

Development of novel nanomaterials based electrocatalysts for energy conversion devices

by

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Abstract

The growing global energy demand, due to the depletion of fossil fuels and accompanied global warming, has compelled the utilization of renewable and sustainable energy sources. This has attracted the investigation of electrochemical renewable energy conversion devices, such as fuel cells and water electrolyzers which can provide higher energy conversion efficiency at lower temperature with negligible environmental pollution. Fuel cells produce electricity from renewable chemicals (liquid methanol, hydrogen, air etc.), while water electrolyzers produce renewable chemicals (hydrogen and oxygen) utilizing electricity and water. The electrocatalysts used in fuel cell and water electrolyzers are key to enhance their performances. Despite the advances in both the technologies, they are not commercially successful yet owing to high cost and poor durability of Pt based electrocatalysts used to catalyze the electrochemical reactions. This dissertation focusses on the development of novel electrocatalysts, and catalyst supports for fuel cells and water electrolyzers using microwave-assisted synthesis methods.

In the first approach, a simple microwave assisted synthesis methods has been developed to prepare multifunctional core-shell catalyst supports and PtRu nanoparticles to employ as methanol oxidation reaction (MOR) anode electrocatalysts in direct methanol fuel cells (DMFC). The specific heating of microwaves has been used to selectively deposit ultra-thin shell of metal oxides (such as TiO_2 and SnO_2) on carbon supports and PtRu nanoparticles on TiO_2/C or SnO_2/C supports. Thermal annealing of these electrocatalysts has resulted in formation of PtRu alloy nanoparticles and defective metal oxide ultra-thin shells. Systematic materials and half-cell electrochemical characterizations has been done in Chapter 2 to show the improved carbon monoxide (CO) oxidation kinetics, superior MOR activity, and excellent stability exhibited by the PtRu alloy nanoparticles deposited on TiO_2 or SnO_2 modified carbon supports, when compared to

commercial PtRu/C catalysts. The enhanced MOR activity and stability is attributed to the strong-metal support interaction (SMSI) and higher oxophilicity offered by the ultra-thin metal oxide shell on PtRu nanoparticles. The effect of different carbon supports and different metal oxides in the activity and stability of PtRu electrocatalysts have been studied in Chapters 3 and 4, respectively, with full DMFC evaluations. The excellent properties imparted by the ultra-thin shells of TiO₂ modified carbon supports have been found to enhance the hydrogen oxidation reaction (HOR) anode kinetics of PtRu electrocatalysts in anion exchange membrane fuel cells (AEMFCs) in Chapter 5. About 20% enhancement in maximum power density in AEMFC has been achieved compared to the commercial PtRu/C anode.

In the second approach, one-dimensional chain like structures of amorphous molybdenum trisulfide (MoS₃) has been deposited on reduced graphene oxides (rGO), using a rapid microwave assisted synthesis method, to employ as a platinum group metal free hydrogen evolution reaction (HER) electrocatalyst to use in proton-exchange membrane water electrolyzers (PEMWEs). A family of MoS_x/rGO hybrid materials with controllable composition and structure, has been produced by subjecting the microwave prepared samples to thermal annealing at different temperatures in reducing atmosphere. The amorphous MoS₃/rGO annealed at 250 degrees Celsius (a-MoS₃/rGO 250) exhibits excellent HER catalytic activity with a low overpotential, a low Tafel slope, a high double layer capacitance and a high turnover frequency value. The enhanced catalytic activity of a-MoS₃/rGO 250 has been attributed to the high density of Mo^V active sites and the abundant sulfur ligands of the a-MoS₃/rGO 250. Overall, microwave assisted synthesis method has been found to be a versatile and a rapid platform to prepare high performance electrocatalysts for fuel cells and water electrolyzers.

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Dedication

To my mom, Revathi

for her love, trust, and support she gave me to pursue my Ph.D.

Preface

The dissertation comprises of following major sections:

Chapter 1: This chapter provides an overview of the motivation of this dissertation. It includes the basic scientific concepts involved in the energy conversion technologies such as DMFC, AEMFC and PEMWE, which are studied in this work. It will provide elaborate discussion on the challenges prevailing in the commercialization of these renewable energy conversion device technologies.

Chapter 2: An accepted paper, published in *ACS Applied Nano Materials*. A rapid microwave-assisted synthesis method is reported to produce a novel core-shell multifunctional catalyst support based on hydrogenated TiO₂ coated on nitrogen doped carbon nanotubes for PtRu anode electrocatalysts to employ in DMFCs. The PtRu/TiO₂/ONCNT-400 demonstrated in this work provide promising CO oxidation, methanol oxidation reaction kinetics with improved stability compared to commercial PtRu/C anodes.

Chapter 3: In this chapter, we extend the study to investigate the effect of TiO₂ modification on various carbon supports, such as ONCNT, Vulcan and KB 600JD, to reveal the critical role of carbon supports in enhancing the MOR activity and stability of PtRu electrocatalysts. Accelerated stress test (AST) protocols were established to understand the degradation mechanism of various PtRu electrocatalysts deposited on hydrogenated TiO₂ modified carbon supports by conducting CO stripping experiments at various stages of ASTs. Full DMFC was assembled to understand the role of different anode catalyst support architecture in DMFC performance at different methanol concentration feeds.

Chapter 4: In this chapter, a rapid microwave-assisted synthesis method is demonstrated to form core-shell SnO₂ modified high surface area carbon support to enhance the stability of PtRu

electrocatalysts. The effect of different annealing atmosphere (such as nitrogen and hydrogen) and different ratio of SnO₂ to carbon were investigated to optimize the MOR activity of PtRu catalyst alloy nanoparticles. Systematic CO stripping studies at different stages of AST were conducted to reveal the excellent MOR stability exhibited by the as-prepared SnO₂ modified carbon support towards strongly anchoring Ru nanoparticles when compared to the TiO₂ modified carbon supports.

Chapter 5: In this chapter, we investigated a multifunctional hydrogenated TiO₂ modified on high surface area carbon support to enhance the hydrogen oxidation reaction (HOR) kinetics of PtRu electrocatalysts in AEMFCs. A full AEMFC was assembled to demonstrate the high performance of PtRu/TiO₂/C-400 HOR anodes compared to commercial PtRu/C anodes. The reason for high performance AEMFC is elucidated by systematic materials and half-cell electrochemical characterization such as CO stripping and RDE voltammetry at different RPMs.

Chapter 6: In this chapter, a novel non-precious platinum metal group free (PGM-free) electrocatalyst based on defect-engineered molybdenum sulfide (MoS_x) deposited on rGO is developed, to employ as cathode to catalyze hydrogen evolution reaction (HER) in proton-exchange membrane water electrolyzer (PEMWE). A rapid microwave-assisted synthesis method was used to prepare the amorphous MoS₃/rGO and subsequent thermal at various temperatures produced MoS_x/rGO hybrids with tunable S to Mo atomic ratio. The HER activity and stability of various MoS_x/rGO hybrids is demonstrated using half-cell electrochemical characterizations.

Chapter 7: The main findings and conclusions of the five major research chapters are provided in this section.

Chapter 1 - Introduction

1.1. Motivation

The rapidly increasing global population of over 8.0 billion and economic growth have increased the global energy demand. The world is in the middle of energy crisis.² The entire humanity is dependent on consumption of non-renewable energy sources such as fossil fuels, to support the current living standards, as shown in Figure 1.1.³ This has led to unacceptable levels of greenhouse gas emissions (especially CO₂) resulting in global warming.⁴ Utilization of renewable energy source is the key for the transition to a less carbon-intensive environment.⁵ In the present, renewable energy sources including solar, wind, and hydropower account for only about 26% of the world's electricity production.⁵

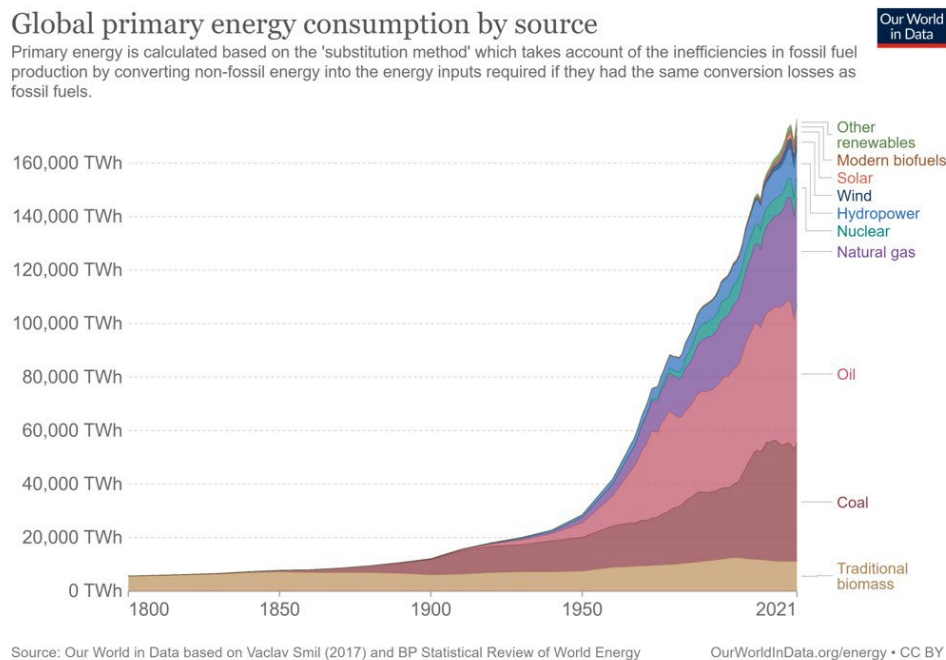


Figure 1.1. Global energy consumption data. BP Statistical Review of World Energy; Vaclav Smil (2017), Energy Transitions: Global and National Perspectives, 2nd edition, Appendix A.³

Another limitation of current renewable energy technologies is that they are from intermittent energy sources. This has led to the need to store energy produced from renewables in

energy storage systems such as batteries to support the continuous usage. Currently, lithium-ion batteries (LIBs) are the commercial forerunners in energy storage systems from electric vehicles to portable electronic devices.⁶ However, increasing energy demand cannot be completely resolved with the use of LIB technology owing to its limited energy density (~ 200 to 270 Wh/kg) when compared to gasoline.⁷ This has attracted the exploration of alternate renewable and sustainable energy sources such as hydrogen (H_2) and methanol which possess high energy density of about 33.6 kWh/kg and 6.1 kWh/kg, respectively.^{8,9} H_2 is a versatile energy carrier as it possesses myriad of applications in both transportation sector (fuel cells and energy storage) and industry sectors. Some of the key industrial applications of hydrogen are in the ammonia synthesis, methanol production, hydrochloric acid production, hydrometallurgical processes, food industry, etc.¹⁰ Renewable energy conversion device such as water electrolyzers is the prime technology being investigated to split water into high value renewable green H_2 and O_2 . On the other hand, the fuel cells can convert chemical energy of renewable fuels (such as H_2 or methanol) to usable electricity and greener byproducts with zero carbon emission or net zero emissions.¹¹ They have promising applications in portable devices, transportation sectors, and stationary power sources.

1.2. Fuel Cells

Fuel cells are electrochemical energy conversion devices which convert the chemical energy of fuel to electrical energy.⁹ It commonly consists of an anode, a cathode, an electrolyte, an ion-selective membrane and an external load. The fuel supplied at the anode compartment is oxidized to generate free electrons and byproducts, whereas the fuel supplied at the cathode compartment is reduced using the electrons and ions supplied from anode via the external load and electrolyte, respectively, to form byproducts and electricity.⁹ Fuel cells are classified based on the electrolyte being used in it, which in turn determines the electrochemical reactions involved, type

of fuel used, operating temperature, etc.¹² The most studied fuel cells are proton exchange membrane fuel cells (PEMFCs), direct methanol fuel cells (DMFCs) and anion exchange membrane fuel cells (AEMFCs), due to their capability to deliver high energy efficiency, high energy density, flexibility to operate at low working temperatures with environmental friendliness.¹² This dissertation focuses on DMFC and AEMFC, hence the following section provides a brief overview of the same.

