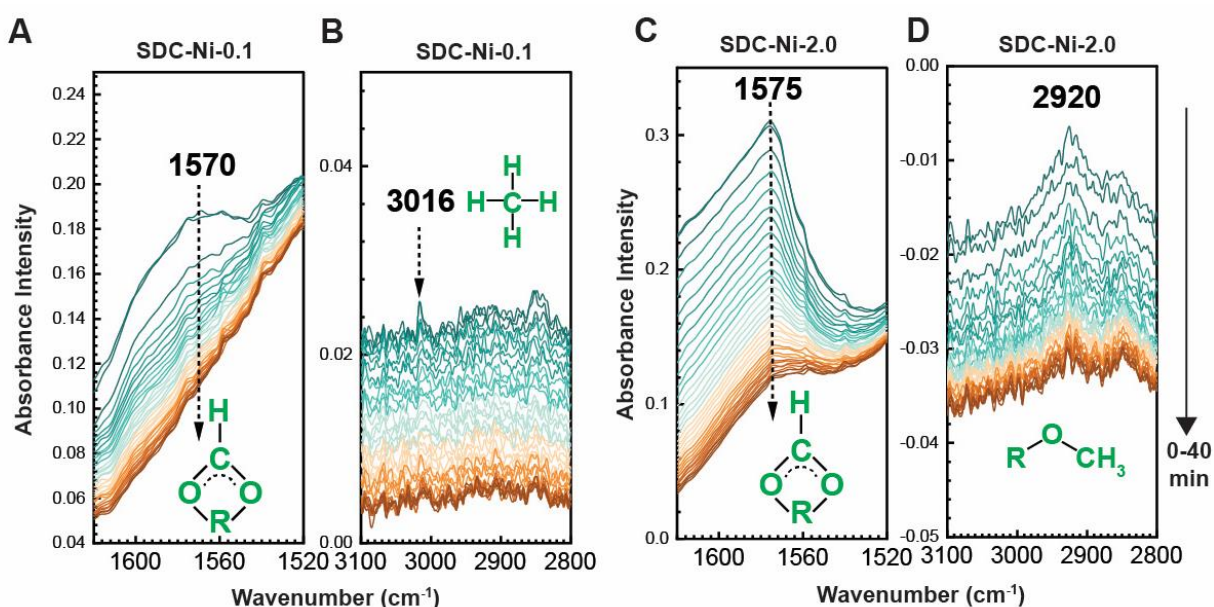


Figure 6.7. Evolution of DRIFT spectra collected at 250 °C over SDC-Ni-0.1(A-B) and SDC-Ni-2.0 (C-D). Both catalysts were pre-treated under a mixture of Ar with HCOOH for 1 hour followed by the degassing under UHP Ar for 1 hour. The spectra were collected after the atmosphere was changed from Ar to 20% H₂ balanced with Ar.

Figure 6.8A displays the proposed CO₂ methanation mechanism over SDC-Ni catalysts, which follows the formate-formyl-methoxy pathway. The C/I ratio does not affect the CO₂ methanation pathway while it impacts the kinetics of intermediate steps. The C-O bond cleavage is the foremost step of formate decomposition to formyl and subsequent methoxy to methane. CO₂

methanation over SDC-Ni therefore involves two kinds of C-O bond cleavage, the rates of which determine the overall CH₄ yields. Both formate decomposition and methoxy-to-methane process need hydrogen to accomplish C-O bond cleavage. The amount of Ni surface sites could determine the available of chemisorbed hydrogen. As shown in Figure 6.8B, SDC-Ni-0.1 has higher metallic Ni surface and larger active interface than that of SDC-Ni-2.0; thus, the C-O bond cleavage during the steps of formate to formyl and methoxy to methane are faster over SDC-Ni-0.1 than SDC-Ni-2.0. Therefore, the CH₄ yield over SDC-Ni-0.1 is much higher than that over SDC-Ni-2.0.

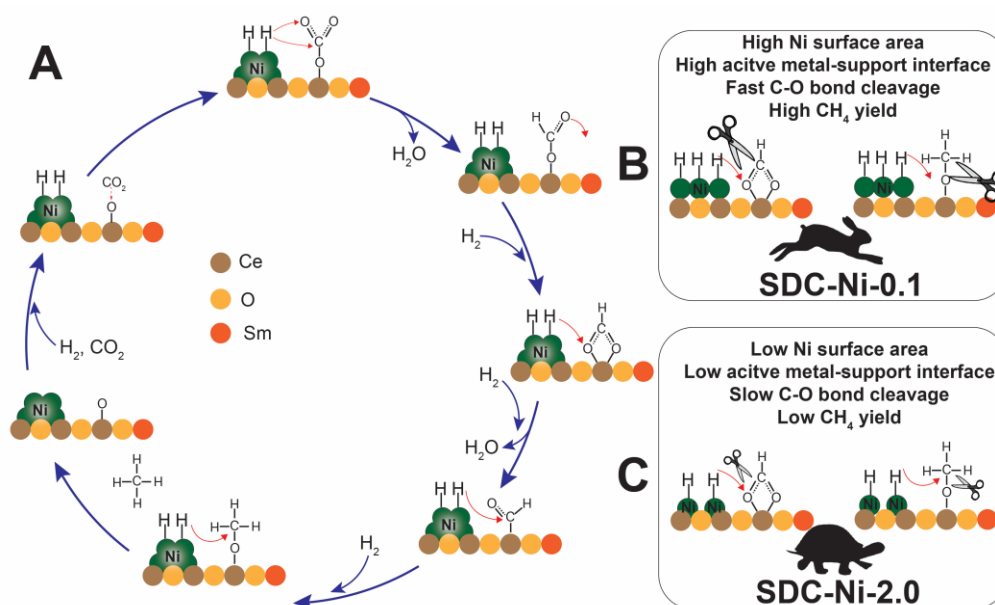


Figure 6.8. (A) Proposed mechanism of CO₂ methanation over SDC-Ni catalysts. (B) The C-O bond cleavage over SDC-Ni-0.1 during formate-to-formyl process and methoxy-to-methane process is fast. (C) The C-O bond cleavage over SDC-Ni-2.0 during formate-to-formyl process and methoxy-to-methane process is sluggish.

6.1.5 Conclusions

We demonstrated an extremely straightforward approach to enhance the CO₂ methanation activity of samarium-doped ceria-supported Ni (SDC-Ni) by altering the chelating agent-to-metal cation ratios (C/I ratios) and tuning the metal-support interactions. This approach can

simultaneously modulate the morphology of Ni, crystal structure, chemical composition, and electronic structure of SDC-Ni. A C/I ratio of 0.1 gives rise to the highest CO₂-to-CH₄ yield at 250 °C (73.6%) among the catalyst studied in this work. The enhanced performances are attributed to the fact that SDC-Ni-0.1 concurrently exhibits the largest metallic Ni surface area, the highest Ni dispersion, high-area active interface, and strong metal-support interaction. These unique properties drastically reduce the C-O bond cleavage activation energy, which significantly facilitate formate decomposition, formyl hydrogenation, and subsequent methoxy-to-CH₄ conversion, leading to exceptional CO₂ conversion and CH₄ yield at 250 °C

6.1.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1021/acsami.1c23881>.

6.2 Rationally designed negative electrode for selective CO₂-to-CO conversion in protonic ceramic electrochemical cells

6.2.1 Abstract

Protonic ceramic electrochemical cells (PCECs) are solid-state electrochemical devices that employ proton-conducting oxides as electrolytes, which offer a promising approach for electrification of chemical manufacturing, including CO₂ reduction to produce value-added chemicals (e.g., CO). The primary advantage of PCECs is their intermediate operating temperatures (300-600 °C), which thermodynamically and kinetically favor the CO₂ reduction chemistry at the negative electrode. However, the conventional negative electrodes of PCECs, such as BaZr_{0.8-x}Ce_xY_{0.2}O_{3-δ}-Ni or BaZr_{0.8-x}Ce_xY_{0.1}Yb_{0.1}O_{3-δ}-Ni, cannot reduce CO₂ to either CH₄ or CO with a selectivity of >99%, leading to the production of a CO and CH₄ mixture. Herein, an oxide-supported *in-situ* exsolved Ni-Fe alloyed nanoparticle electrocatalyst, Sr₂Fe_{1.4}Mo_{0.5}O_{6-δ}-Ni_{0.175} (SFM-Ni_{0.175}), is first employed as the negative electrode of PCECs. The PCECs equipped with this new negative electrode selectively favor the CO₂-to-CO conversion. A selectivity of ~100% toward CO has been demonstrated over a wide range of operating temperatures (400-600 °C) and applied potentials/current densities. The negative electrode demonstrated in this work fully suppresses the CH₄ production. *In situ* diffuse reflectance infrared spectroscopy (DRIFTS) was performed to probe the CO₂ reduction mechanisms over both SFM-Ni_{0.175} and the traditional negative electrode (BCZYYb7111+Ni), which indicates SFM-Ni_{0.175} inhibits the formation of formate species, leading to selective production of CO. This work validates that PCECs equipped with the rationally designed negative electrode can selectively manufacture chemicals.

6.2.2 Introduction

The growing CO₂ emissions and increasing atmospheric CO₂ concentration necessitate the exploration of economically viable approaches to achieving CO₂ capture, storage, conversion, and utilization^{156,325-330}. Converting CO₂ into value-added chemicals (e.g., CO, CH₄, light olefins, alcohol, and aromatics) is attracting enormous attention, especially the electrochemical CO₂ reduction using solar- or wind-based renewable electricity, which can mitigate the CO₂ emissions while manufacturing carbon-containing chemicals with a reduced carbon footprint³³¹⁻³³⁶. Current efforts to electrochemically convert and utilize CO₂ center around high-temperature (>700 °C) oxygen-ion solid oxide electrolysis cells (O-SOECs)³³⁷⁻³³⁹ for synthesizing carbon monoxide (CO) or syngas (a mixture of CO and H₂) and low-temperature (<100 °C) proton exchange membrane (PEM) and anion exchange membrane (AEM) CO₂ electrolyzers that produce chemicals beyond syngas, such as ethylene, methanol, formate acid, and dimethyl ether³⁴⁰⁻³⁴². Both technologies are capable of converting a fraction of the anthropogenic CO₂ back into valuable chemicals. However, the low-temperature CO₂ conversion is kinetically limited while high-temperature CO₂ conversion is constrained by thermodynamics and has a low versatility in producing diverse chemicals.

Protonic ceramic electrochemical cells (PCECs), which operate in the reversed mode of protonic ceramic fuel cells (PCFCs), have been successfully demonstrated for converting CO₂ into value-added chemicals^{31,55,343}. Thanks to the lower activation energy of proton conduction than that of oxygen-ion conduction, PCECs achieve comparable or higher energy efficiency at intermediate operating temperatures (e.g., 350-600 °C). Its intermediate operating temperature thermodynamically and kinetically favors the production of chemicals beyond CO, such as CH₄^{343,344}. However, the versatility in products also poses challenges to the purity of chemicals, which means a mixture of CO and CH₄ can be normally produced.

As CO₂ conversion in PCECs (CO₂-PCECs) is a truly nascent technology, there is a limited demonstration of CO₂-PCECs^{56-58,60,343,345,346}. Irvine et al.⁵⁷ have validated CO₂ reduction in an electrolyte (BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-δ}) supported PCEC, which employs Pt as the positive electrode and Fe as the negative electrode, for converting CO₂ to CO at 600 °C. However, a low current density of 40 mA/cm² is achieved, implying the CO₂ conversion is poor, and the product yield is low. Despite that the CO₂-PCECs equipped with BCZYZn+Ni as the negative electrode greatly improve the CO₂ reduction, this Ni-based cermet negative electrode suffers from coking and oxidation of Ni, leading to a poor durability⁵⁸. Due to the high ohmic resistance ascribed to the electrolyte and manufacturing complexity of PCECs, CO₂-PCECs remained quiet for a while. The most recent advancements in proton-conducting materials, PCFCs, and PCECs are reviving the development of CO₂-PCECs^{31,47,48}. For instance, Duan and co-workers demonstrated CO₂-PCECs that achieve a CO₂ conversion of ~10% at 500 °C³¹. The following work reports that large-area CO₂-PCECs can efficiently convert CO₂ to CH₄ with a CH₄ production rate of 0.13 sccm cm⁻² at 450 °C³⁴³. Unfortunately, as displayed in Figure 6.9A, these CO₂-PCECs with conventional Ni-based cermet negative electrodes exhibit poor product selectivity^{31,55,58,343,347}. A mixture of CO and CH₄ is produced. Although adjusting the operating temperatures and current densities can alter the selectivity toward CO or CH₄, changing the operating conditions fails to achieve a selectivity of >99% toward a specific product. Therefore, tailoring the negative electrode, which enables selective production of a certain chemical, is essential for the implementation of CO₂-PCECs. Ding et al. have demonstrated an approach to modulating the Ir-O interaction on Sm-doped CeO₂ (SDC), which was then applied as the negative electrode of PCECs, leading to the production of CO or CH₄ with a selectivity of >99%⁵⁵. Their work validates the feasibility of tuning product selectivity by engineering the negative electrode. However, noble metal-based negative electrodes are used

in their work. So far, there are few low-cost transition metal-based negative electrodes that have been developed for selective CO₂ reduction in PCECs. It has been widely recognized the oxide support and metallic phase synergize to control the product selectivity^{348,349}, implying that rationally designing the oxide support and metallic phase of the negative electrode could be an effective approach to realizing selective CO₂ reduction in PCECs.

Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} (SFM) has been developed as the electrodes for CO₂ electrolysis in solid oxide electrolysis cells, which is benefited by its relatively high chemical bulk diffusivity and high surface reaction rate constant for CO₂ reduction reaction (CO₂RR)^{350,351}. Additionally, bimetallic heterogeneous catalysts can lead to synergistic effects, which significantly enhance the catalytic activity and product yield^{164,352,353}. However, there is little work on using bimetallic catalysts for converting CO₂ in PCECs, which is due to the lack of effective tools to create uniformly distributed and thermally stable alloyed nanoparticles in the negative electrode scaffold. Thus, creating an SFM-supported bimetallic catalyst as the negative electrode could potentially help to achieve efficient and selective CO₂ reduction in PCECs.

In this work, Sr₂Fe_{1.4}Mo_{0.5}O_{6-δ} (SFM-Ni0), Sr₂Fe_{1.4}Mo_{0.5}Ni_{0.175}O_{6-δ} (SFM-Ni0.175), and Sr₂Fe_{1.4}Mo_{0.5}Ni_{0.225}O_{6-δ} (SFM-Ni0.225) were synthesized and employed as the negative electrodes of CO₂-PCECs. Upon reduction, Ni-Fe alloyed nanoparticles exsolved from SFM-Ni0.175, forming oxide-supported bimetallic nanoparticles. The PCECs with an SFM-Ni0.175 negative electrode significantly reduces the overpotential ascribed to the negative electrode and simultaneously increase CO production rate. Furthermore, the SFM-Ni0.175 negative electrode enables the selective production of CO with a selectivity of >98% at an operating temperature ranging from 400-600 °C and over a wide range of current densities (50-400 mA/cm²), which represents the first transition metal-based negative electrode that achieves selective CO₂ reduction

in PCECs. Moreover, its stability has also been validated. Additionally, the CO₂ reduction mechanism over SFM-Ni_{0.175} was probed by using *in situ* DRIFTS and compared with conventional Ni-based cermet negative electrode (BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-δ}-Ni), which illuminates the CO₂ reduction pathways over two kinds of negative electrodes, aiming to guide the future development of CO₂-PCEC negative electrodes.

6.2.3 Methods and materials

6.2.3.1 Negative electrode materials synthesis

Sr₂Fe_{1.4}Mo_{0.5}O_{6-δ}-Ni_{0.075} (SFM-Ni_{0.075}), Sr₂Fe_{1.4}Mo_{0.5}O_{6-δ}-Ni_{0.175} (SFM-Ni_{0.175}), Sr₂Fe_{1.4}Mo_{0.5}O_{6-δ}-Ni_{0.225} (SFM-Ni_{0.225}), and Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ}-Ni₀ (SFM-Ni₀) were synthesized via the conventional sol-gel method²³⁶. A stoichiometric amount of Sr(NO₃)₂, Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O, and (NH₄)₆Mo₇O₂₄·4H₂O were first dissolved in DI water. The ethylenediaminetetraacetic acid (EDTA) and citric acid (CA) were then added to the above solution with a molar ratio of 2:2:1 (EDTA: CA: total metal ions). The above solution was subsequently stirred and heated at 250 °C until a gel was formed. The gel was immediately moved to a drying oven that was held at 175 °C, in which the gel will be dried for 24 h. The obtained black powder was then calcined under air at 1000 °C for 5 hours to synthesize SFM-Ni_x (x=0, 0.075, 0.175, and 0.225).

6.2.3.2 Characterization

The as-fired catalysts were reduced under 40% H₂ balanced with N₂ (20 sccm H₂+30 sccm N₂) at 600 °C for 2 hours. The crystal structures of as-fired SFM-Ni_x and reduced SFM-Ni_x powder were determined using X-ray diffraction (XRD) (Rigaku MiniFlex diffractometer with a Cu Kα

radiation source operated at 30 kV and 15 mA. The scan speed was 1°/min). The morphology of reduced SFM-Nix powder was examined using transmission electron microscopy (TALOS F200X, Thermo Fisher Scientific)). The microstructure of CO₂-PCECs was examined by using the scanning electron microscope (Hitachi/S-3400N). *In situ* DRIFTS was performed using a Thermo Fisher iS50 FTIR spectrometer equipped with the Praying Mantis high-temperature reaction chamber.

6.2.3.3 CO₂-PCEC fabrication and electrochemical performance testing

As this work focuses on studying the negative electrode materials, BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3- δ} -Ni (BCZYYb7111-Ni) is employed as the positive electrode support to simplify the manufacturing of CO₂-PCECs. H₂ is fed to this positive electrode for providing protons to the negative electrode. Feeding H₂ to the positive electrode can minimize the overpotential ascribed to the positive electrode, which allows for better comparing the performance of different negative electrodes.