1.2.1. Proton Exchange Membrane Fuel Cells

1.2.1.1. Working Principle

PEMFCs are fuel cells which use proton exchange membrane (PEM), commonly Nafion, to selectively conduct protons from anode to cathode compartment.¹³ It uses renewable H₂ gas and oxygen gas as anode fuel and cathode oxidant, respectively.¹⁴ Hydrogen oxidation reaction (HOR) happens at the anode to release electrons and protons, which pass through the external circuit and the PEM, respectively, to reach the cathode, where oxygen reduction reaction (ORR) happens. The reaction steps are shown in the equations below,



1.2.1.2. Challenges in PEMFC

The advantage of using a PEMFC is that electricity is produced as a result of anode and cathode electrochemical reactions with just water as by product, without any environmental unfriendly byproducts. But it suffers from several problems which mitigate its widespread commercialization. Firstly, both the HOR and ORR require electrocatalysts to drive the electrochemical reactions. Platinum is the gold-standard active electrocatalyst for both HOR and

ORR.¹³ This is because Pt holds an optimum adsorption binding energy for the key intermediates involved in the electrochemical reactions.^{15, 16} It is important that the intermediate species involved in electrochemical reaction doesn't adsorb too strong or too weak to the electrocatalyst surface, as it will make it difficult to release the product or limit the reaction rate, respectively.¹⁵ Compared to the reaction kinetics of HOR, ORR has sluggish kinetics which involves a four electron transfer process.¹⁷ In addition, the Pt-based electrocatalysts suffer from carbon monoxide (CO) poisoning, from the CO impurities found in fuel feeds, which degrades its kinetics and stability.¹⁷ Hence, extensive research on developing highly active electrocatalysts are undergoing. Secondly, the Pt is usually dispersed as nanoparticles with size of ~ 2 to 3 nm on high surface area carbon supports, to enable exposure of abundant active sites. These carbon supports suffer from corrosion during the startup/shutdown processes of fuel cell. This is because the voltage of the PEMFC can rise to 1.5 V from its theoretical 1.23 V voltage which cause corrosion of carbon.¹⁸ Carbon corrosion in turn degrades the PEMFC performance, as the Pt nanoparticles dispersed on carbon supports either dissolve or agglomerate resulting in loss of surface-active sites.¹⁸ Thirdly, the main hurdle is the expensiveness of the Pt-based electrocatalysts used for the HOR and ORR, which make up to 40% of the total cost of PEMFC.¹⁷ Owing to the instability of most of the transition metals in acidic environments, Pt is the only best choice of catalysts for ORR and HOR. Hence, researchers are intensively developing intermetallic Pt alloy with other inexpensive metal such as Ru, Co and Ir to enhance the stability and activity towards ORR.¹⁹ Nevertheless, it highly demanded to further reduce the Pt loading in PEMFCs. Fourthly, the H_2 used in the PEMFC are flammable which makes them difficult to store or transport due to safety issues.²⁰ In addition, the green H_2 fuel produced from renewable water electrolysis technology makes it an expensive fuel. Hence, other

fuel cell technologies such as direct methanol fuel cells are investigated, which use relatively cheaper methanol liquid fuel which possess higher energy density.

1.2.2. Direct Methanol Fuel Cells

1.2.2.1. Working Principle

DMFC is a type of PEMFCs that employ methanol as anode fuel which has an energy density of 6.08 kWh/kg.¹¹ Unlike hydrogen, methanol is cheaper, ease to transport and store.¹¹ Methanol is considered as carbon-neutral and renewable fuel if produced from biomass. This makes DMFC a good choice for application in automobile, portable electronic devices and stationary power sources. DMFC use methanol as anode fuel and oxygen from air as cathode fuel to produce electricity and byproducts such as carbon dioxide (CO₂) and water.⁸ A schematic of working principle of DMFC is shown in Figure 1.2. It consists of an anode and a cathode compartment separated by the proton exchange membrane (PEM).²¹ In anode compartment, an anode current collector with fuel channels, an anode gas diffusion layer (GDL) and an anode catalyst layer are present. Similarly, cathode compartment comprises of a cathode current collector with fuel channel, a cathode GDL and a cathode catalyst layer is present. The catalyst is coated as a thin layer either on the porous GDL or on the PEM.¹¹

Methanol is fed to the anode compartment, and it diffuses through the porous GDL to reach the anode catalyst layer for methanol oxidation reaction (MOR) to happen. Methanol is oxidized to CO₂ and produce 6-electrons and 6 protons, as shown in eqn. 1.4. Methanol has a theoretical standard oxidation potential of -0.02 V vs. SHE.^{21, 22} The 6 protons and 6-electrons produced are transferred to the cathode compartment through the PEM and the external circuit, respectively. Oxygen from air is fed to the cathode and it diffuses through the porous cathode GDL to reach the cathode catalyst layer to perform oxygen reduction reaction (ORR).

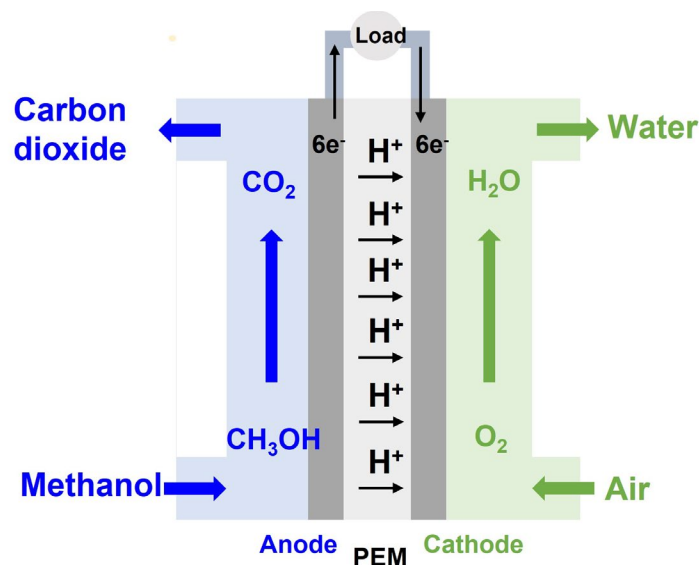
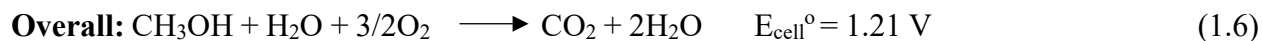


Figure 1.2. Schematic working principle of DMFC.

The oxygen is reduced to water by reacting with 6 protons and 6-electrons transferred from anode, as shown in eqn. 1.5.¹¹ The theoretical standard oxygen reduction potential is 1.23 V vs. SHE. The overall reaction is shown in eqn. 1.6. The overall cell voltage for DMFC is 1.21 V.²² Nevertheless, due to the kinetic and ohmic losses, the overall output voltage of DMFC is less than the theoretical voltage.



1.2.2.2. Methanol Oxidation Reaction

The electrode reaction kinetics of both MOR and ORR are sluggish, and it requires highly active catalysts to perform the electrochemical reactions. Platinum (Pt) is the active electrocatalyst for both MOR and ORR.^{11, 21} MOR is a more sluggish reaction when compared to the ORR (4-electron process), owing to the 6-electron transfer process associated with MOR.²³ The oxidation

of methanol happens through, indirect pathway on Pt. MOR is a multistep reaction which involves several dehydrogenation steps which produce intermediate products like CO as shown in Figure 1.3.^{23, 24}

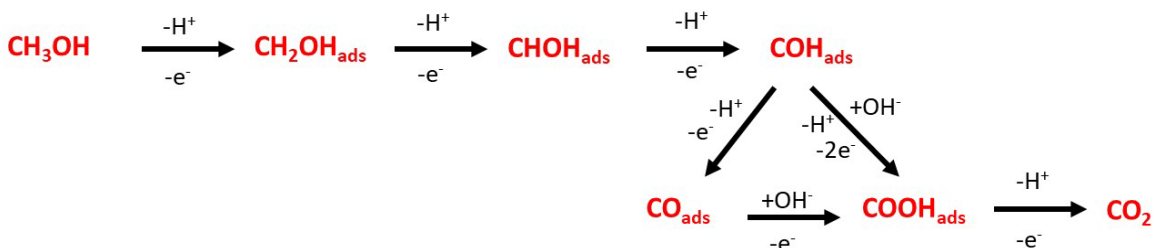


Figure 1.3. Methanol oxidation mechanism on Pt surface.

CO adsorbs strongly on the surface of Pt causing CO poisoning, and it requires hydroxyl (OH⁻) species to oxidize the CO to CO₂ as shown in eqn. 1.7 to 1.9. Pt dissociates water to form OH species at a high potential of 0.7 V vs. RHE, by that time all the Pt sites are poisoned by CO.²⁵ CO poisoning on Pt is one of the most critical issues which slows down the reaction kinetics of MOR.



* denotes free surface site

1.2.2.3. Challenges in DMFC

Regardless of the advantages of DMFC, it suffers from several technical barriers which hinders its commercialization,¹¹ such as (1) sluggish MOR kinetics accompanied by poisoning of activity Pt electrocatalysts. (2) Expensiveness of Pt metal which makes the catalyst cost to take up more than 40% of the total cost in fuel cell manufacturing, as DMFC requires massive

electrocatalyst loading compared to PEMFC to achieve decent performances.²⁶ (3) Catalyst nanoparticles dissolution from carbon support due to carbon support corrosion during fuel cell operations, particularly at the start-up/shut-down processes, majorly limits the durability of MOR catalysts.¹⁸ (4) Methanol crossover, which is the crossover of methanol from anode to cathode compartment due to diffusion and electro-osmotic drag. Typically, diffusion is the major contributor of methanol crossover, which happens due to the concentration gradient of methanol.¹¹ When methanol reaches the cathode compartment, Pt/C being the cathode catalyst, it will undergo MOR instead of ORR resulting in loss of cathode voltage due to cancellation of oxidation (MOR) and oxygen reduction current (ORR), thereby lowering the overall cell voltage. Due to this fact, low concentration of methanol is used in DMFC to reduce methanol crossover, and this substantially lowers the deliverable power density.²¹ Nevertheless, DMFC has attracted researchers to address the challenges because of their advantages of using liquid methanol fuel.

Popular strategy adopted to enhance the sluggish MOR kinetics and suppress CO poisoning is to alloy Pt with an oxophilic metal such as Ru which can provide abundant -OH species at much low potential than Pt to aid with CO oxidation to CO₂ as shown in Figure 1.4.²³ In addition, alloying such secondary metals into Pt lattice causes strain which modifies the binding energy of different adsorbates (such as CO and OH) on the Pt surface which can eventually accelerate the CO oxidation.²⁷ To date, PtRu nanoparticles (NPs) deposited on nanostructured carbon support, i.e., PtRu/C, is the commercial benchmark MOR catalyst in acidic medium owing to its excellent mass activity.²⁸ Hence, designing catalyst structures with modified strain is an effective strategy to tune the catalytic activity.^{19, 27}

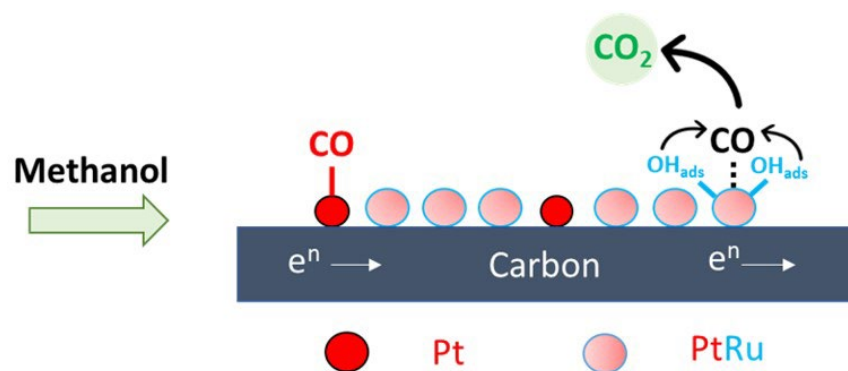


Figure 1.4. Schematic of methanol oxidation on PtRu catalyst.

Apart from the expensiveness of the Pt based electrocatalysts required for hydrogen based PEMFC or DMFC, it requires corrosion resistant fuel cell components to withstand the harsh acidic environment, which overall makes it an expensive technology.²⁰ Despite this, a high peak power density of 1.24 W/cm² is achieved with just 0.125 mg_{Pt}/cm² using hydrogen fuel with ambient air as oxidant.²⁹ The long-term goal of U.S. Department of Energy for light duty fuel cells vehicles cost is \$30/kW at 500 000 units per year.^{30, 31} But the cost of the current commercially available Toyota Mirai is at \$200/kW, with < 3000 units/year.²⁹ This shows the pressing demand to reduce the cost of PEMFC fuel cells systems to make it affordable. A promising approach is to switch to an alternative cell chemistry, i.e., transition to alkaline medium. Alkaline medium offers less corrosive environment which permits the utilization of inexpensive platinum metal group free (PGM-free) active electrocatalysts for HOR, MOR and ORR with relatively cheaper materials for anion membranes and cell components.^{20, 32} On this note, anion or hydroxide exchange membrane fuel cells (AEMFCs) have attracted enormous research interest.

1.2.3. Anion Exchange Membrane Fuel Cells

1.2.3.1. Working Principle

AEMFCs commonly use anion exchange membrane (AEM) based electrolyte which selectively conduct hydroxide ions (OH^-) for driving the electrochemical reactions.³³ Humidified H_2 and O_2 gas are supplied as anode and cathode fuels, respectively. Figure 1.5 shows the schematic working principle of an AEMFC. The major advantage of AEMFCs comes from the relatively less corrosive environment which makes it attractive to utilize inexpensive PGM-free electrocatalysts with low-cost materials for AEMFCs components when compared to PEMFCs.²⁰ U.S. Department of Energy has set a targeted cost of $\sim \$26/\text{kW}$ for AEMFC to surpass the PEMFC technology cost.³⁴

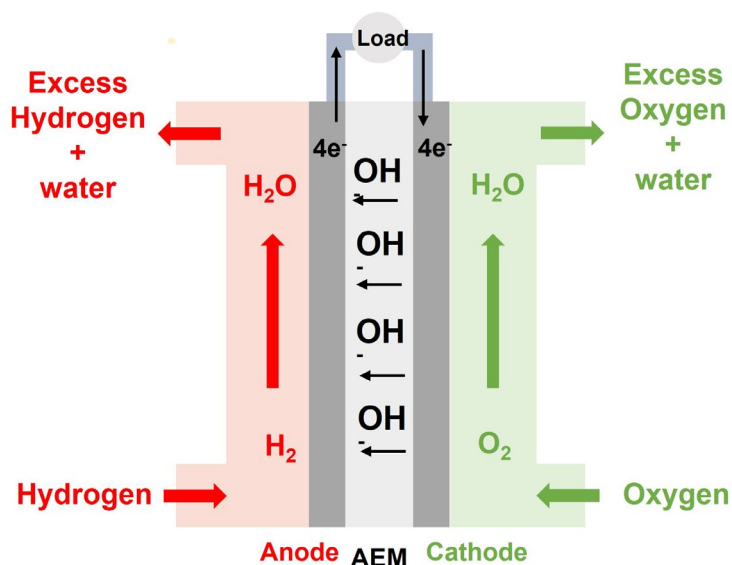


Figure 1.5. Schematic working principle of AEMFC.