The CO₂-PCECs were manufactured via the conventional solid-state sintering process²². The positive electrode-supported CO₂-PCEC half cells were prepared via tape casting. The positive electrode support layer is a composite of 50 wt. % NiO, 33.3 wt. % BCZYYb7111, and 16.7 wt. % corn starch. The positive electrode function layer is made of 60 wt. % NiO and 40 wt. % BCZYYb7111. The BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_{3- δ} -Ni (BCZYYb4411) electrolyte layer was applied on the positive electrode function layer via spray coating and sintered at 1460 °C for 5 hours. The SFM-Nix negative electrode ink was brush painted on the BCZYYb4111 electrolyte and calcined at 1000 °C for 5 hrs to build the full CO₂-PCECs. The active area of the CO₂-PCECs was 0.5 cm².

The electrochemical characterization was performed using the high-temperature electrochemical testing stand. A gas stream of 20% H₂ (20 sccm H₂+80 sccm N₂) was fed to the positive electrode while the negative electrode was supplied with pure CO₂ gas with a flow rate of 10 sccm. Before characterizing the performance of CO₂-PCECs, a current density of 100 mA/cm² was applied on CO₂-PCECs for 2 hours to pump the H₂ from positive electrode to negative electrode for *in situ* exsolution of Ni-Fe alloyed nanoparticles in negative electrodes. The *I-V* curves and electrochemical impedance spectroscopy (EIS) measurements were performed using a Gamry Reference 3000. Galvanostatic EIS was carried out over a frequency ranging from 50 kHz to 0.1 Hz with an AV amplitude of 10 mV under different applied current densities. The applied current densities range from 50 mA/cm² to 400 mA/cm², and the outlet gas compositions were analyzed using an online gas chromatography (INFICON 3000 Micro GC). The selectivity of CO (%) and CO production rate (ml/min/cm²) is calculated using the following equations:

$$\text{CO selectivity (\%)} = \frac{F_{CO,out}}{F_{CO,out} + F_{CH_4,out}} \times 100\% \quad (1)$$

$$\text{CO production rate (ml min}^{-1}\text{cm}^{-2}\text{)} = \frac{F_{CO,out}}{A} \times 100\% \quad (2)$$

where F_{out} represents the outlet gas flow rate. The A represents the active area of the negative electrode, which is 0.5 cm². The electrical energy-to-CO chemical energy conversion efficiency is calculated using equation (3):

Electrical energy to CO chemical energy conversion efficiency: ε (%)

$$= \frac{\Delta H_{CO} \times n_{CO}}{i \times V} \times 100\% \quad (3)$$

where ΔH_{CO} is the absolute value of CO₂ reduction to CO (CO₂ (g)+H₂ (g)=CO (g) + H₂O(g), STP, 25°C), which is 41.2 kJ/mol. n_{CO} is the production rate of CO (mol s⁻¹). i is the current applied (A). V is the voltage (V).

6.2.4 Results and discussion

6.2.4.1 Current research and development status of CO₂-PCECs

As mentioned above, CO₂-PCECs are a novel technology; thus, there are limited PCECs that have been developed for CO₂ reduction. To better understand the current status of CO₂-PCECs and identify their critical barriers, Figure 6.9A and Table S1 are developed to summarize the CO selectivity achieved in CO₂-PCECs. The CO selectivity achieved in previous CO₂-PCECs tends to increase with increasing the temperature, which is consistent with the thermodynamics of endothermic reversed water gas shift reaction. Therefore, the CO₂ reduction in prior CO₂-PCECs is governed by thermodynamics, which indicates CO₂ is reduced by gaseous H₂ rather than electrochemically reduced by protons. These CO₂-PCECs are equipped with conventional Ni-based cermet as the negative electrode, implying Ni-based cermet negative electrode cannot selectively produce CO. As shown in Figure 6.9B, *in situ* DRIFTS was conducted to further understand the CO₂ reduction mechanism over a representative Ni-based cermet negative electrode (BCZYYb7111+Ni). The DRIFTS spectrum shows both CH₄ and CO are produced over BCZYYb7111-Ni, suggesting an alternative negative electrode should be developed.

Ding et al. have successfully demonstrated a novel negative electrode, PBM-BZY-Ir (SDC) for CO₂ reduction in CO₂-PCECs. By creating a negative electrode with SDC-supported single Ir atoms or relatively small Ir clusters, CO can be synthesized in PCECs with a selectivity of ~100% at 400 °C⁵⁵. So far, however, there are few negative electrode materials that achieve selective CO production in PCECs. Therefore, enhancing the selectivity toward one specific carbon-containing chemical remains to be the critical barrier of CO₂-PCECs, especially at intermediate operating temperatures. In this work, an oxide-supported bimetallic catalyst, SFM-Ni_{0.175}, was synthesized and applied as the negative electrode for CO₂-PCECs. As shown in Figure 6.9C, the *in-situ*

exsolved Ni-Fe alloyed nanoparticles are anchored on the oxide support, which is expected to favor CO production and enhance CO₂ conversion. Figure 6.9A shows the CO₂-PCECs with SFM-Ni_{0.175} negative electrode obtains a CO selectivity of ~100% at an operating temperature ranging from 400 to 600 °C at an applied current density of 100 mA/cm². It has been noted that the applied current density also impacts the product selectivity because it is proportional to the proton, or the hydrogen could be available for reducing CO₂. Operating the CO₂-PCECs at a high current density can increase the selectivity towards CH₄ as CH₄ production consumes more proton/hydrogen than CO production³⁴³. The SFM-Ni_{0.175} negative electrode leads to selective CO production at a wide range of current densities (50-400 mA/cm²). Figure 6.9D presents a CO selectivity of >98% achieved in this wide range of current densities, indicating the CO₂ reduction over this negative electrode is governed by the kinetics. *In situ* DRIFTS of CO₂ reduction over SFM-Ni_{0.175} was conducted, as shown in Figure 6.9B, no band assigned to CH₄ is detected over SFM-Ni_{0.175}, which further validates our observation. A detailed analysis of the DRIFTS spectra is discussed in the following section to better present the CO₂ reduction pathways over both conventional Ni-based cermet negative electrode and SFM-Ni_{0.175}.

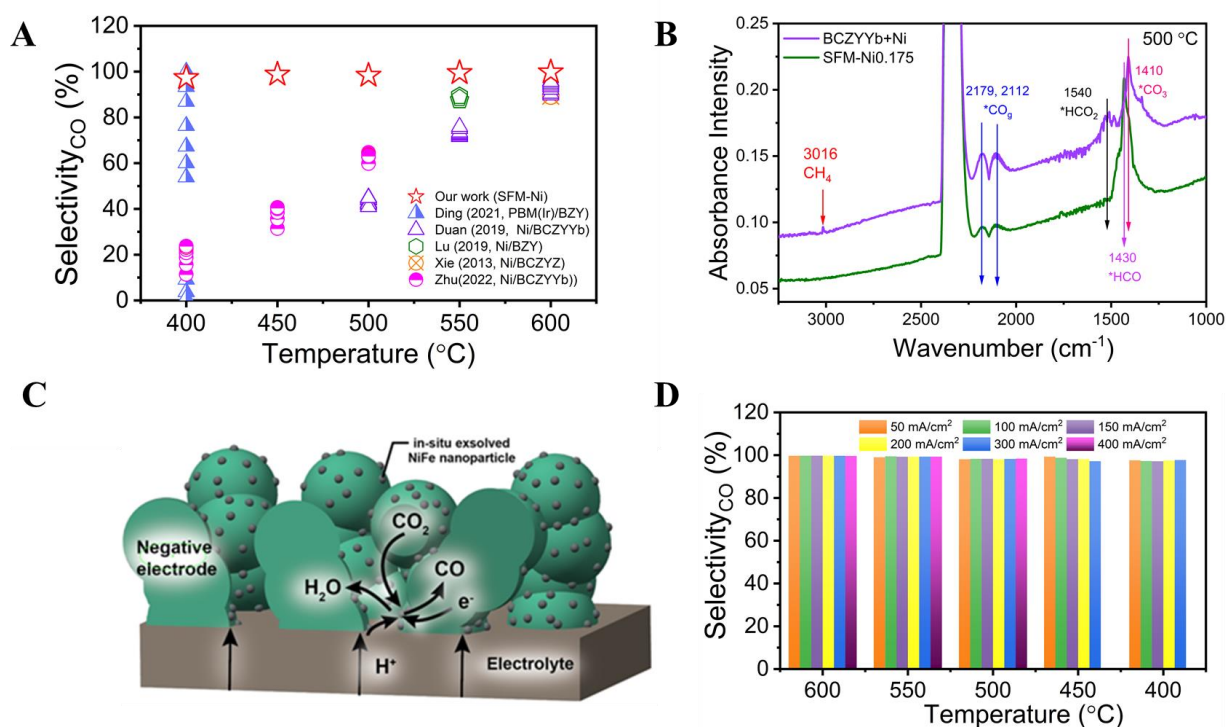


Figure 6.9. CO₂ reduction in protonic ceramic electrochemical cells. (A) A survey of CO selectivity achieved in CO₂-PCECs as a function of operating temperature^{31,55,60,343,347}. (B) DRIFTS spectra collected at 500 °C over SFM-Ni_{0.175} and BCZYYb₇₁₁₁-Ni. The spectra were collected under CO₂ reduction conditions. (C) An illustration of the SFM-Ni_{0.175} negative electrode developed in this work. (D) CO selectivity achieved in CO₂-PCECs with SFM-Ni_{0.175} negative electrode at various operating temperatures and current densities.