HOR and ORR occurs at the anode and cathode of an AEMFC, as shown in equations below:

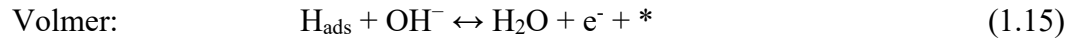




1.2.3.2. Hydrogen Oxidation Reaction

Pt is also the gold-standard active electrocatalyst for HOR and ORR in alkaline medium. ORR kinetics based on Pt catalysts in alkaline medium are superior to that in acid medium. But the HOR kinetics is sluggish by two orders of magnitude (using exchange current density as factor), compared to acidic medium.³⁵ The exact reason for the sluggish HOR kinetics on Pt in alkaline medium is still unknown.³⁴ Some researchers attribute this to the stronger binding of hydrogen to Pt surfaces.³⁶

The HOR reaction mechanism follows either a Tafel-Volmer (eqn 1.13 & 1.15) or a Heyrovsky-Volmer (eqn 1.14 & 1.15) pathway³³ in alkaline medium:



As a first step, hydrogen adsorbs on metal surface either via Tafel or Heyrovsky pathway and leads to formation of water with the reaction with OH^- by Volmer pathway. Volmer step is the rate-determining step (RDS) in alkaline medium.

1.2.3.3. Challenges in AEMFC

Despite the advantages of AEMFCs, they have their known drawbacks which hinder them from commercialization. Firstly, durability issues associated with the AEM used in AEMFCs. This is mainly because of the inferior chemical stability of organic cationic polymer backbones in AEM in high pH conditions.³⁷ They are susceptible to degradation. Researchers focused on developing several stable AEMs, such as, alkyl chain tethered polymers,^{37, 38} and more stable cationic

functional groups as piperidinium.^{39, 40} However, the stability of such AEMFCs is less than 1000 h (one order of magnitude less than PEMFCs).³⁷ Secondly, there is a critical voltage loss due to the cell carbonation. CO₂ from the air input at the cathode, has a high solubility in aqueous alkaline environments. AEMs and OH⁻ ions from cathode ORR reaction are highly susceptible to the reaction with CO₂ which causes voltage loss up to 400 mV during AEMFC operation which result in kinetic and mass transport losses.^{20, 37} Finally, the sluggish reaction kinetics of the HOR and the expensiveness of Pt-based HOR electrocatalysts are still issues.⁴¹

Development of highly active HOR electrocatalysts are of compelling interests in the research community right now. Despite the poor kinetics for HOR on Pt, it is still the best electrocatalyst for HOR. Other less expensive transition metals such as Ru, Pd and Ir are studied as active electrocatalysts owing to their HBE close to Pt and the ability to form abundant hydroxyl (OH⁻) groups.⁴² The elements that can provide OH species are called as oxophilic metals. Oxophilicity is found to play a critical role in HOR Volmer step, where the reaction between H_{ads} and OH species results in water formation. Hence, oxophilic metals have found to have high HOR electrocatalytic activity.³² Ru was one of the best oxophilic metals chosen as active HOR electrocatalysts, however, owing to the fast surface oxide formation at low potentials, its surfaces becomes unavailable for further H_{ads}.⁴³ This makes it a poor standalone HOR electrocatalysts.⁴⁴ However, researchers alloyed the oxophilic Ru with Pt to form PtRu alloys, where the OH spillover effect helps to enhance the HOR activity.³⁶ The PtRu alloy not only enhanced the HOR kinetics by oxophilicity but also altered the electronic structure of Pt to attain an optimum hydrogen binding energy (HBE).⁴⁵ So far, PtRu dispersed on carbon is the state-of-the-art HOR electrocatalysts. On the other hand, transition metal oxides such as CeO₂, TiO₂, SnO₂, ZrO₂, etc., with high oxophilic

properties are also explored as novel catalysts supports for Pd and Pt to enhance the HOR kinetics.^{46, 47}

1.3. Water Electrolyzer

Previous sections discussed the renewable energy conversion technologies to convert renewable fuels such as H₂ or methanol to electricity with green by products. This section focuses on a technology used to produce renewable H₂ fuel from water. As discussed earlier, H₂ is a promising energy carrier which has plethora of application in transportation sectors such as in fuel cells and energy storage (metal hydrides) and in industrial sectors (ammonia production, methanol production, hydrometallurgy, etc).¹⁰ Most of the H₂ produced today is from steam reforming of fossil fuels, which causes emission of carbon dioxide. Hence, it is of worldwide interests, right now, for generation of H₂ by clean, renewable, and efficient technique to successfully realize the hydrogen economy.⁴⁸

Electrochemical splitting of water into hydrogen and oxygen gases is considered the clean, sustainable, and efficient way to produce hydrogen gas.⁴⁹ 99.9999% purity of hydrogen can be obtained by electrochemical water splitting.⁵⁰ As water is the only by product in the cycle of hydrogen economy, it has widespread research interest. Water electrolyzer is the technology which performs the electrochemical water splitting. Proton exchange membrane water electrolyzer (PEMWE) will be discussed in this section.

1.3.1. Proton Exchange Membrane Water Electrolyzer

1.3.1.1. Working Principle

Figure 1.6 shows the schematic of working principle of PEMWE. PEMWE uses proton exchange membrane (PEM), as a solid polymer electrolyte.⁵¹ It consists of an anode and cathode, where water oxidation and reduction happens, respectively. The cathode reaction is called the

hydrogen evolution reaction (HER) and anode reaction is called the oxygen evolution reaction (OER) as given by the following equations:

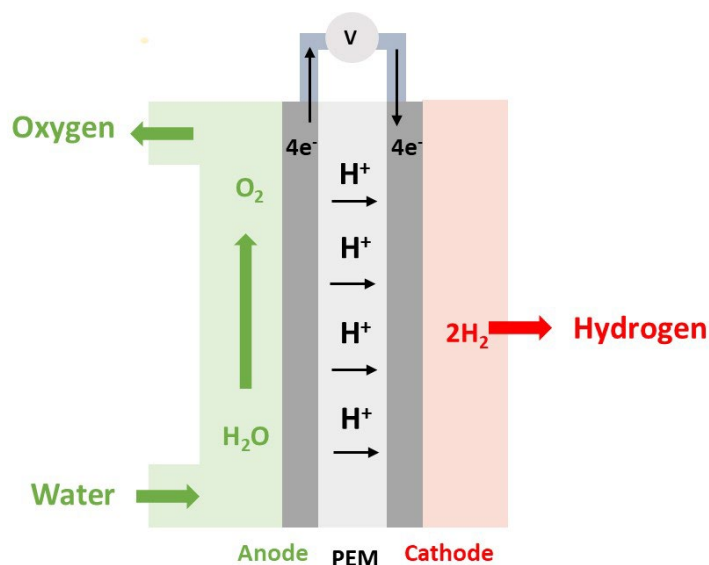
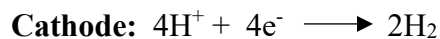
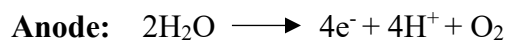


Figure 1.6. Schematic working principle of PEMWE.

It requires a $\Delta G^\circ = 237.2 \text{ kJ}$ corresponding to a cell voltage of 1.23 V to split water into H_2 and O_2 .⁴⁸ Water is fed to the anode compartment of the PEMWE, where oxidation of water results in formation of protons and electrons. The protons pass through the PEM to reach the cathode where reduction of protons results production of hydrogen gas.⁵⁰ Both HER and OER require suitable active catalysts to catalyze the electrochemical reactions. Platinum and platinum group metals are the best known efficient electrocatalysts for HER. While RuO_2 and IrO_2 are the efficient OER electrocatalysts in acidic medium.⁵²

1.3.1.2. Hydrogen Evolution Reaction

The HER is key electrochemical reaction responsible for hydrogen production in PEMWE.

The HER mechanism follows the equation as below,



The first step in HER is the adsorption of proton to the metal active site surface and then it is followed by the electrochemical (Heyrovsky pathway) and/or chemical (Tafel pathway) hydrogen desorption process.⁵¹ Pt is the active electrocatalyst for HER in acid medium due to the optimum HBE and hydrogen desorption energy on its surface.⁵² It has nearly ~ 0 eV hydrogen adsorption free energy ($\Delta G_{\text{H}} = 0$ eV) on its surface.⁴⁹ Pt delivers the least overpotential for HER with low Tafel slope and high exchange current density.

1.3.1.3. Challenges in PEMWE

The main hurdle of PEMWE is the cost of active precious metal HER and OER electrocatalysts. Hence, the prime target is to reduce the loading of the precious metal loading at both anode and cathode of PEMWE. The reduction of Pt loading at cathode shows good performance.⁵⁰ However, it is necessary to investigate inexpensive (PGM-free) electrocatalysts to achieve HER performance comparable to Pt. Recently, The U.S. Department of Energy's first energy earth shot has announced to reduce the cost of green H_2 to 80% to \$1/kg of H_2 in a decade to realize the hydrogen economy.⁵³ This has attracted researchers to actively investigate non-precious HER electrocatalysts. In that line, transition metal dichalcogenides such as MoS_2 have shown promising HER activity like Pt owing to their low values of $\Delta G_{\text{H}} = 0.8$ eV at the edge sites.⁵⁴ Several reports focusing on increasing the edge active sites by modifying morphology, doping of basal planes, phase engineering have been investigated.⁵⁵ On the other hand, low-cost

earth abundant materials such as Co-doped FeS_2/CNT , WO_2/C , $\text{Mo}_2\text{C}/\text{CNT}$ were reported as alternates for Pt.⁴⁸ Part of this dissertation focuses on developing a novel PGM-free cathode for HER.

1.4. Experimental Methods

1.4.1. Performance Evaluation of Electrocatalysts in Fuel Cell

To test anode and cathode electrocatalysts, a fuel cell is assembled by making membrane electrode assemblies (MEA) as shown in Figure 1.7.⁵⁶ MEAs comprises of five components following the order of anode gas diffusion layer (GDL), anode catalyst layer, polymer electrolyte membrane, cathode catalyst layer and cathode GDL as shown in Figure 1.7. The catalyst layer is prepared by coating few milligrams ($1 - 2 \text{ mg}_{\text{Pt}}/\text{cm}^2$) of electrocatalyst on to the GDL or directly on to the membrane by spray coating techniques.⁵⁷

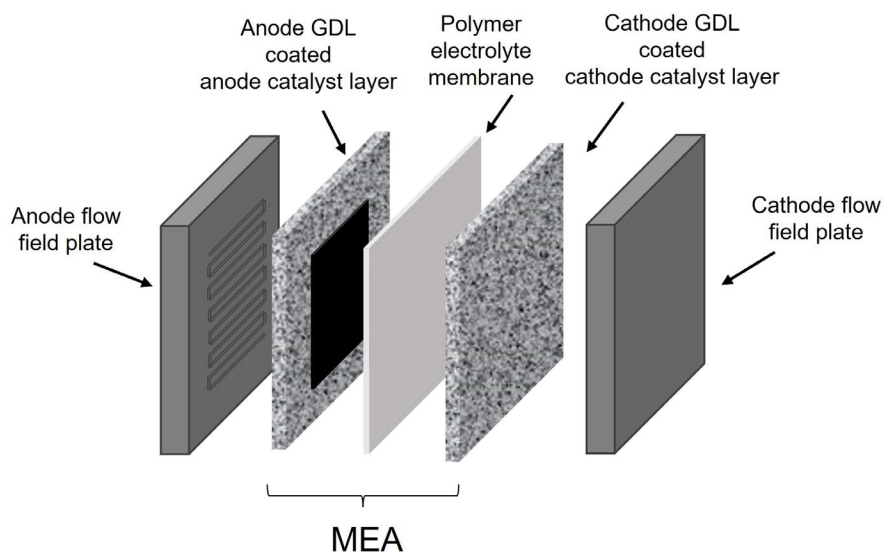


Figure 1.7. Parts of membrane electrode assembly.

All these components are compressed together by applying certain pressure and temperature to make the MEA. This is then assembled along with the anode and cathode fuel channels and bipolar plates to form the fuel cell.⁵⁸ For a PEMFC or a AEMFC, humidified H_2 gas

and air/O₂ gas are used as anode and cathode fuels, respectively. While for a DMFC, different concentration of liquid methanol mixed with water and air/O₂ gas are used as anode and cathode fuels, respectively. The cell temperature, gas pressures, liquid fuel flow rate are controlled/monitored using appropriate temperature, pressure, mass flow controllers, respectively.