6.2.4.2 Rationally design negative electrodes for CO₂-PCECs

To the best of our knowledge, there are few negative electrodes have been published for selective CO₂ reduction in PCECs. To build highly efficient and durable CO₂-PCECs with selective CO₂-to-CO conversion, the negative electrode must concurrently exhibit excellent catalytic activity, high electronic conductivity, exceptional CO₂ tolerance, and good compatibility with the electrolyte. SFM has been used in SOFCs and SOECs with validated electronic conduction and CO₂ tolerance^{54,354}. Additionally, it possesses outstanding phase stability under both reducing and oxidizing atmospheres, SFM can therefore function as a negative electrode

where the atmosphere is reducing. Moreover, SFM was applied as the CO₂ reduction electrode of high-temperature SOECs (>650 °C)⁵⁴. Combining these properties suggests SFM could potentially be the negative electrode for CO₂-PCECs. However, as SFM was originally designed for high-temperature SOECs, its catalytic activity at 400-600 °C is poor, which requires to build a SFM-supported metallic nanoparticles to further enhance the catalytic activity. It has been demonstrated that creating a bimetallic phase leads to synergistic effects, which significantly enhances the catalytic activity and stability^{355,356}. For example, a computational investigation has revealed that the Ni-Fe bimetallic catalyst exhibits comparable catalytic activity with Ru^{357,358}. Additionally, Ni-Fe bimetallic catalysts have been recently employed to selectively convert CH₄ to syngas³⁵⁹. By tuning the Ni/Fe ratio, the selectivity to CO can be dramatically enhanced, suggesting Ni-Fe bimetallic catalysts could be also used for selective CO₂-to-CO conversion³⁵⁹. However, the conventional impregnation or infiltration method cannot be used for synthesizing highly dispersed bimetallic catalysts. Creating metallic nanoparticles via *in-situ* exsolution from the perovskite oxides is attracting growing attention³⁶⁰. The *in-situ* exsolved metallic nanoparticles are uniformly dispersed on the oxide support can significantly enhance their electrocatalytic activity. Moreover, the nanoparticles anchored on the oxide support exhibit enhanced thermal stability, suppressing their agglomeration³⁶¹. It has been widely recognized that *in-situ* exsolved bimetallic nanoparticles from the SFM lead to improved activity for oxygen reduction reaction in fuel cell mode or CO₂ reduction in electrolysis mode^{353,362-364}. In this work, therefore, we have deliberately designed the negative electrode by decorating SFM with *in-situ* exsolved Ni-Fe bimetallic nanoparticles, aiming to achieve higher CO₂-to-CO selectivity and improve energy conversion efficiency in PCECs.

The XRD patterns of as-fired and reduced SFM-Ni_x ($x = 0, 0.175, 0.225$) are shown in Figure S1. Before reduction, both SFM-Ni₀ and SFM-Ni_{0.175} display a single phase of double

perovskite, indicating that Ni is fully dissolved into SFM. With further increasing the Ni amount to 0.225, additional NiO impurity was detected. Additionally, increasing the amount of Ni tends to shift the XRD pattern peaks to a lower degree, suggesting the Fe^{3+} ions, which have a relatively smaller ionic radius (0.64 Å), are substituted by the relatively larger Ni ions (0.72 Å)²⁴⁷. After reduction, SFM-Ni0 maintains its original crystal structure, implying SFM is stable under a reducing atmosphere and no metallic phase is exsolved. A new peak at $\sim 44.2^\circ$ shows on the XRD patterns of SFM-Ni0.175 and SFM-Ni0.225 samples, which are indexed well with a Ni-Fe alloy. It should be noted that the NiO phase in SFM-Ni0.225 is also reduced to metallic Ni, resulting in a relatively high peak intensity at $\sim 44.2^\circ$. Additionally, the CO_2 electrode with a lower amount of Ni, SFM-Ni0.075, was prepared. As shown in Figure S2, before reduction, the SFM-Ni0.075 displays a single phase of double perovskite, indicating that Ni is fully dissolved into SFM. After reduction, the SFM-Ni0.075 maintains its original crystal structure, and no obvious Ni-Fe alloyed phase was observed via XRD, implying a much lower number of Ni-Fe nanoparticles have been exsolved from SFM-Ni0.075 than SFM-Ni0.175. Therefore, the catalytic activity of SFM-Ni0.075 is expected to be worse than that of SFM-Ni0.175.

The morphology and chemical composition of the exsolved Ni-Fe bimetallic nanoparticles were subsequently identified via transmission electron microscopy (TEM). The reduced SFM-Ni0 powder displays a highly porous structure with a glossy particle surface, validating that there is no second phase formation upon reduction (Figure S3). In contrast, the TEM images of reduced SFM-Ni0.175 show that exsolved nanoparticles (~ 10 nm) are uniformly dispersed on the oxide support (Figure 6.10). To identify the crystal structure of the exsolved nanoparticles and oxide support, the interface between the oxide support and Ni-Fe alloyed nanoparticles was investigated by using high-resolution transmission electron microscopy (HR-TEM). As shown in Figure 6.10D, the

oxide support displays an observed lattice-fringe distance of $\sim 2.68 \text{ \AA}$, which can be assigned to the (110) plane of SFM-Ni_{0.175}. The reduced SFM-NiO (110) interplanar spacing is $\sim 2.78 \text{ \AA}$, which is relatively larger than that of SFM-Ni_{0.175}, affirming the fact that Ni is doped into the SFM lattice and Ni is not fully exsolved after reduction, which is consistent with the XRD analysis results. The lattice-fringe distance of the exsolved nanoparticles is $2.02 \text{ \AA}$, which is designated as the (110) plane of the Ni-Fe alloy. The energy dispersive spectroscopy (EDS) mapping displayed in Figure 6.10 E-G shows that the elements are homogeneously distributed. Additionally, it is observed that these nanoparticles are Ni-rich. As the oxide support and bimetallic nanoparticle contain Fe, the EDS mapping of Fe does not clearly show the nanoparticles. To further confirm the composition of the exsolved Ni-Fe alloyed nanoparticles, the high-magnification EDS mapping on one single nanoparticle was conducted, as shown in Figure 6.10H, which distinctly shows these metallic nanoparticles have both Ni and Fe. A detailed quantitatively analysis of EDS results determined that these bimetallic nanoparticles have 73.4 at. % Ni and 26.6 at. % Fe (Table S2). It should be noted that SFM-Ni_{0.175} was first reduced under hydrogen in an atmosphere-controlled furnace and transferred to the TEM sample chamber. The sample was exposed to air for a certain time. As the Ni-Fe particles are nanosized, the surface of Ni-Fe alloyed nanoparticles can be partially oxidized. Therefore, the EDS mapping images also show the oxygen elements (Figure 6.10H). Similar results have been reported in the literature³⁶⁵. The TEM images and EDS mapping of SFM-Ni_{0.225} also present the exsolved Ni-Fe alloyed nanoparticles (Figure S4) and relatively bigger Ni particles (Figure S5). Since the as-synthesized SFM-Ni_{0.225} is a composite of Ni-doped SFM and relatively big NiO particles (Figure S1A). Upon exposure to hydrogen, these NiO particles were reduced to metallic Ni particles (Figure S1B) with a relatively larger particle size than that of *in-situ* exsolved Ni nanoparticles. The Ni to Fe atomic ratio in SFM-Ni_{0.225} is slightly

lower than that of SFM-Ni_{0.175} (Table S2), this relatively low Ni/Fe ratio might be ascribed to less amount of Ni incorporates into the oxide lattice while some of them formed bulk NiO, consequently leading to a low Ni/Fe ratio in the exsolved nanoparticles after reduction.

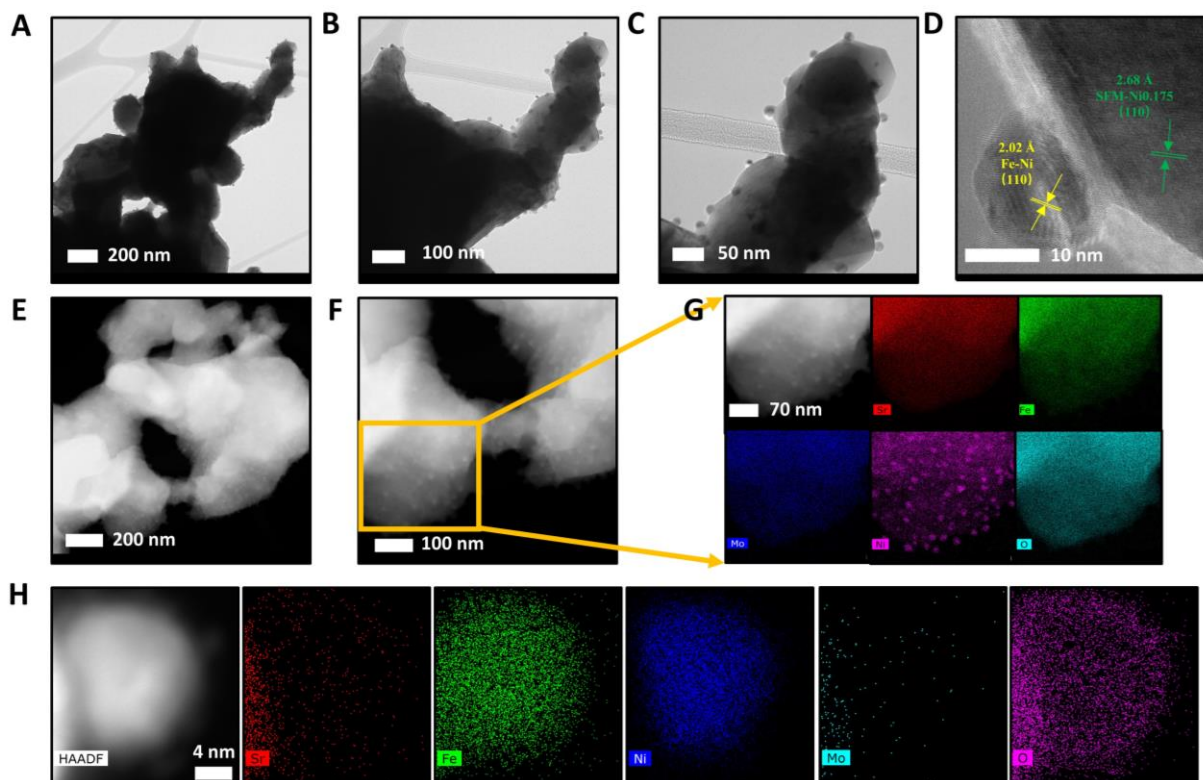


Figure 6.10. TEM images of the reduced SFM-Ni_{0.175}. (A-D) Bright-field TEM images at different magnifications. (E-G) High-angle annular dark-field (HAADF) images and EDS mapping at low magnification. (H) HAADF images and EDS mapping of a single bimetallic nanoparticle at high magnification.

6.2.4.3 CO₂-PCECs performance and stability evaluation

The CO₂ reduction in CO₂-PCECs with SFM-Ni₀, SFM-Ni_{0.175}, and SFM-Ni_{0.225} negative electrodes was conducted. Figure 6.11A shows the electrode potential as a function of current density at 600 °C. To better compare the electrocatalytic activity of negative electrodes, the applied overpotential shown in Figure 6.11A is normalized to solely present the overpotential ascribed to the electrodes. Moreover, H₂ is fed to the positive electrode, and the overpotential of

hydrogen oxidation reaction at the positive electrode is much lower than the negative electrode overpotential. Therefore, Figure 6.11A can fairly compare the activity of these three negative electrodes. SFM-Ni_{0.175} does show a much lower overpotential than that of SFM-Ni₀, indicating the *in-situ* exsolved Ni-Fe bimetallic nanoparticles drastically accelerate the electrochemical reaction that occurs at the negative electrode. SFM-Ni_{0.225} does not further improve the performance as the excess Ni creates big Ni particles and reduces the Ni/Fe ratio of alloyed nanoparticles. In addition, the CO selectivity for those three negative electrodes is all >98% at 600 °C under the applied current density ranging from 50 to 400 mA/cm² (Figure S6), suggesting exceptional CO selectivity hinges on the SFM support. Furthermore, as shown in Figure 6.11B, the highest CO production rate is achieved in CO₂-PCECs with the SFM-Ni_{0.175} negative electrode in a wide range of current densities. For example, the CO production rate reaches ~18 ml/h/cm² at a current density of 0.2 A/cm², which is 44% higher than that of SFM-Ni_{0.225} and 800% higher than that of SFM-Ni₀. Referring to Figure 6.11B, the selectivity toward CO at the SFM-Ni_{0.175} negative electrode is >98%, indicating the CO production rate is proportional to the CO₂ conversion. It should be noted that the CO production rate over these three negative electrodes displays the same trend as the overpotentials shown in Figure 6.11A. Therefore, it has been identified that SFM-Ni_{0.175} is more active than SFM-Ni_{0.225} and SFM-Ni₀.

To understand how can operating temperatures impact CO₂ reduction in CO₂-PCECs with SFM-Ni_{0.175} negative electrode, Figure 6.11C presents the overpotential as a function of the applied current density at 400-600 °C. Although the overpotential increases with decreasing the operating temperature, an overpotential of 0.68 V is achieved at a current density of 300 mA/cm² and an operating temperature as low as 400 °C, suggesting this rationally designed transition metal-based negative electrode cannot only contribute to reduced catalyst cost but also improve the

energy conversion efficiency (Figure S7). It is clear that SFM-Ni0.175 significantly enhances the energy efficiency, which is ~ 10 times higher than that of SFM-Ni0 and SFM-Ni 0.225. The enhanced energy efficiency is attributed to low overpotential and high CO yield. The overall energy conversion efficiency is relatively low at high current densities because there is considerable hydrogen production at the CO₂ reduction electrode, suggesting future work should also center on inhibiting hydrogen evolution reaction while increasing CO₂ conversion at a high current density. In addition, it should be recognized the CO production rate is relatively low at 400 °C. Therefore, the catalytic activity at 400 °C should be further improved in future work to enhance CO₂ conversion.

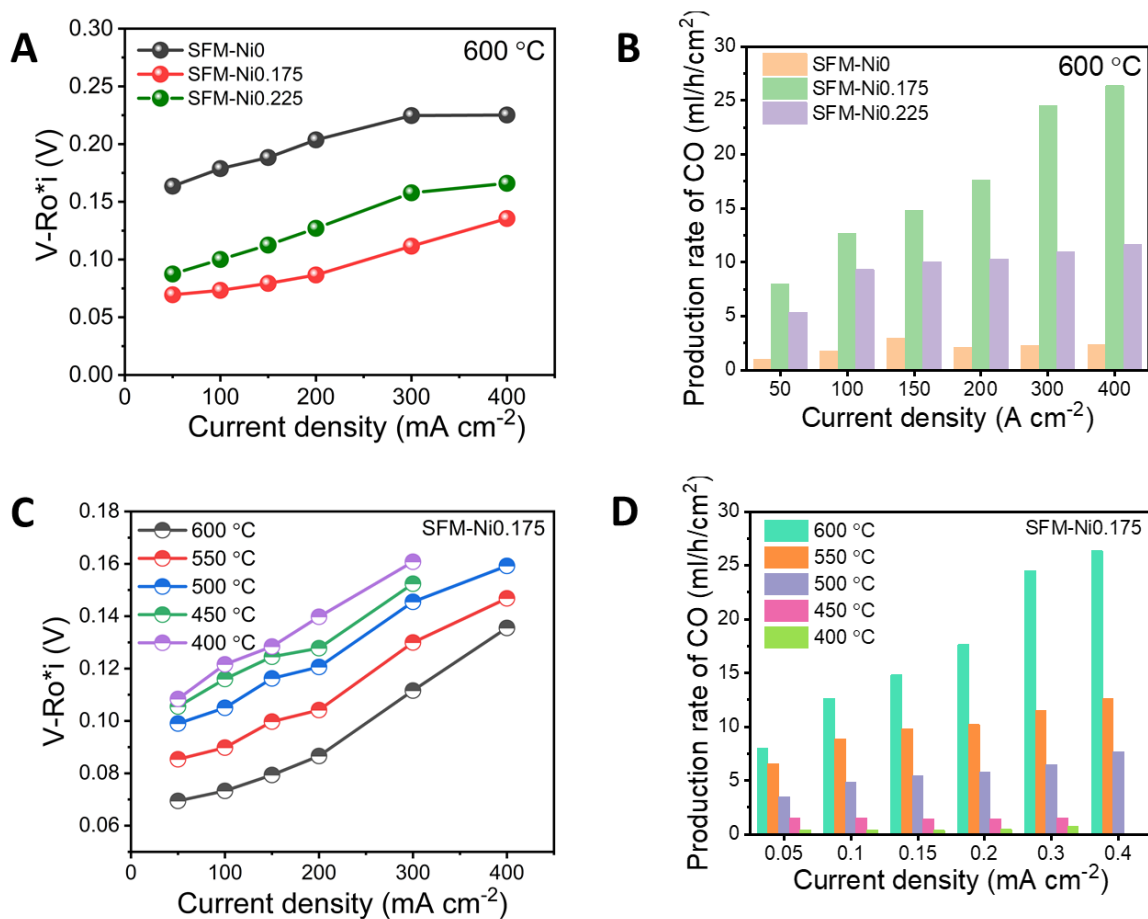


Figure 6.11. CO₂ reduction in CO₂-PCECs with three different negative electrodes, including SFM-Ni0, SFM-Ni0.175, and SFM-Ni0.225. (A) *I-V* curves of the CO₂-PCECs. The voltage is normalized by subtracting the potential ascribed to ohmic resistance from the applied voltage. (B) CO production rate in CO₂-PCECs with three negative electrodes at 600 °C. (C) *I-V* curves of the CO₂-PCECs with SFM-Ni0.175 negative electrode at 400-600 °C. The voltage is normalized by subtracting the potential ascribed to ohmic resistance from the applied voltage. (D) CO production rate as a function of current density in CO₂-PCECs with SFM-Ni0.175 negative electrode at 400-600 °C.