A typical fuel cell polarization, shown in Figure 1.8, is a plot of voltage vs current density load obtained using a potentiostat or galvanostat. The polarization curves are obtained by drawing a constant current from the fuel cell and by measuring the output voltage. The load current density is slowly ramped up to measure the changes in cell voltage. The open circuit voltage (OCV), which is the voltage at zero current of the polarization curve is an indicator of the theoretical cell voltage. But practically, it is difficult to obtain the theoretical OCV, owing to some fuel crossover from anode to cathode, in case of both PEMFC and DMFC. As discussed in earlier sections, this causes mixed potential at the cathode resulting in overall loss in cell voltage. Ideally, polarization curve is expected to be a straight line (see dashed line in Figure 1.8).

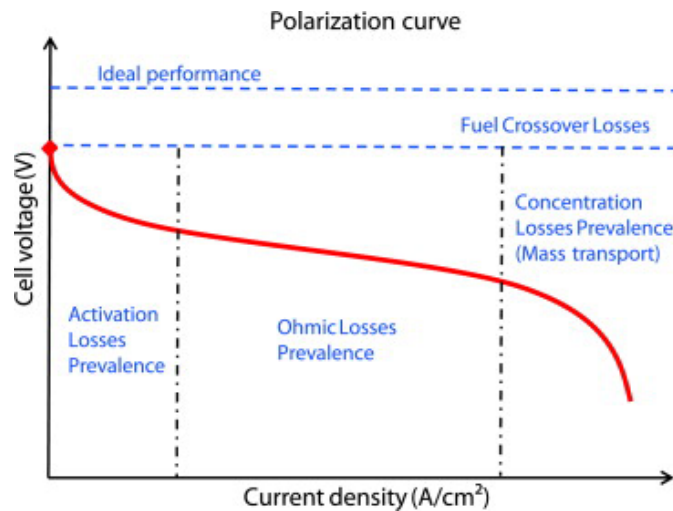


Figure 1.8. Visualizing losses: the polarization curve. Reprinted from Prognostics and Health Management of PEMFC – State of the art and remaining challenges, Volume 38, Issue 35, Marine Jouin, Rafael Gouriveau, Daniel Hissel, Marie-Cécile Péra, Nouredine Zerhouni, 15307-15317, Copyright (2013), with permission from Elsevier.

But it is impossible to achieve such curve owing to several loss mechanisms such as activation polarization, ohmic polarization and concentration polarization.⁵⁶ There are three characteristic loss regions of the polarization curves as shown by dotted lines in Figure 1.8. *The activation polarization* is the voltage loss due to overpotential needed to achieve the anode/cathode electrochemical reaction on the electrocatalyst. These activation polarization losses are observed at the low current density region of the polarization. This region will show the kinetic activity of a given electrocatalyst and is governed by Butler-Volmer equation.⁵⁹ A good electrocatalyst must have low activation polarization loss. *The ohmic polarization* is the voltage loss due to the ohmic resistance of the cell components such as catalyst layers, gas diffusion layers, electrolyte and terminal contacts.⁵⁶ This is typically dominated in the mid-current region, where a linear voltage loss is observed, as it is simply governed by ohm's law. While *the concentration polarization* is the voltage loss due to inefficient mass transport of fuel. It is important to have the continuous fuel flow through the fuel cell for efficient removal to product, otherwise there will be poor energy conversion efficiency. Mass transport in fuel cell is dominated by convection and the porous catalyst support structures are used to achieve better mass transport.²² These losses are observed at the high current density regions. The power density of the MEA is obtained by multiplying the obtained voltage response of the fuel cell and the corresponding current density load. A plot of power density vs. current density is drawn to obtain the peak power density ($P_{\max}$). The peak power density is considered as the parameter to compare the performance of various anode and cathode electrocatalysts of a fuel cell.

Testing electrocatalysts in MEA level is the most promising method. However, it is very time consuming (few days to weeks) and requires a lot of electrocatalyst (mg to g) to make catalyst layers. Also, it requires instrumentation to accurately control the gas pressure, fuel flow,

temperature, and relative humidity.⁵⁷ This makes it very difficult for researchers to develop and test new electrocatalysts. Hence, half-cell measurement protocols using three electrode setups were established as an electrocatalyst screening method. The advantage is that it only takes a few hours and requires micrograms ($10 - 600 \mu\text{g}/\text{cm}^2$) of electrocatalysts for the study.⁵⁷ Electrochemical half-cell characterizations can provide the kinetic activity of the different electrocatalysts of any fuel cell reactions. Electrocatalyst for various electrochemical reactions of fuel cell or water electrolysis have different protocols to study its reaction kinetics.

1.4.2. Performance Evaluation of Electrocatalysts in Half-Cell

To test an electrocatalysts in half-cell, a three-electrode setup is used as shown in Figure 1.9. It consists of a working electrode, a reference electrode, and a counter electrode.

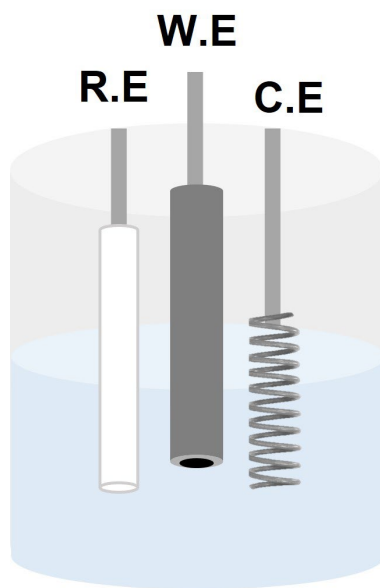


Figure 1.9. Schematic of standard three electrode setup with reference electrode (R.E), working electrode (W.E) and counter electrode (C.E).

The working electrode is usually a flat (3 mm or 5 mm in diameter) glassy carbon electrode encased in a PEEK body. Electrocatalyst ink is prepared using certain amount of electrocatalyst dispersed in solvent such as ethanol and water with addition of ionomer binders (Nafion or any AEM ionomer). The ink is drop casted on to the flat glass carbon electrode and dried at room

temperature before testing for the electrochemical reaction. Reference electrodes such as Ag/AgCl (1.0 M KCl), Hg/H₂SO₄ (sat'd K₂SO₄) or Hg/HgO (1.0 M NaOH) were used in this dissertation depending on the pH value of electrolyte used in the electrochemical reaction under study. Inert platinum wire/mesh with surface area of ten times higher than the surface area of working electrode is chosen as the counter electrode. While studying non-PGM electrocatalysts, to avoid contamination from Pt counter electrode to the electrochemical study, graphite counter electrodes are used.

A potentiostat, CHI 760 D electrochemical workstation, was used for performing the electroanalytical experiments such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA), chronopotentiometry (CP), etc. to study the electrochemical reactions on different electrocatalysts. The measured potentials from the experiments versus the reference electrode are converted versus the reversible hydrogen electrode (RHE) for proper comparison with the literature. The following equation is used to convert the reference electrode potential values to RHE:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Ref})} + E_{(\text{Ref vs. SHE})} + 0.059 \text{ pH} \quad (1.20)$$

where $E_{(\text{vs. Ref})}$ is the experimentally measured potential versus the any of the reference electrode mentioned above. $E_{(\text{Ref vs. SHE})}$ is the standard potential of the reference electrode vs. NHE.

The following shows the reference electrode potentials of,

$$E_{(\text{Ag/AgCl (1M KCl)})} = 0.122 \text{ V vs. SHE,}$$

$$E_{(\text{Hg/H}_2\text{SO}_4(\text{sat'd K}_2\text{SO}_4))} = 0.640 \text{ V vs. SHE,}$$

$$E_{(\text{Hg/HgO (1M NaOH)})} = 0.140 \text{ V vs. SHE,}$$

where pH is the pH value of the electrolyte used in the electrochemical reaction.

1.4.2.1. Evaluation of MOR electrocatalysts

In principle, CV technique is used to monitor surface of any electrocatalyst before studying its reaction kinetics. As this research focus on Pt based electrocatalysts, we show the characteristic CV curve of Pt/C obtained in 0.50 M H_2SO_4 solution in Figure 1.10. Generally, the electrolyte solution is purged with inert gas such as Ar or N_2 to remove the dissolved oxygen present to avoid the contribution/ contamination from oxygen to the electrocatalyst.

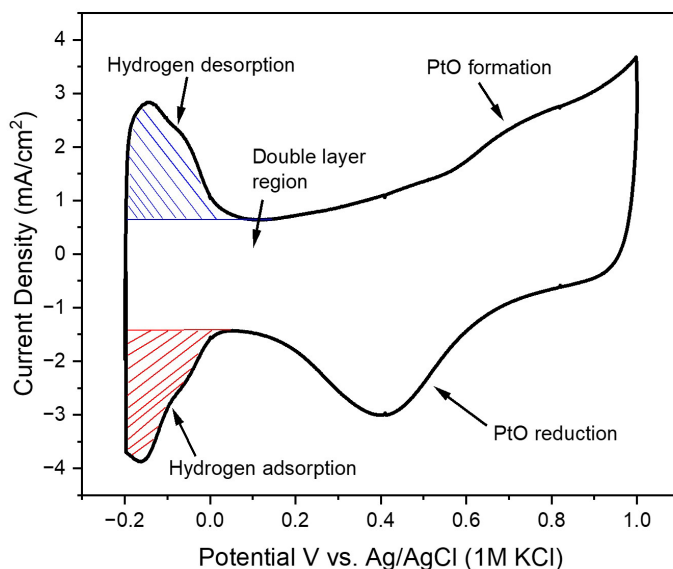


Figure 1.10. Characteristic CV curve of Pt/C in 0.50 M H_2SO_4 collected at 50 mV/s scan rate.

The CV shows the oxidation and reduction of Pt surface while sweeping the potential from negative to positive and positive to negative, respectively. Apart from that, we do observe characteristic hydrogen adsorption and desorption peaks for Pt surface lattices. As the hydrogen adsorption and desorption is specific to Pt surface sites, it is characteristic of Pt. This is also commonly referred as butterfly curve. The charge under the hydrogen adsorption region or

desorption region can be used to calculate the electrochemical active surface area (ECSA) of the Pt based electrocatalysts. As only a monolayer adsorption of protons occurs on the Pt surface, the charge can be correlated to ECSA using the following equations:

$$\text{ECSA} = \frac{Q_a}{Q_{H_{\text{upd}}}^0 \times m_{\text{Pt}}} \quad (1.21)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of H_{upd} oxidation peak; $Q_{H_{\text{upd}}}^0 = 210 \mu\text{C}/\text{cm}^2$ is the charge associated with hydrogen atoms on 1 cm^2 of flat Pt surface and m_{Pt} ($\text{g}_{\text{Pt}}/\text{cm}^2$) is the mass loading of Pt on the working electrode surface.

This dissertation focuses on development of MOR electrocatalysts for DMFC which operates in acidic condition. Hence, CV technique is used to study the MOR kinetics in half-cell in an acidic electrolyte ($0.50 \text{ M H}_2\text{SO}_4$ or 0.10 M HClO_4) containing 0.75 M methanol solution. A characteristic MOR CV curve, swept between 0 to 1.0 V vs. RHE,⁸ of commercial Pt/C is shown in Figure 1.11 (a). The arrows in Figure 1.11 (a) guide us through the CV potential sweep directions. It is to be noted that MOR CV is different from the usual CV curves we observe in electrochemistry. This MOR CV curve has two oxidation peaks both in anodic and cathodic scans rather observing a cathodic reduction peak during the cathodic scan.

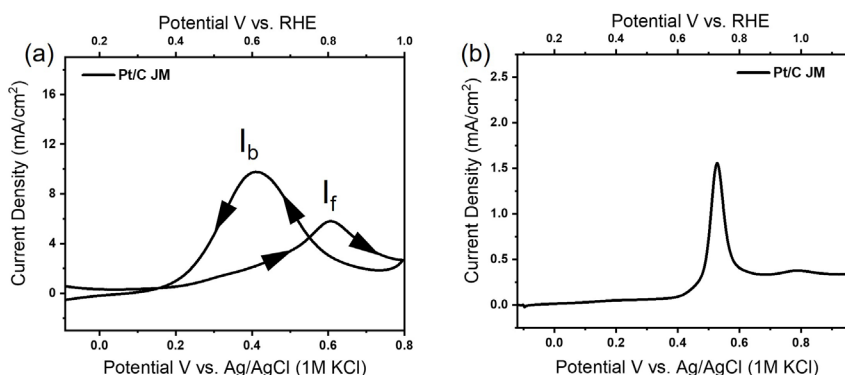


Figure 1.11. (a) MOR CV curve of Pt/C collected in $0.50 \text{ M H}_2\text{SO}_4$ containing 0.75 M methanol at a scan rate of 50 mV/s and (b) CO stripping LSV curve of Pt/C collected in $0.50 \text{ M H}_2\text{SO}_4$ at a scan rate of 10 mV/s .