It is also observed that increasing the current density tends to increase the CO production rate as more proton/hydrogen is supplied to reduce CO₂ (Figures 6.9B, 6.11B, and 6.11D). Furthermore, increasing the current density does not reduce the CO selectivity, suggesting an excessive supply of proton/hydrogen does not lead to the production of CH₄, which indicates the SFM-Ni0.175 negative electrode favors a specific CO₂ reduction pathway where the CH₄ production is suppressed.

Figure S8 presents the electrochemical impedance spectra (EIS) of CO₂-PCECs with SFM-Nix as the negative electrodes. Figure S9 shows the electrolyte layers of these three PCECs have the same thickness; thus, three CO₂-PCECs exhibit similar ohmic resistance. To better understand how can negative electrodes affect the kinetic of CO₂ reduction in PCEC, Figure 6.12 presents the normalized electrochemical impedance spectra (EIS) of CO₂-PCECs with SFM-Nix as the negative electrodes and the corresponding distribution of relaxation time analysis (DRT).

The CO₂-PCECs are composed of a CO₂ electrode, electrolyte, and positive electrode. The same electrolyte and positive electrode are used to fabricate the PCEC half cells for evaluating different CO₂ electrodes. As shown in Figure 6.12A, at 600 °C, the CO₂-PCEC with SFM-Ni0.175 negative electrode possesses the lowest electrode polarization area-specific resistance (*ASRp*) at a current density of 50 mA/cm², indicating SFM-Ni0.175 is more active than SFM-Ni0.225 and SFM-Ni0, which is consistent with the CO₂-PCEC performance shown in Figure 6.12. Increasing

the current density accelerates the electrochemical reactions, reducing the $ASRp$ (Figure 6.12B). As shown in Figure 6.12C, the DRT analysis is performed to identify the specific steps of CO_2 conversion and understand how SFM-Ni0.175 improves the catalytic performance. The EIS spectra have been deconvoluted into four main regions/peaks, which are denoted as P1 in the low-frequency zone (1-50 Hz), P2 in the intermediate-frequency zone (100-1000 Hz), P3 in the relatively high-frequency zone (~ 5000 Hz), and P4 in the high-frequency zone (~ 50000 Hz).

As shown in Figures 6.12C and 6.12D, both P1 and P2 vary significantly with using different CO_2 electrodes and changing the current density, suggesting P1 and P2 correspond to the essential current-dependent processes occurring at CO_2 electrodes, which mainly include CO_2 reduction reaction and hydrogen evolution reaction⁵⁶. At an electrode that does not favor CO_2 reduction reaction while favors hydrogen evolution reaction, the CO_2 reduction reaction exhibits a higher energy barrier than that of hydrogen evolution reaction³⁶⁶. In this case, the peak associated with CO_2 reduction reaction has a higher resistance than that of hydrogen evolution reaction. The CO_2 reduction performance in CO_2 -PCECs equipped with SFM-Ni0 and SFM-Ni0.225 is poor, suggesting the CO_2 reduction over SFM-Ni0 and SFM-Ni0.225 is unfavorable. Figure 6.12C shows the P1 of SFM-Ni0 and SFM-Ni0.225 is higher than P2, indicating P1 could be related to CO_2 reduction reaction and thus P2 could be assigned as hydrogen evolution reaction. On the other hand, SFM-Ni0.175 exhibits a lower P1 and higher P2 than that of SFM-Ni0 and SFM-Ni0.225 (Figure 6.12C), implying SFM-Ni0.175 favors CO_2 reduction and suppresses hydrogen evolution reaction, which is consistent with the CO_2 -PCEC performance shown in Figure 6.11. Therefore, SFM-Ni0.175 is a promising CO_2 electrode for PCECs.

DRT analysis was also conducted to correlate the CO_2 reduction kinetics with the applied current densities (Figures 6.12D). Increasing the current density can accelerate the charge transfer

and electrochemical reactions^{56,367}. Therefore, as shown in Figure 6.12D, both P1 and P2 decrease with increasing the current density. At a current density of 50 mA/cm², there are insufficient protons supplied to the CO₂ electrode to activate and reduce CO₂ adsorbed on the electrode surface. Therefore, at a relatively low current density, the CO₂ reduction kinetics is slower than hydrogen evolution reaction, and the corresponding resistance (P1) is higher than that of hydrogen evolution reaction (P2). With increasing the current density, both CO₂ reduction and hydrogen evolution reactions are facilitated, reducing P1 and P2. At a current density of 200 mA/cm², there are sufficient protons provided to reduce CO₂. The beneficial impact of increasing current density on CO₂ reduction is more significant than that on hydrogen evolution reaction. Therefore, at a relatively high current density, the CO₂ reduction is more favorable than hydrogen evolution reaction and the corresponding resistance (P1) is lower than that of hydrogen evolution reaction (P2). Referring to the DRT results, the P1 (CO₂ reduction reaction) is smaller than P2 (hydrogen evolution reaction) at 200 mA/cm² while it is reversed at a low current density of 50 mA/cm². As shown in Figure 6.12D, at 600 °C, both P3 and P4 are constant with increasing the current density, indicating P3 and P4 are current-independent processes^{368,369}, which could include the external mass transport of CO₂ to the negative electrode surface, CO₂ absorption, desorption of CO and CH₄. There is limited work has been conducted to reduce CO₂ in PCECs, especially probing the CO₂ reduction processes in PCECs, suggesting additional efforts should be devoted to understanding the electrochemical reactions that occur at CO₂ electrodes

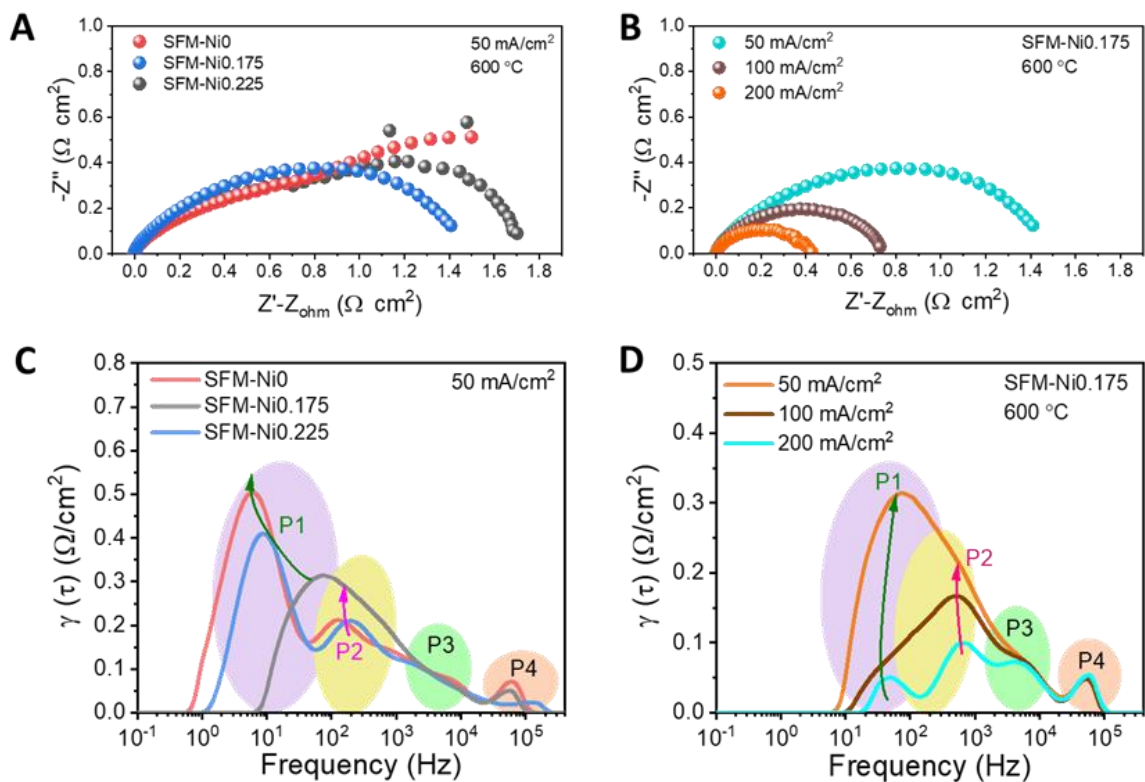


Figure 6.12. EIS spectra of CO₂-PCECs with three different negative electrodes (A) Nyquist plots of CO₂-PCECs with three different negative electrodes under a current density of 50 mA/cm² at 600 °C. (B) Nyquist plots of the CO₂-PCEC with SFM-Ni0.175 negative electrode under a current density of 50, 100, and 200 mA/cm² at 600 °C. (C) DRT analysis of EIS spectra shown in Figure 6.12A. (D) DRT analysis of EIS spectra shown in Figure 6.12B.

The durability of CO₂-PCECs is also critical for comprehensively evaluating the negative electrodes. Prior work has revealed that the conventional BCZYYb7111-Ni negative electrode is prone to react with CO₂ and form BaCO₃, leading to poor CO₂-PCEC stability²⁷. Therefore, herein, BCZYYb4111 is employed as the electrolyte to mitigate potential degradation attributed to the electrolyte. Furthermore, as shown in Figure 6.13A, the stability of the CO₂-PCECs with SFM-Ni0.175 negative electrodes was determined by recording the voltage and measuring the CO production rate under a constant current density at 400 °C and 500 °C. The CO₂-PCEC stability was first evaluated at 400 °C for 10 hours at a current density of 50mA/cm². The degradation rate is around 0.15mV/min. The operating temperature was then increased to 500 °C. The applied

terminal voltage was stable at ~ 0.2 V for ~ 50 hours. There was no observable degradation in voltage, CO production rate, and CO selectivity, demonstrating remarkable stability for selectively converting CO_2 to CO at intermediate temperatures. Post-mortem characterization of the CO_2 -PCEC was performed. Figure 6.13C shows the SEM image of the CO_2 -PCEC after stability testing. The negative electrode layer maintained good adhesion with the electrolyte while no delamination was observed. To better confirm the coking tolerance of SFM-Ni0.175, the high-resolution post-mortem SEM image were presented in Figure S10. There is no apparent carbon on the surface of CO_2 electrode, indicating the SFM-Ni0.175 exhibits good coking tolerance.

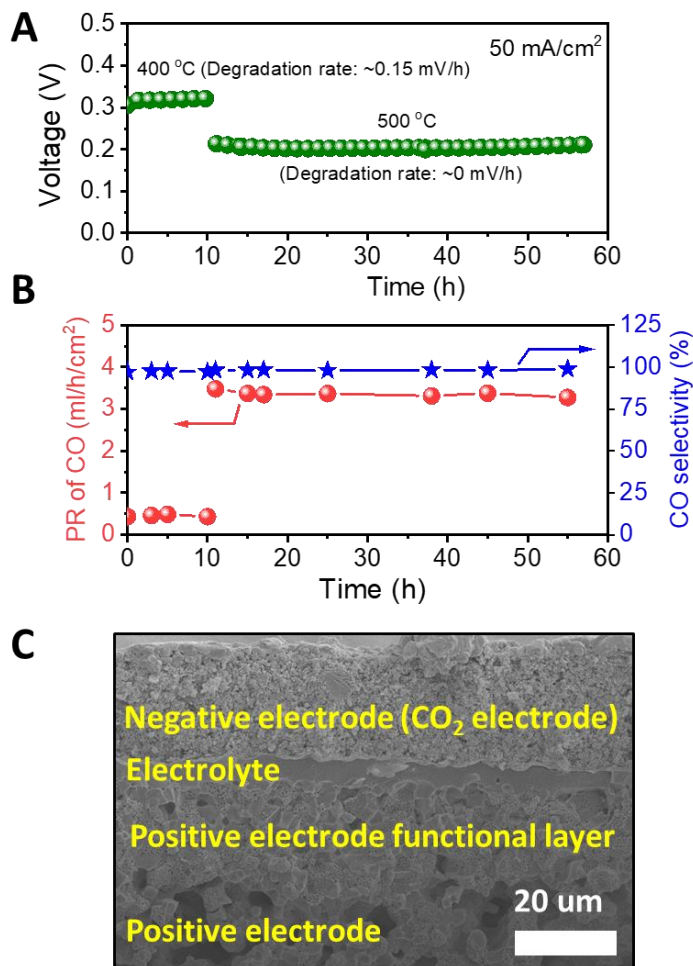


Figure 6.13. Stability testing of CO_2 -PCECs with SFM-Ni0.175 negative electrodes. (A) The terminal voltage as a function of time under a current density of 50 mA/cm² at 400 °C and 500 °C. (B) The CO production rate and selectivity toward CO as a function of time under a current density

of 50 mA/cm² at 400 °C and 500 °C. (C) Cross-section SEM image of CO₂-PCECs after stability testing.

6.2.4.4 In situ DRIFTS to probe the CO₂ reduction mechanism

In situ DRIFTS was performed to probe the CO₂ reduction mechanisms over both an SFM-Ni_{0.175} negative electrode and a conventional cermet negative electrode. As shown in Figures 6.10 and 6.14, a mixture of CO and CH₄ is produced over a BCZYYb-Ni negative electrode at an intermediate temperature ranging from 350 °C to 550 °C. On the other hand, SFM-Ni_{0.175} can selectively reduce CO₂ to CO across a wide range of operating temperatures. The DRIFTS spectra are consistent with PCEC testing results in this work and reported in the literature^{190,320,347}.

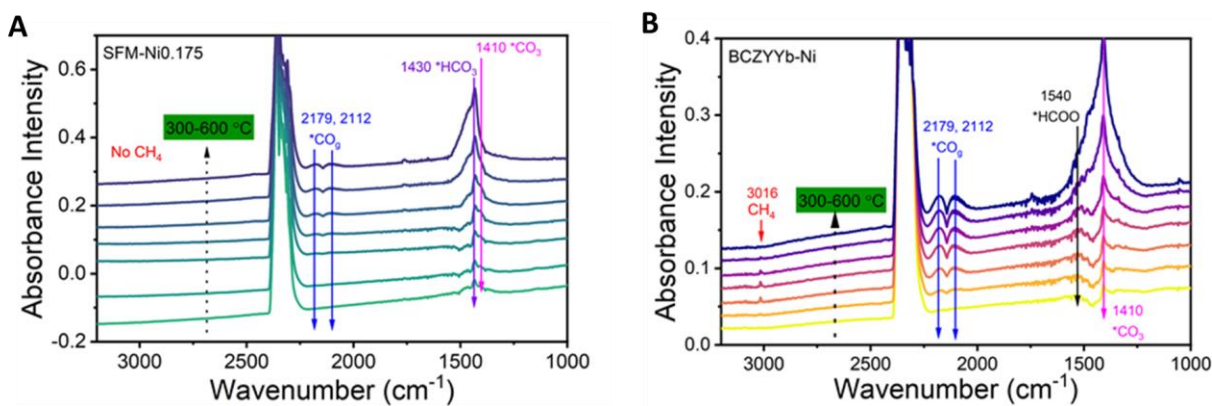


Figure 6.14. In situ DRIFTS spectra of CO₂ reduction over (A) SFM-Ni_{0.175} and (B) BCZYYb-Ni cermet negative electrode. Both samples were reduced at 600 °C for 2 hours and cooled down to 25 °C under H₂. The atmosphere was then changed to Ar to collect the background. Upon changing the feeding gas from Ar to 10 sccm CO₂, 10 sccm H₂, and 20 sccm Ar, the spectra were collected with gradually increasing the operating temperature.

An in-depth analysis of the DRIFTS spectra shows that formate species (~1540 cm⁻¹) were presented over BCZYYb-Ni while the formate species were not observed on SFM-Ni_{0.175}. Additionally, the temperature range at which the formate species were present is consistent with the temperature range that CH₄ is produced. Therefore, the CH₄ production could be attributed to the formate species. Accordingly, we propose the CO₂ reduction mechanisms over both negative

electrodes, which are displayed in Figure 6.15. As shown in Figure 6.14A, both bicarbonate ($\sim 1430\text{ cm}^{-1}$) and monodentate carbonate species ($\sim 1410\text{ cm}^{-1}$) show on SFM-Ni_{0.175}, which can lead to the production of CO. Figure 6.15A shows the associative path where CO₂ is associatively adsorbed on SFM-Ni_{0.175} to form bicarbonate, which is subsequently reduced to CO. Alternatively, as shown in Figure 6.15B, CO₂ can be dissociatively adsorbed on SFM-Ni_{0.175} to form monodentate carbonate that can be further reduced to CO. Figure 6.15C shows the CH₄ can be produced on BCZYYb-Ni via the formate path. CO simultaneously forms on BCZYYb-Ni via the dissociative path where monodentate carbonate is the key functional group. The formation of formate on BCZYYb-Ni results in the production of CH₄. SFM-Ni_{0.175} inhibits the formation of formate; thus, it can selectively reduce CO₂ to CO.