The MOR starts to occur from 0.3 V vs. RHE showing an increase in current till 0.85 V vs. RHE forming a forward peak current (I_f).⁶⁰ After that, a decrease in current is observed from 0.8 V to 1.0 V vs. RHE, owing to the PtO formation. As PtO is inactive to MOR, thus the current starts to decrease. When the potential is switched to cathodic direction, the PtO will reduce back to form fresh Pt surface, however the reduction current corresponding to this is so small that it is buried under the oxidation peak current in the cathodic direction. The current increase in the backward scan (I_b) is attributed to the oxidation of methanol on the fresh Pt surface.⁶⁰ Absence of a reduction peak corresponding to the forward methanol oxidation peak shows that MOR is an irreversible reaction. The I_b is dependent on the upper potential of CV curve.²³ As the upper potential of CV is increased the I_b starts to decrease, due to the presence of PtO formed during forward scan.²³ One of the key information one may require is from the I_f and I_b ratio. The I_f/I_b ratio provides the degree of oxophilicity of the catalyst, which means the ability of electrocatalyst to provide hydroxyl species to oxidize CO to CO₂. For a good MOR electrocatalyst, literature show an I_f/I_b ratio > 1.²⁸

As CO is a poisonous intermediate for MOR electrocatalyst, it is important to study the kinetics of CO oxidation for MOR. CO gas is intentionally purged in the electrolyte to adsorb a monolayer on the surface of Pt based electrocatalysts while the electrode is held at 0.1 V vs. RHE for 5 mins. Then the purging gas is switched to inert gas such as Ar or nitrogen while the electrode is held at 0.1 V vs. RHE for 30 min to remove the CO from electrolyte. After that, a linear sweep voltammetry is done from 0.1 V vs. RHE to 1.0 V vs. RHE to obtain the CO stripping voltammetry.⁸ Figure 1.11 (b) shows a typical CO stripping voltammetry curve. An earlier onset potential for CO oxidation peak is preferred for a good MOR electrocatalyst. As that highlights the ability of the electrocatalyst to produce abundant OH species to assist the CO oxidation process according to equation. In addition, the integral area under this CO oxidation curve is used to

calculate the electrochemical active surface area (ECSA) of a catalyst. The ECSA of Pt in the catalysts was determined using the following equation:

$$\text{ECSA} = \frac{Q_a}{Q_{\text{CO}}^0 \times m_{\text{Pt}}} \quad (1.22)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of CO oxidation peak; $Q_{\text{CO}}^0 = 420 \mu\text{C}/\text{cm}^2$ is the charge required to oxidize a monolayer of CO adsorbed on 1 cm^2 of flat Pt surface and m_{Pt} (g/cm^2) is the mass loading of Pt on the working electrode surface.

1.4.2.2. Evaluation of HOR electrocatalysts

Linear sweep voltammetry (LSV) technique is used to sweep the potential of working electrode from two set potentials at certain scan rate. It is either swept from negative potential to positive potential to study the oxidation reaction or vice versa. Rotating disk electrode (RDE) technique is the widely used method to study the HOR kinetics owing to the well-defined mass transport behaviors obtained from the hydrodynamic.

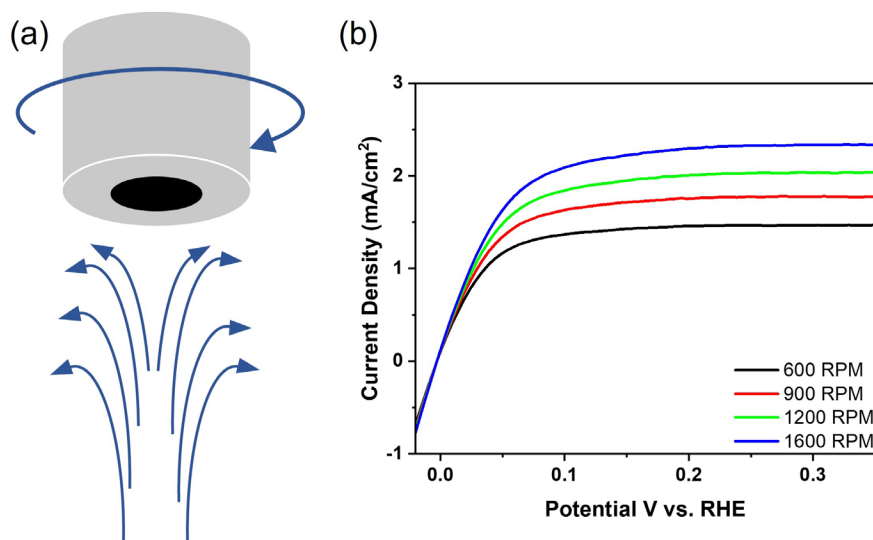


Figure 1.12. (a) Schematic of fluid flow near RDE surface and (b) HOR LSV curves of PtRu/C obtained at different rotation speeds in 0.10 M KOH at 10 mV/s scan rate.

Generally, H₂ gaseous analyte will be purged until saturation in the electrolyte used for RDE study. It is a hydrodynamic voltametric technique, which use working electrodes which can be rotated at constant rotation speeds to attain a steady-state concentration of gaseous analyte near the electrode surface, see Figure 1.12 (a). By rotating or convection, fresh solution from bulk approaches near the electrode surface to maintain a constant diffusion layer thickness which translates to a steady-state current density (called as limiting current density), as shown in Figure 1.12 (b). The diffusion layer thickness decreases with increasing rotation speed, showing an increase in limiting current density with rotation speeds.

HOR electrocatalyst is drop casted on the surface of glassy carbon in the RDE. LSV is performed by rotating the RDE at different rotation speeds (rpm) between 500 rpm to 2000 rpm. A characteristic HOR LSV curve is shown in Figure 1.12 (b) for PtRu/C. The current at low potentials correspond to the kinetic current due to HOR. When the potential is swept more positive, the current reaches a plateau indicating the mass transport limited current density (J_{lim}). The limiting current density can be theoretically derived from Levich equation shown below,

$$J_{lim} = 0.62 n F C D^{2/3} \nu^{-1/6} \omega^{1/2} \quad (1.23)$$

where n is the number of electrons transferred, F is the Faraday's constant (96485 C/mol), C is the concentration of dissolved hydrogen (0.7 mM) in 0.1 M KOH, D is the diffusion coefficient of hydrogen in 0.1 M KOH (3.40×10^{-5} cm²/s), ν is the kinematic viscosity of 0.1 M KOH (0.01 cm²/s) and ω is the rotation speed. For a rotation speed of 1600 rpm, theoretical J_{lim} is found to be 2.44 mA/cm². A good electrocatalyst must have low onset potential, half-wave potential for HOR and has to reach the maximum theoretical limiting current density at set rotation speed.

1.4.2.3. Evaluation of HER electrocatalysts

For HER electrocatalysts, LSV is done from a positive potential (typically 0 V vs. RHE) to negative potential to study the HER kinetics. A typical HER LSV curve of Pt/C is shown in Figure 1.13 (a). The theoretical HER onsets at 0 V vs. SHE. Like any other electrochemical reaction, it requires overpotential, i.e., excess potential to overcome the energy barrier to perform the reaction.⁴⁹ Hence, the overpotential (η) at 10 mA/cm² is considered as standard parameter to compare the performance of HER among different electrocatalysts from literatures. Pt/C is the best-known HER electrocatalyst with lowest η of < 40 mV for HER at 10 mA/cm².⁵²

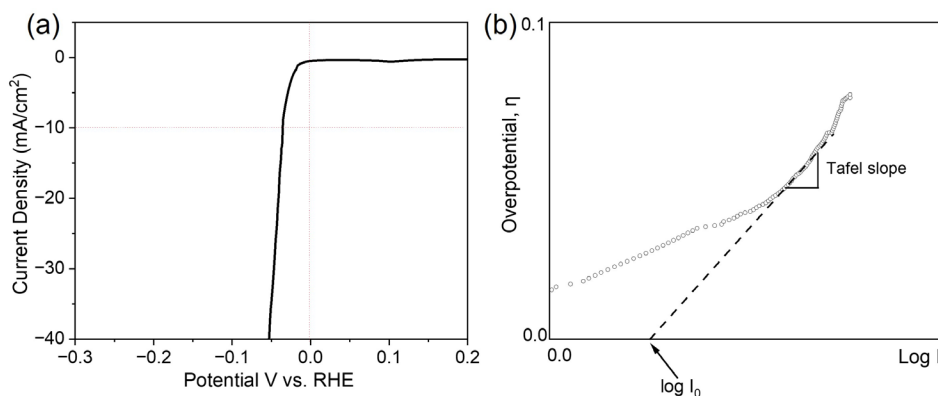


Figure 1.13. (a) HER LSV curve of Pt/C collected in 0.50 M H₂SO₄ at 10 mV/s scan rate and (b) Tafel plot of Pt/C showing the Tafel slope and log I₀ determination.

For a good electrocatalyst, η close to 0 mV is expected. Tafel analysis from the LSV polarization curve will provide kinetic information of the HER electrocatalysts. To understand the kinetic parameters derived from Tafel analysis, it is important to clearly know the basics of how Tafel equations are formed. For any electrochemical/ faradaic reaction, the current and overpotential at an electrode-electrolyte interface is governed by the Butler-Volmer equation,⁵² as shown below,

$$I = I_0 \left[\exp \left(\frac{\alpha_A n F}{RT} \eta \right) - \exp \left(\frac{\alpha_C n F}{RT} \eta \right) \right] \quad (1.24)$$

Where I is the current obtained in the polarization curve, I_0 is the exchange current density (kinetic current at equilibrium potential), α_A and α_C are the charge transfer coefficients for anodic and cathodic reactions, n is the number of electrons transferred, F is the Faraday constant (96485 C/mol), T is the absolute temperature in K and η is the overpotential. At equilibrium potential, the contribution of anodic and cathodic terms equals and results in $I = I_0$. At high overpotentials (either cathodic or anodic), when $\eta > 0.1$ V, one part of the Butler-Volmer equation becomes negligible resulting in Tafel equations.⁶¹ The Tafel equation for anodic and cathodic polarization is given as,

$$\text{Anodic polarization: } \ln I = \ln I_0 + \left(\frac{\alpha_A n F}{RT} x \eta \right) \quad (1.25)$$

$$\text{Cathodic polarization: } \ln I = \ln I_0 + \left(-\frac{\alpha_C n F}{RT} x \eta \right) \quad (1.26)$$

which has an equation form of straight line, $y = mx + c$. Hence, a plot of $\log I$ vs. η can be made to obtain the slope of this curve to determine the reaction rate, as shown in Figure 1.13 (b). This plot is commonly called a Tafel plot and slope derived from this plot is called Tafel slope. The Tafel slope provides the overpotential required to increase the reaction rate (current density in our case) by 10-fold of magnitude. For general cases, the slope of this Tafel plot is given as⁵²,

$$\text{Anodic reaction: slope } d(\log I)/d\eta = 2.303 RT/\alpha_A n F \quad (1.27)$$

$$\text{Cathodic reaction: slope } d(\log I)/d\eta = 2.303 RT/(-\alpha_C n F) \quad (1.28)$$

For HER electrocatalysts, the Tafel slopes can reflect the HER reaction pathways. The theoretical Tafel slopes for different HER steps^{51, 62} are given below:

$$\text{Volmer: } H^+ + e^- = H_{ads}; \text{ Tafel slope} = 2.303 RT/\alpha F = 118.2 \text{ mV/decade} \quad (1.29)$$

$$\text{Heyrovsky: } H_{ads} + H^+ + e^- = H_2; \text{ Tafel slope} = 2.303 RT/2F = 29.5 \text{ mV/decade} \quad (1.30)$$

$$\text{Tafel: } 2H_{ads} = H_2; \text{ Tafel slope} = 2.303 RT/(1 + \alpha) F = 39.4 \text{ mV/decade} \quad (1.31)$$

The transfer coefficient α is considered as 0.5 to calculate the theoretical Tafel slope values shown in equation 1.29 to 1.31.⁶² The surface coverage of the protons on the active sites determines the rate-determining step of HER. A constant H_{ads} coverage ($\theta_H \approx 1$) at high overpotentials results in high Tafel slope value of 118.2 mV/decade. A very low H_{ads} coverage ($\theta_H \ll 1$) at low overpotentials results in a low Tafel slope value of 29.5 mV/decade.⁶³ Another important parameter that can be derived from Tafel plot, is the exchange current density (I_0) which also reflects the intrinsic catalytic activity of a electrocatalyst. The I_0 can be determined by extrapolating the linear fit curve of Tafel slope to intercept at $\eta = 0$, as represented in Figure 1.13 (b).

Chapter 2 - PtRu Catalysts on Nitrogen-Doped Carbon Nanotubes with Conformal Hydrogenated TiO₂ Shells for Methanol Oxidation

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2.1. Introduction

The ever-increasing demand for replacing fossil fuels has stimulated the investigation of renewable energy conversion devices such as fuel cells.^{64–66} Direct Methanol Fuel Cells (DMFCs), a type of proton exchange membrane fuel cell (PEMFC), have attracted considerable attention owing to the low cost, high energy density (6.08 kWh/kg for liquid methanol), and ease in handling methanol fuels.⁶⁴ However, sluggish kinetics of the methanol oxidation reaction (MOR) and severe methanol crossover limit the power density and conversion efficiency that can be obtained, which hinders the commercialization of DMFCs. At present, platinum (Pt) is the primary choice of electrocatalyst for catalyzing MOR.^{67, 68} However, the strong adsorption of methanol oxidation intermediates such as carbon monoxide (CO) on Pt surface causes poisoning of the Pt catalysts and impedes the MOR.^{66, 69} General strategies to overcome this issue is to incorporate other precious platinum group metals (PGMs) or transition metals (TMs) to form binary alloys, such as PtRu, PtPd, PtCu, PtRh, PtCo, and PtMo⁷⁰, which can provide abundant hydroxyl species and exhibit electronic ligand effects on Pt to efficiently oxidize CO to CO₂, thus improving the MOR kinetics. To date, PtRu nanoparticles (NPs) on nanoscale carbon supports, i.e., PtRu/C, is the state-of-the-art MOR catalyst in acidic medium owing to its excellent mass activity.⁷¹ Nevertheless, the dissolution of PtRu NPs due to carbon corrosion during fuel cell operations, particularly at the start-up/shut-down processes¹⁸ still limits the durability of PtRu/C catalysts in DMFCs. There is a

strong demand for design and development of highly active electrocatalyst and catalyst supports which can impart a strong metal-support interaction (SMSI)^{72, 73} to improve the catalyst stability.

Various graphitic nanocarbon supports such as carbon nanotubes (CNTs),⁷⁴ carbon nanofibers (CNFs) and graphene were studied to reduce carbon corrosion in PEMFCs owing to their intrinsic high chemical stability and outstanding electronic conductivity.^{73, 75-77} Among these, several reports demonstrate that nitrogen (N) doping in graphitic carbon supports not only enhances the stability but also increases the activity of PGM NPs towards MOR due to the SMSI provided at the doped graphitic edges of the support.⁷⁸⁻⁸⁰ Recently, our group reported the enhanced MOR activity and stability of Pt and PtRu NPs deposited on N-doped vertically aligned carbon nanofibers (N-VACNFs) owing to the SMSI provided by the graphitic edge and N-doping.²³ We revealed that the electron transfer between PGM catalysts and the N-VACNF support promotes the binding of OH⁻ over CO on the Pt surface, which accelerated the oxidation of CO to CO₂. In addition, the oxygenated functional groups present on the N-VACNFs made the carbon surface more oxophilic, which assisted efficient CO oxidation at the neighboring Pt sites.^{23, 81} Hence, graphitic carbon supports with synergistic enhancement by N-doping and oxygenation are potential candidates for MOR co-catalysts and catalyst supports.

In other circumstances, metal oxides such as IrO₂, CeO₂, RuO₂, and TiO₂ were studied as co-catalysts, non-carbon catalyst supports and hybrid catalyst supports to enhance the catalytic activity and stability of Pt-based electrocatalysts since the metal oxides can effectively hinder carbon corrosion in PEMFCs, including DMFCs.^{72, 82} Among them, TiO₂ is the most promising candidate due to its low cost, superior corrosion resistance in fuel cell operation conditions, and strong interaction with PGM NPs. TiO₂ serves multiple functions, including preventing the PGM NP agglomeration during high-temperature annealing and providing abundant hydroxyl species to

accelerate CO oxidation to CO₂.⁸³⁻⁸⁶ For example, Huang et al. showed enhanced power density and stability of Pt electrocatalysts using corrosion-resistant TiO₂ as the support based on SMSI.⁸⁷ However, the wide bandgap (3.2 eV) makes the pristine TiO₂ an intrinsically poor electronic conductor (with a conductivity in the order of 10⁻⁷ S/cm).⁸⁸ To increase the electronic conductivity, Ioroi *et al.* reported the synthesis of sub-stoichiometric Magneli phase TiO₂ (Ti_nO_{2n-1}) by reducing TiO₂ in a hydrogen atmosphere at ~1050 °C and using it as a Pt catalyst support for PEMFCs.⁸⁹ Ti₄O₇ phase exhibit increased electronic conductivity to the order of 10³ S/cm.^{89, 90} Several other researchers reported that doping metal or non-metal atoms into TiO₂ lattice can increase the electronic conductivity.⁹¹⁻⁹⁴ However, the above-mentioned strategies involve thermal treatment of metal oxides at high temperatures (> 1000 °C), which cause particle agglomeration and decrease the specific surface area (SSA). This limits its ability to support well-dispersed electrocatalysts. Recent studies show that defect engineering in TiO₂ lattice, without phase change, by inducing oxygen vacancies with thermal annealing TiO₂ at relatively lower temperature (~ 300 °C to 500 °C) in hydrogen atmosphere, has the potential in improving the electronic conductivity of TiO₂, as the delocalized electrons near the oxygen vacancies can be excited easily to the conduction band.⁹⁵

⁹⁶ For example, the black TiO₂ anatase nanocrystals (otherwise called hydrogenated TiO₂) synthesized by Chen et al. have attracted a lot of attention due to enhanced solar light absorption for photocatalysis provided by the oxygen vacancies and Ti³⁺ lattices in the disordered black TiO₂ layers.^{95, 97, 98} Followed by that, Myung et al. reported the synthesis of black TiO₂ anatase nanocrystals (bandgap of about ~ 1.8 eV) for ultra-fast Li⁺ insertion into and extraction from the anatase TiO₂ host, making it a unique high-rate electrode for Li-ion batteries.⁸⁸ Zhang et al. showed improved activity and stability of Pt NPs when hydrogen-treated TiO₂ nanotube was used as the catalyst support for PEMFCs, owing to the SMSI and enhanced electronic conductivity.⁹⁹ To the

best of our knowledge, there is no report so far on studying the effect of the defective hydrogenated TiO_2 for MOR in DMFC applications.

Another approach to mitigating the low electronic conductivity of TiO_2 is to make it as a hybrid structure with highly conductive carbon materials. The morphology of the metal oxide in the hybrid support has a significant effect on the electrochemical performance of catalysts.⁷² Amid the various morphologies (such as NPs, nanotubes, nanoarrays) of TiO_2 that have been studied as the catalyst supports, ultrathin-films or nanocoating on carbon supports attracted special attention due to the SMSI and maximal -OH groups that it can provide to the PGM NPs. In addition, they can provide a continuous electron conductive network, mimic the high surface area of underlying carbon support for better NP dispersion while effectively protecting the underlying carbon from corrosion.^{72, 92} Until today, only a few vacuum-based and/or energy-intensive methods have been reported for TiO_2 thin-film synthesis/deposition, such as atomic layer deposition (ALD),¹⁰⁰ chemical vapor deposition (CVD),¹⁰¹ and hydrothermal/solvothermal methods^{102, 103}. Microwave-assisted synthesis has attracted a lot of attention due to its low cost, facile, rapid, and scalable nature.¹⁰⁴ In addition, since carbon materials have a higher microwave absorptivity than the solvent (as reflected in its high dielectric tangent loss values), the “specific heating” by microwave irradiation can be used to enable preferential TiO_2 nucleation and thin film growth on the carbon support, unlike the presence of large bulk reaction in conventional synthesis methods.¹⁰⁵ Manthiram et al. and Vigil et al. reported TiO_2 thin film deposition from solution on conductive ITO substrate using the microwave-assisted method at a relatively low temperature 150 °C when compared to those used in conventional TiO_2 synthesis.^{105, 106} However, deposition of TiO_2 as thin-films or core-shell structures on carbon supports using microwaves has not been explored for developing MOR electrocatalysts.

Herein, we report the microwave-assisted deposition of a conformal ultrathin TiO_2 film (or shell) on oxygen functionalized N-doped carbon nanotubes (ONCNT), to form a core-shell hybrid support for PtRu alloy NPs to enhance the MOR activity and stability. The PtRu NPs were also deposited on TiO_2 /ONCNT support by the rapid microwave-assisted synthesis followed by a post-deposition thermal annealing process at 400 °C in a reducing atmosphere (3% H_2 /97% Ar). Crystalline PtRu alloy NPs anchored on the defective hydrogenated ultrathin TiO_2 shell, named as PtRu/ TiO_2 /ONCNT-400, have been obtained. The as-prepared PtRu/ TiO_2 /ONCNT-400 catalyst exhibited enhanced CO oxidation kinetics, superior MOR activity, and excellent stability when compared to two types of benchmark commercial PtRu/C catalysts from Johnson Matthey (JM) and Tanaka KiKinzoku (TKK), respectively. We illustrate that this is attributed to the SMSI, continuous electron conductive network, and the increased hydroxyl groups provided by the ultrathin defective hydrogenated TiO_2 coating on the ONCNT. The systematical materials and electrochemical characterization reveal that the SMSI between the PGM catalyst and TiO_2 coating is critical in reducing the CO poisoning on Pt sites by enhancing the CO oxidation kinetics via stronger OH^- adsorption and abundant $-\text{OH}$ groups on the underlying TiO_2 surface. Such multifunctional hybrid MOR catalysts can be synthesized in a scalable process for future DMFCs.

2.2. Experimental Section

2.2.1. Chemical and Materials

The potassium hexachloroplatinate (K_2PtCl_6), ruthenium chloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), and Nafion[®] solution (5 wt% in lower aliphatic alcohols) were purchased from Sigma-Aldrich (St. Louis, MO). The titanium tetraisopropoxide (TTIP), ethylene glycol (EG), sulfuric acid (H_2SO_4), nitric acid (HNO_3), pure ethanol 200 proof, and methanol (ACS grade) were purchased from Fisher

Scientific (Hampton, NH). Ultrapure water (18.2 M Ω .cm at 25 °C) purified from a Millipore water system (EASYPURE II, Thermo Scientific, Waltham, MA) was used to prepare all aqueous solutions for the experiments. The commercial Pt/C catalyst (20 wt% Pt on carbon, HiSPEC[®] 3000) and PtRu/C catalyst (48.0 wt% Pt and 23.1 wt% Ru on carbon, HiSPEC[®] 12100) by Johnson Matthey (JM) were purchased from Alfa Aesar (Tewksbury, MA) as the benchmark reference. Another benchmark commercial PtRu/C catalyst (TEC 66E50 – 32.8 wt% Pt and 16.9 wt% Ru on carbon) was purchased from Tanaka Kikinzoku International (America) Inc. (Schaumburg, IL), referred as TKK.

2.2.2. Material Synthesis

2.2.2.1. Preparation of NCNTs

N-doped CNTs (NCNTs) were synthesized from the pristine CNTs (obtained from Zhongshan CNM Plastic Co., Ltd., Zhongshan, China) by chemical vapor deposition of pyridine on the cleaned pristine CNTs. Briefly, CNT was placed into a quartz tube and heated from room temperature to 760 °C at a rate of 10 °C/min under N₂ atmosphere. Pyridine solution was charged into the quartz tube at 2 mL/min for 4 h. After that, the furnace was cooled down in N₂ atmosphere and NCNT was obtained.

2.2.2.2. Preparation of TiO₂/ONCNT

The NCNT was first oxygenated by treating 1.0 g of NCNT in an aqueous mixture of 2.0 M H₂SO₄ and 4.0 M HNO₃ at 120 °C for 12 h under constant stirring. The obtained oxygenated NCNT (ONCNT) was washed with ultrapure water till the pH reached 7.0, filtered, and dried at 80 °C in a vacuum oven. Then, 10.0 mg of ONCNT was dispersed in 6.0 ml of ethanol by ultrasonication for 30 min. Further, 10.0 mg of TTIP was added to this dispersion and sonicated in a water bath. After 30 min sonication, this mixture was transferred to a 10 ml Pyrex glass

microwave vessel and put into Discover[®] SP microwave synthesizer (CEM Corporation., Matthews, NC). A microwave irradiation was applied in the dynamic mode with the power up to 300 W to maintain a reaction temperature of 150 °C for 5 min. The reaction pressure rose to ~ 19 bar during the process. After reaction, the naturally cooled product mixture was washed 2-3 times using ethanol to remove the unreacted precursors and dried at 80 °C in a vacuum oven to obtain the TiO₂-coated ONCNTs, referred as TiO₂/ONCNT.

2.2.2.3. Preparation of PtRu/TiO₂/ONCNT-400

To deposit PtRu catalysts, 12.5 mg of K₂PtCl₆, 5.1 mg of RuCl₃.xH₂O, and 16.0 mg of TiO₂/ONCNT were dispersed in 20 ml of mixture of ethylene glycol and water (at 4:1 volume ratio) by ultrasonication for 1 hour. The solution was then transferred to 35 ml Pyrex glass microwave vessel. The weight ratio of Pt and Ru is maintained at 2:1 in the precursors. Ethylene glycol serves as a reducing agent and solvent in this reaction. The mixture was irradiated with a 300 W microwave under the dynamic mode to maintain a reaction temperature of 190 °C for 20 min in Discover[®] SP microwave synthesizer to deposit Pt and Ru NPs onto TiO₂/ONCNT. The reaction pressure rose to ~8 bar during this process. The cooled product mixture was washed several times using acetone to remove residual ethylene glycol and then dried at 80 °C in a vacuum oven to obtain PtRu/TiO₂/ONCNT. The dried catalyst material was annealed in a tube furnace at 400 °C for 2 h in 3% H₂/ 97% Ar atmosphere at a ramp rate of 10 °C/min, to form crystalline PtRu alloyed NPs and defective hydrogenated TiO₂ shell on the ONCNT. The as-prepared catalyst is named as PtRu/TiO₂/ONCNT-400. Synthesis of control samples was carried out using the same reaction conditions as mentioned above with appropriate precursors but skipping some specific intermediate steps.