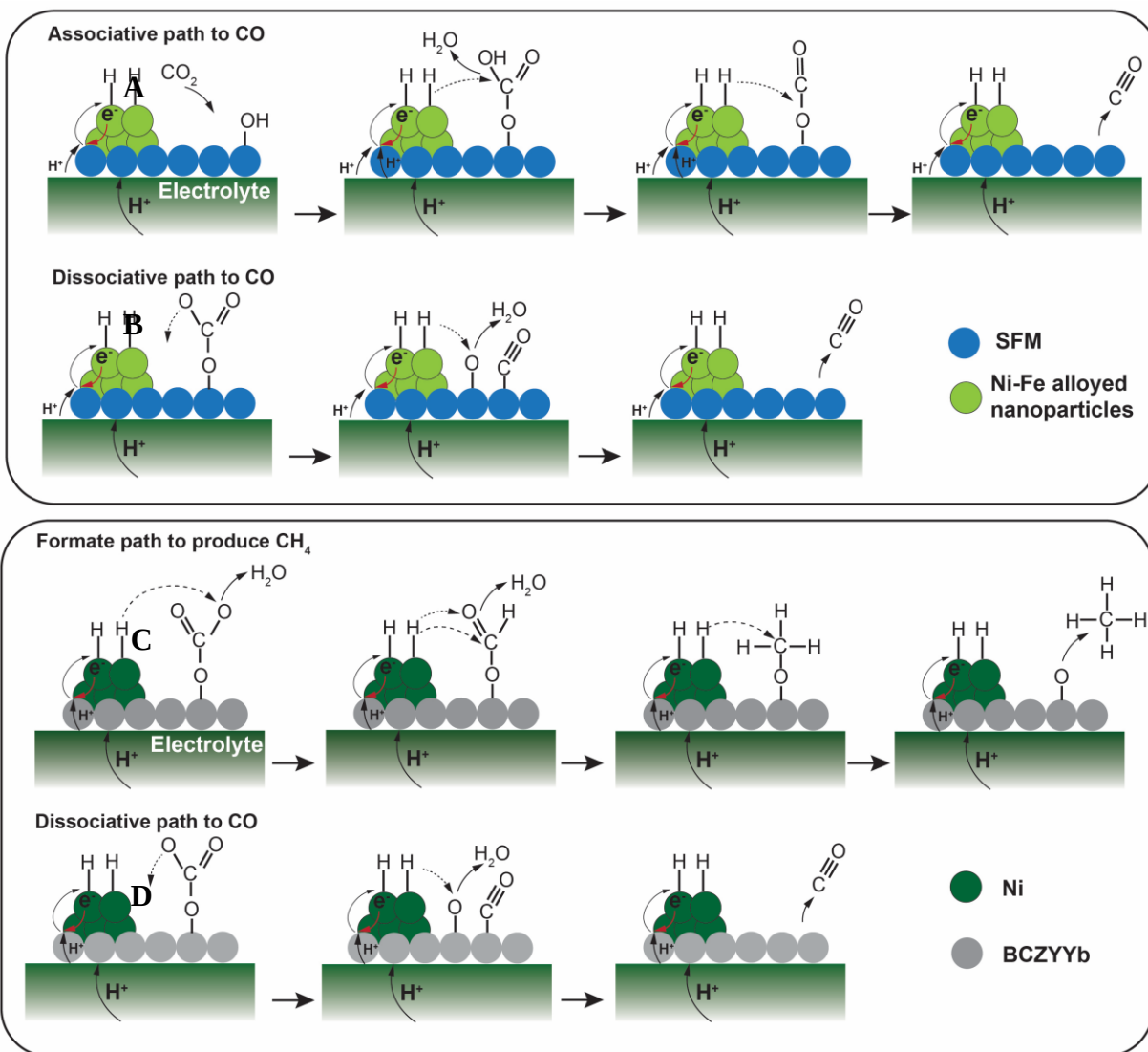


Figure 6.15. Proposed CO₂ reduction pathways over the SFM-Ni_{0.175} negative electrode and conventional Ni-cermet negative electrode. (A) Associative path to produce CO over SFM-Ni_{0.175}. (B) Dissociative path to produce CO over SFM-Ni_{0.175}. (C) Formate path to produce CH₄ over BCZYYb-Ni negative electrode. (D) Dissociative path to produce CO over BCZYYb-Ni negative electrode.

6.2.5 Conclusions

In this work, SFM-Ni_{0.175} is rationally designed and employed as the negative electrode of CO₂-PCECs. Upon reduction, Ni-Fe alloyed nanoparticles exsolve from SFM-Ni_{0.175}, creating a novel negative electrode that is constituted of an oxide phase and *in-situ* exsolved bimetallic

nanoparticles, which significantly increases the CO production rate and reduces the negative electrode overpotential. Furthermore, this novel negative electrode leads to CO production with a CO selectivity of ~100%. It is identified that SFM-Ni_{0.175} suppresses the formation of formate species which inhibit the production of CO. This work further validates that PCECs can selectively reduce CO₂ to value-added chemicals at intermediate temperatures by engineering the negative electrode.

6.2.6 Data and materials availability

All data are available in the main text or the supplementary materials. The supplementary materials can be found at <https://doi.org/10.1016/j.nanoen.2022.107722>.

Chapter 7 – Summary and conclusion

This thesis is dedicated to the design, manufacturing, and testing/verification of advanced ceramic electrochemical cells aimed at efficient power generation, green hydrogen production, and CO₂ conversion. Throughout this research, numerous challenges were addressed, leading to significant breakthroughs and the demonstration of world-record performance and durability of PCECs and SOFCs.

One of the primary achievements of this thesis is the successful reduction of the operating temperature of PCECs to below 450 °C. This was accomplished through the rational development of a low Ba-deficiency, bamboo-structured, ultrathin, and chemically homogeneous electrolyte, coupled with the design of highly active positive electrodes. These innovations have paved the way for enhanced efficiency and durability of PCECs, setting new standards in ceramic electrochemical cell technology.

Furthermore, the thesis explores the concept of process-intensified DRM-PCFCs, showcasing their ability to concurrently generate power, produce chemicals, and mitigate greenhouse gas emissions. These DRM-PCECs exhibit unprecedented performance at intermediate temperatures (<650 °C), demonstrating their potential to revolutionize energy conversion processes.

Additionally, the thesis validates the potential of PCECs for CO₂ electrochemical conversion, achieving a remarkable selectivity of approximately 100% towards CO over a wide range of operating temperatures (400-600 °C) and applied potential/current densities. This accomplishment underscores the versatility and efficacy of PCECs in facilitating sustainable chemical manufacturing processes.

Comprehensive characterization tools were employed throughout the research to understand the structure, composition, and electrochemical properties of the developed ceramic electrochemical cells. Specifically, the integration of in-situ operando spectroscopy combined with DFT calculations, provided invaluable insights into catalytic mechanisms and advanced our understanding of materials science and electrochemistry.

In summary, this PhD thesis presents an extensive and thorough investigation into the advanced design and development of ceramic electrochemical cells. By enhancing their efficiency, durability, and sustainability, this research contributes significantly to the advancement of energy conversion and storage technologies, ultimately fostering the realization of a more sustainable energy future.

Chapter 8 – Suggestions for future directions

PCECs that run at $<450\text{ }^{\circ}\text{C}$ could transform the architecture and operation of ceramic electrochemical cells, leading to enhanced energy conversion efficiency, reduced costs of producing green hydrogen and the realization of long-term chemical energy storage. The scalable PCEC fabrication processes developed in this thesis might also accelerate the scale-up and commercialization of this technology. Moreover, the demonstration of high-performance PCECs that operate at relatively low temperatures creates opportunities for using proton-conducting ceramics for other applications, including electrochemical membrane reactors, gas separation membranes and electrochemical sensors. Producing chemicals in PCECs on the other hand opens an attractive avenue for chemical energy storage as PCECs interconvert the electrical energy and chemical energy. Nevertheless, several challenges remain in the development of PCECs:

- (1) Although the Faradaic efficiency (FE) of our PCECs is comparable to or higher than that of other reported PCECs, the FE of PCECs is still low compared with that of high-temperature oxygen-ion conductor solid oxide electrolysis cells. This suggests that additional strategies are required to further increase the FE of PCECs, especially at a high current density.
- (2) The active area of our PCECs should be greatly increased to validate the performance under industrially relevant conditions. However, suitable interconnector and sealing materials first need to be developed before the performance of large-area PCECs can be evaluated.
- (3) Substantial increasing efforts have been devoted to validating the concepts of using PCECs for chemical production. There is a lack of fundamental understanding of the electrochemical reactions and reaction pathways. Therefore, it is necessary to design

- and build the experimental tools to assist in probing mechanisms of nitrogen reduction reaction, CO₂ reduction reaction, and methane aromatization in PCECs. A deeper understanding of the reaction mechanisms could be of great benefit to rationally designing electrodes and catalysts for PCECs.
- (4) Thinking beyond synthesizing chemicals via a single reaction, intensifying two or more reactions in one PCEC to produce more chemicals can enhance energy efficiency, reduce capital cost, and improve economic benefits. For example, N₂ or CO₂ reduction PCEC can be integrated with the CH₄ dehydroaromatization reactor to utilize the H₂ produced via CH₄ conversion. N₂ or CO₂ reduction electrodes can be applied as the negative electrodes of the CH₄ conversion reactor; thus, H₂ will directly reduce N₂ to ammonia or convert CO₂ to value-added chemicals. This process intensified reactor increases the hydrogen utilization and reduces the carbon footprint of producing ammonia, carbon monoxide, and hydrocarbons.
- (5) The economic viability of producing chemicals in PCECs depends on both capital and operational costs. The reduction in electricity cost, especially the renewable electricity cost, is essential for facilitating the future implementation of PCECs for synthesizing chemicals in the real world. To accurately evaluate the economic viability of producing chemicals in PCECs, it is suggested to conduct a comprehensive techno-economic analysis to quantitatively determine the chemical production cost in PCECs and compare it with conventional manufacturing processes.
- (6) The configurations of PCECs employed for producing chemicals vary with feedstocks and products, which limits the flexibility and versatility of PCECs. For example, the positive electrodes of PCECs for CO₂ reduction should be modified to use different

reactants delivered to the positive electrode. With a positive electrode that is active for the oxidation of various feedstocks, PCECs will be more capable of converting broader reactants to high-value chemicals.

- (7) We have recognized that operating conditions, including temperature, atmosphere, current density or voltage, and pressure, can affect PCEC performance and stability, suggesting a detailed computational system can be developed to control and optimize the processes, aiming to further enhance the economic viability of producing chemicals in PCECs.

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