2.2.3. Materials Characterization

The structure of the catalysts was characterized using three transmission electron microscopes (TEM) at different stages of the project, including: a Tecnai Osiris Scanning/Transmission Electron Microscope (S/TEM, FEI, Hillsboro, OR) at a 200 kV acceleration voltage, located at University of Nebraska, Lincoln; a Hitachi H-8100 TEM (Hitachi, Krefeld, Germany) at a 200 kV acceleration voltage, located at University of Kansas, Lawrence and a Philips CM 100 TEM at a 100 kV acceleration voltage, located at Department of Biology, KState. The crystal structure of the catalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 1 mm, located at Department of Chemistry, KState. XRD reference spectra are used from Joint Committee on Powder Diffraction Standards (JCPDS). The composition of the catalysts was determined using a Thermogravimetric Analyzer (TGA) Q50 system (TA instruments - Waters LLC, New Castle, DC) from the room temperature to 900 °C in a compressed air atmosphere, located at Department of Chemistry, KState. The surface chemical composition of the catalysts was characterized using a PHI 5000 Versa XPS system (Chanhasen, MN) with a monochromatized Al K α source (1486.7 eV), located at University of Nebraska, Lincoln. All the XPS spectra were obtained using a 400 μ m spot size. Shirley background was used in the curve fitting. The binding energy (B.E.) of all XPS data was calibrated vs. the standard sp² C 1s peak at 284.60 eV.

2.2.4. Electrochemical Characterization

All the half-cell electrochemical experiments were performed in a standard three-electrode setup using a CHI 760D electrochemical workstation (CH Instruments, Austin, TX) at room temperature. A silver-silver chloride (Ag/AgCl in 1.0 M KCl) reference electrode and a coiled Pt

counter electrode (0.55 mm in diameter and 23 cm in length) were used. The working electrode was prepared by drop-casting the catalyst ink onto a 3 mm diameter glassy carbon electrode (GCE) encased in a PEEK rod. Before drop-casting the catalyst ink, the GCE was polished using 0.05 μm alumina slurry. The catalyst ink was prepared by dispersing the required amount of catalyst powder in 1.0 ml of mixture of ethanol and ultrapure water (at 3:1 volume ratio) with addition of the 30 μl of Nafion[®] solution (5 wt% in lower aliphatic alcohols). The loading of the platinum group metal (PGM, specifically Pt and Ru in this study) was maintained at 54 $\mu\text{g}/\text{cm}^2$ for all catalysts in the half-cell studies. Before studying the MOR catalytic activity, the catalyst-coated electrodes were subjected to activation by cyclic voltammetry (CV) in the potential range of -0.2 V to 0.8 V vs. Ag/AgCl (1.0 M KCl) at a sweep rate of 100 mV/s for 50 cycles in Ar-purged 0.50 M H₂SO₄ electrolyte. The MOR experiments were performed by recording CV in the potential range of -0.2 V to 0.8 V vs. Ag/AgCl (1.0 M KCl) at a scan rate of 50 mV/s for 500 cycles in Ar-purged 0.5 M H₂SO₄ solution containing 0.75 M methanol. The CV curves of the 100th cycle was chosen to compare the MOR activity of various catalysts in this paper unless otherwise specified. For direct comparison of the potentials with literature, the measured electrode potential vs. the Ag/AgCl (1.0 M KCl) reference electrode is converted to the value vs. the reversible hydrogen electrode (RHE) using the following equation:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Ag/AgCl})} + E_{(\text{Ag/AgCl vs. SHE})} + 0.059\text{pH} = E_{(\text{vs. Ag/AgCl})} + 0.222 \text{ V} \quad (2.1)$$

where $E_{(\text{vs. Ag/AgCl})}$ is the measured potential vs. the Ag/AgCl (1.0 M KCl) reference electrode, $E_{(\text{Ag/AgCl vs. SHE})} = 0.222 \text{ V}$ is the Ag/AgCl (1.0 M KCl) reference electrode potential vs. SHE, and $\text{pH} = 0$ for 0.50 M H₂SO₄.

The CO stripping voltammetry experiments were performed in 0.50 M H₂SO₄ to evaluate the catalyst activity towards CO oxidation and to determine the active electrochemical surface area

(ECSA) of the catalyst. In CO stripping experiments, the electrolyte was first purged with Ar gas to remove any dissolved oxygen species in the electrolyte. Then, a pure CO gas was used to purge the electrolyte for 10 min while the potential of the working electrode was held at 0.10 V vs. RHE. After 10 min, the purging gas was switched back to pure Ar to purge for 30 min to remove the dissolved CO gas from the electrolyte, while the potential of the working electrode was still held at 0.10 V vs RHE which retained the adsorbed CO monolayer on the Pt surface. Subsequently, the CO monolayer on the Pt surface was stripped off with a linear anodic sweep at 10 mV/s from 0.10 V to 1.222 V vs. RHE. A few CV cycles were taken following CO stripping to evaluate the baseline of the electrode.

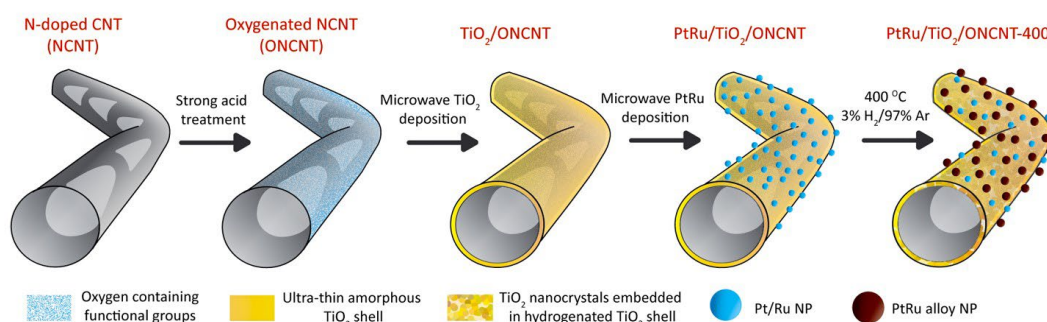
The ECSA of Pt in the catalysts was determined using the following equation:

$$\text{ECSA} = \frac{Q_a}{Q_{\text{CO}}^0 \times m_{\text{Pt}}} \quad (2.2)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of CO oxidation peak; $Q_{\text{CO}}^0 = 420 \mu\text{C}/\text{cm}^2$ is the charge required to oxidize a monolayer of CO adsorbed on 1 cm^2 of flat Pt surface and m_{Pt} ($\text{g}_{\text{Pt}}/\text{cm}^2$) is the mass loading of Pt on the working electrode surface.

2.3. Results And Discussion

The process to synthesize the PtRu/TiO₂/ONCNT-400 catalyst is illustrated in Scheme 2.1 and is detailed in the experimental section. The final catalyst as well as the control samples are carefully characterized to reveal the structure and properties. The key features obtained at each step are highlighted.



Scheme 2.1. Schematic of synthesis process for PtRu/TiO₂/ONCNT-400. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

2.3.1. Morphology of the catalysts by TEM

Figure A1 shows the low-magnification TEM images of the as-prepared PtRu/TiO₂/ONCNT-400 and two benchmark commercial PtRu/C catalysts (JM and TKK). The catalyst support used in this study, i.e., NCNT, has a long fiber-like structure with the diameter ranging from 20 - 40 nm and the length ranging from 2 – 10 μ m. This is drastically different from the amorphous carbon support of $\sim$ 30 – 50 nm diameter spherical NPs in the two state-of-the-art commercial PtRu/C catalysts. In addition, the NCNT catalyst support consists of characteristic bamboo-like graphitic internal structures which consist of stacks of conical graphitic layers along

the fiber axis. This unique structure presents abundant electrochemically active graphitic edge sites at the sidewall which are expected to have stronger interaction with metal oxides and PGM NPs. More details of the internal conically stacked graphitic structure of the NCNT are illustrated with the high-magnification TEM image in Figure A2 (a).

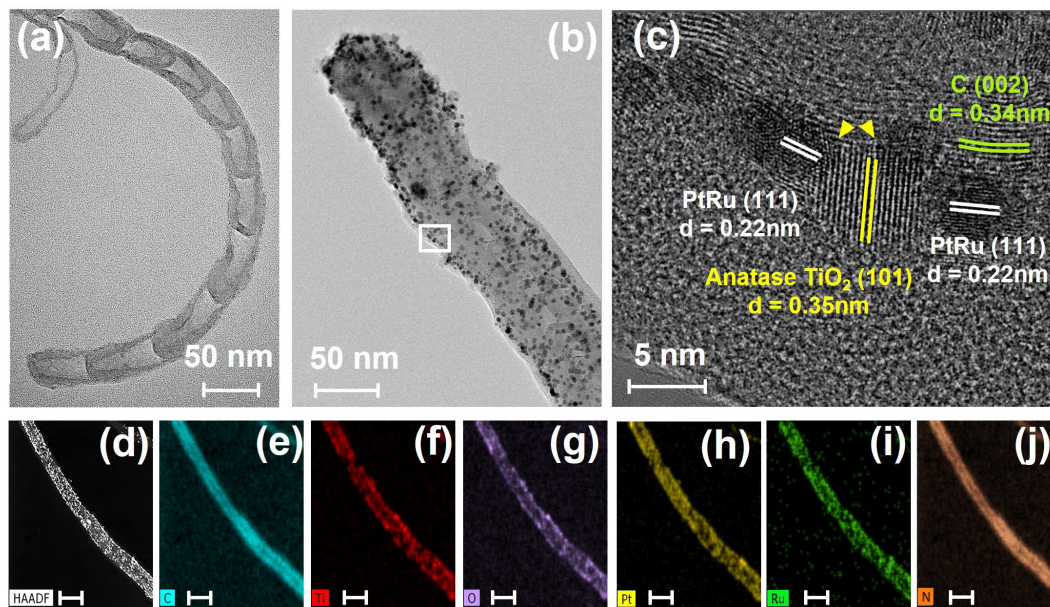


Figure 2.1. (a) TEM image of TiO₂/ONCNT. (b) TEM image of PtRu/ TiO₂/ONCNT-400. (c) High-resolution TEM (HRTEM) image of the rectangular portion of panel (b) with the lattice fringes corresponding to C(002), anatase TiO₂ (101) and PtRu(111). (d) HAADF-STEM image and (e-j) STEM-EDX elemental mapping of C, Ti, O, Pt, Ru and N in PtRu/ TiO₂/ONCNT-400. The scale bar in the (d-j) is 100 nm. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

As NCNTs are hydrophobic, they tend to aggregate and are not easy to form a stable well-dispersed solution. This was improved by treating it with strong acids to incorporate oxygenated functional groups at the graphitic edges along the sidewall. The resulted hydrophilic ONCNT (Figure A2 (b)) enabled uniform dispersion in aqueous solutions for subsequent reactions. After microwave-assisted deposition, an ultrathin conformal TiO₂ shell was formed on the ONCNT core

making it a TiO₂/ONCNT hybrid material as shown by the TEM image in Figure 2.1 (a). As will be discussed later, the as-deposited TiO₂ shell is a disordered amorphous material. Thus, the TEM contrast between TiO₂ and ONCNT was quite low and inadequate to clearly reveal the interface. However, after thermal annealing the as-produced TiO₂/ONCNT at 400 °C for 2 h in 3% H₂/97% Ar atmosphere, denoted as TiO₂/ONCNT-400, the contrast was improved, and a clear core-shell structure can be observed by TEM in Figure A2 (c), with the TiO₂ shell thickness about 5 nm.

The TiO₂ shell was found to efficiently improve the nucleation and anchoring of Pt or PtRu NPs in the subsequent microwave process for PGM catalyst deposition. As shown in Figure 2.1 (b), uniform and well-separated PtRu NPs are retained on the surface of TiO₂/ONCNT support after post-PGM-deposition thermal annealing at 400 °C for 2 h in 3% H₂/97% Ar atmosphere, denoted as PtRu/TiO₂/ONCNT-400. The average particle size was found to be 3.8 ± 0.6 nm as shown in the histogram in Figure A3. This is in the right range for highly active PGM catalysts. The nature of the TiO₂ shell and PtRu NPs in PtRu/TiO₂/ONCNT-400 is clearly illustrated in the high-resolution TEM image in Figure 2.1 (c). The lattice fringes match that for anatase TiO₂ (101), PtRu (111) and C (002), respectively. It confirms that the crystalline PtRu catalyst NPs are anchored on the surface of a TiO₂ shell consisting of anatase TiO₂ nanocrystals (about 5 to 8 nm in dia.) embedded in a continuous amorphous TiO₂ film. The yellow arrows highlight the region where the PtRu NPs are in direct contact with the crystalline TiO₂ support. The HAADF-STEM elemental mapping of PtRu/TiO₂/ONCNT-400 (shown in Figures 2.1 (d) – (j)) further confirms the presence and uniform distribution of C, Ti, O, Pt, Ru and N elements. It is to be noted that the diameter of the ONCNT is increased in Ti and O mapping (see Figures 2.1 (f) and (g)) when compared to C mapping (Figure 2.1 (e)), depicting that the formation of TiO₂ shell around the ONCNT. This further reveals that the average thickness of the TiO₂ shell is ~ 5 nm. Comparing

Figures 2.1 (d) – (j) with the HAADF-STEM elemental mapping of TiO₂/ONCNT (before PtRu deposition) in Figures A4 (a) – (e), the microwave-assisted PtRu deposition and subsequent thermal annealing process did not change the morphology and distribution of C, Ti, O and N in the TiO₂/ONCNT support.

Additional TEM images and NP size distribution histograms of Pt and PtRu catalysts deposited on three types of supports, including ONCNT, TiO₂/ONCNT and TiO₂/ONCNT-400, are shown in Figure A5 and Figure A6, denoted as Pt/ONCNT, Pt/TiO₂/ONCNT, Pt/TiO₂/ONCNT-400, PtRu/ONCNT, PtRu/TiO₂/ONCNT and PtRu/TiO₂/ONCNT-400. The particle size distribution of these samples is quite similar, with the average size of ~3.2 to 3.8 nm. In contrast, the average size of PGM NPs increases to 4.8 ± 1.3 nm in Pt/ONCNT-400 (Figure A7 (a)) and 5.4 ± 1.4 nm in PtRu/ONCNT-400 (Figure A7 (b)), respectively, which do not have the TiO₂ coating. Clearly, the TiO₂ shell helps to prevent PtRu agglomeration during thermal annealing, presumably due to stronger PGM-TiO₂ interaction as reported in literature.^{84, 85, 107}

2.3.2. Composition of the catalysts by TGA

TGA analyses of PtRu/TiO₂/ONCNT-400 and its corresponding control samples were carried out in air atmosphere to determine the weight percentage (wt%) of each element or compound present in the catalyst, as shown in Figure A8 (a). In the temperature range of 440 to 640 °C, the control carbon support ONCNT-400, i.e., ONCNTs annealed at 400 °C in 3% H₂/97% Ar, is almost burnt out, leaving only ~4% graphitic residue. In the TGA measurements, Ru atoms in the NPs are oxidized into RuO_x (with $x = 1.20$) in the range of 400 to 625 °C leading to increase of the weight to ~119% as shown in the control Ru NPs (purple curve of Figure A8 (a)). The weight of Pt and TiO₂ control samples remain nearly constant in the whole temperature range from room temperature to 900 °C. Based on these observation and reaction stoichiometry, the wt% of

each component can be derived. Detailed explanations and calculations of TGA are given in Supporting Information file. The wt% of Pt, Ru, TiO₂ and ONCNT in the PtRu/TiO₂/ONCNT-400 catalyst is found to be 25.5%, 10.2%, 20.4% and 43.9%, respectively. The total PGM wt% is 35.7%.

The TGA curves of commercial PtRu/C catalysts from JM and TKK are compared with our PtRu/TiO₂/ONCNT-400 catalyst in Figure A8 (b). While all curves show decrease in the weight in a well-defined step function due to burning off carbon supports, the starting and ending temperatures of our PtRu/TiO₂/ONCNT-400 catalyst are more than 100 °C higher than those of the two commercial catalysts. The graphitic NCNT support is indeed more stable than the amorphous carbon supports in the commercial catalysts. The wt% in the stabilized region above 600 °C are 78.9% for the PtRu/C JM and 55.6% for the PtRu/C TKK. By applying the above TGA analysis method to the commercial PtRu/C catalysts, the derived PtRu wt% are 73.2% (JM) and 50.6% (TKK), which are within ~1 to 2% from the vendor specified values of 71.1% (JM) and 49.7% (TKK) (see details in Supporting Information file). This validates the reliability of TGA in determining the wt% of individual components in the catalyst and support.

2.3.3. Crystal structure of the catalysts by XRD

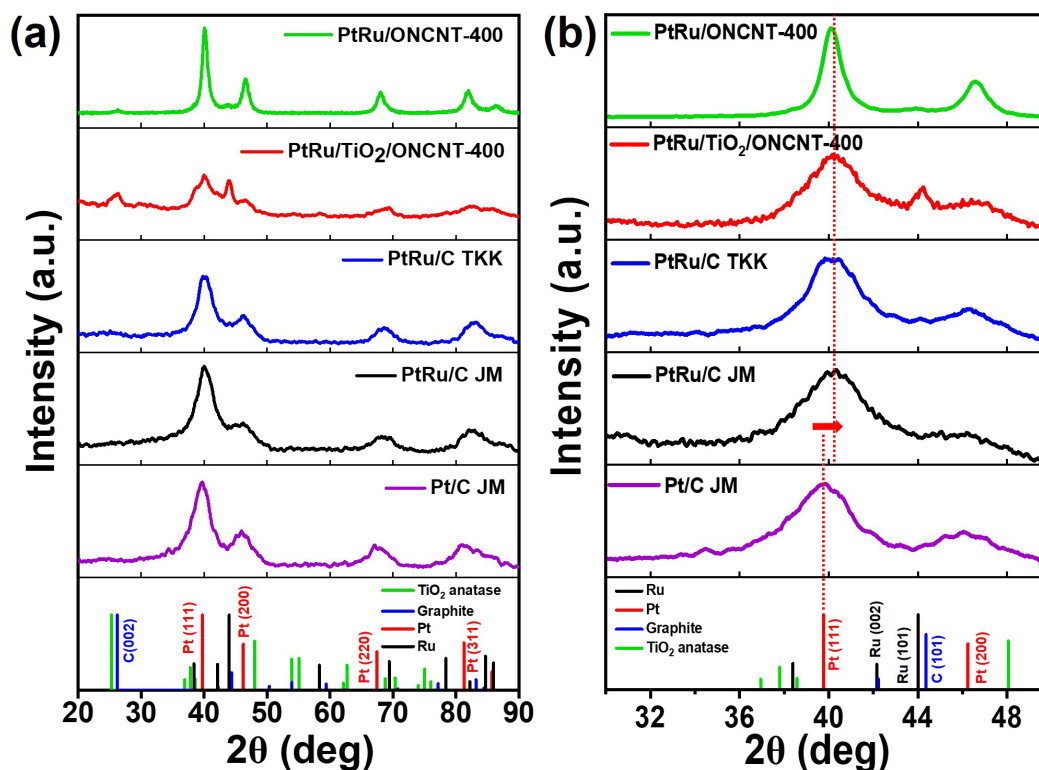


Figure 2.2. XRD patterns (a) in the full 2θ range of 20° to 90° and (b) in the narrower 2θ range of 30° to 50° of TiO_2 anatase (JCPDS# 21-1272), graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), Ru reference (JCPDS # 06-0663) compared with Pt/C JM, PtRu/C JM, PtRu/C TKK, PtRu/ TiO_2 /ONCNT-400 and PtRu/ONCNT-400. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

The as-deposited PtRu catalysts by the microwave process was found to be disordered. Thermal annealing at 400°C in 3% H_2 /97% Ar was applied to convert them into crystalline PtRu alloys. XRD analysis was carried out to understand the crystal structure of the catalysts as shown in Figure 2.2 and Figure A9. The diffraction peaks of the PtRu/ TiO_2 /ONCNT-400 at 2θ angle of 26.1° , 40.3° , 44.2° , 46.72° , 68.4° and 82.8° are indexed as C(002), Pt(111), Ru(101), Pt(200), Pt(220) and Pt(311), respectively. In expanded plots in Figure 2b, the Pt(111) peak of thermal

annealed PtRu catalysts, i.e., PtRu/ONCNT-400 and PtRu/TiO₂/ONCNT-400 shifts slightly to higher 2 θ angles compared to 2 θ = 39.76° in PtRu/TiO₂/ONCNT (before annealing, see Figure A10) and Pt reference spectrum (JCPDS: 04-0802).¹⁰⁸ A similar peak shift is observed in both JM and TKK commercial PtRu/C catalysts comparing to Pt/C from JM. The shift to higher 2 θ angles reveals the successful incorporation of Ru atoms into the Pt lattice to form a crystalline PtRu alloy with a contracted lattice since the atomic radius of Ru is smaller than Pt.¹⁰⁹ The atomic fraction of Pt and Ru in the PtRu alloy in PtRu/TiO₂/ONCNT-400 can be calculated as 1.6:1 using Vegard's law,^{110, 111} as described in the Appendix A. The average crystallite size of PtRu alloy NPs is estimated to be 3.2 nm in PtRu/TiO₂/ONCNT-400 and 5.6 nm in PtRu/ONCNTs-400 using the Scherrer's formula¹¹²:

$$D = K\lambda/\beta\cos \theta \quad (2.3)$$

where D is the crystallite size, K is the shape factor (0.89), λ is the X-ray source wavelength (1.5418 Å for Cu K α radiation), β is the full width at half-maxima of the diffraction peak (in radians), and θ is the half of the 2 θ angle of the diffraction peak. The resulting values are close to the average particle size measured with TEM, which further reveals that TiO₂ coating is critical in confining PtRu NPs on the surface and preventing their agglomeration during the thermal annealing.

Figure A9 (b) show that Pt(220) diffractions also shift to higher 2 θ angles after forming PtRu alloy in the annealed samples and the two PtRu/C commercial catalysts. In contrast, the XRD patterns of the bare supports, including TiO₂/ONCNT and TiO₂/ONCNT-400 (see Figure A9 (c)), only show a clear C(002) peak and a very weak C(101) peak. It is to be noted that, the diffraction peaks for anatase TiO₂ were not observed (when compared to TiO₂ anatase (JCPDS: 21-1272) reference spectra) in any of the TiO₂-coated ONCNT samples, which could be due to the

dominance of the defective disordered nature of the TiO₂ coating. Only a small amount of TiO₂ anatase nanocrystals are embedded in the amorphous shell as shown in the HRTEM image in Figure 2.1 (c). Furthermore, the XRD patterns of Pt/ONCNT, Ru/ONCNT and PtRu/ONCNT in Figure A9 (c) reveal that Pt and Ru form separate nanocrystal matching the standard reference spectra of Pt (JCPDS: 04-0802) and Ru (JCPDS: 06-0663). XRD results provide further evidence that thermal annealing is essential for forming crystalline PtRu alloy NPs that are required for high catalytic activities while the TiO₂ coating on the carbon support, though in a disordered form, is effective in anchoring the PGM NPs during thermal annealing to prevent agglomeration.

2.3.4. Chemical analyses of the catalysts by XPS

The strong PGM-TiO₂ interaction and the surface chemical composition of all catalysts were investigated by XPS. Figure A11 shows the XPS survey spectra of the catalysts. The at% of each element calculated from the survey spectra are summarized in Table A1. The surface atomic nitrogen content in NCNT and ONCNT was found to be ~ 9 at% and ~ 10 at%, respectively, which confirms the high nitrogen-doping in the pristine NCNT and oxygenated NCNT (ONCNT). The surface oxygen content in ONCNT (16 at%) was slightly higher than in the pristine NCNT (15 at%).

The high-resolution spectra of C 1s, N 1s, and O 1s were first collected from NCNT and ONCNT to investigate the surface chemical environment changes before and after strong acid treatment. The C 1s of NCNT and ONCNT were deconvoluted into six components with binding energies (BEs) of 284.60 eV, 285.12 eV, 286.20 eV, 287.35 eV, 289.03 eV, and 291.10 eV, as shown in Figure A12 (a). It is dominated by the sp² hybridized carbon atoms at 284.60 eV with a much smaller content of sp³ hybridized carbon atoms in the NCNT planes.^{113, 114} The peaks at 285.12 eV, 286.20 eV, 287.35 eV, 289.03 eV, and 291.10 eV correspond to sp³ hybridized C

atoms, C–O/C–N, C=O, O–C=O bonds and π - π^* of the shake-up satellite peak from sp^2 C,¹¹⁴ respectively. C–N bond at 285.12 eV further validates the nitrogen doping in NCNT. Similarly, the O 1s of NCNT and ONCNT were deconvoluted into three components with BEs of 531.23 eV, 532.10 eV, and 533.57 eV corresponding to carboxylic O–C=O group, C–O group and hydroxyl C–OH bonds,¹¹⁵ respectively, as shown in Figure A12 (b). The N 1s of NCNT and ONCNT were deconvoluted into five components with BEs of 398.57 eV, 400.00 eV, 401.20 eV, 403.32 eV, and 405.19 eV, which corresponds to pyridinic N, pyrrolic N, graphitic N, pyridinic-N-oxide and C–O–N,^{115, 116} respectively, as shown in Figure A12 (c). Table A2 summarizes and compares the relative at% of each component of deconvoluted peaks in C 1s, O 1s, and N 1s of NCNT and ONCNT. With strong acid functionalization, some sp^3 carbon has converted to C–O, C=O, and O–C=O, showing an increase in the relative at% of carbonyl and carboxyl groups in ONCNT when compared to NCNT. Similarly, some of the O–C=O was transformed to C–O (~7.2 at%) and –OH (~3.2 at%) groups in O 1s of ONCNT when compared to the C–O (~4.2 at%) and –OH (~2.2 at%) in NCNT. The increase of carboxyl and carbonyl groups at the edge sites of ONCNT can promote the TiO₂ deposition in the subsequent process.^{81, 117, 118}

The chemical composition of TiO₂ coating on ONCNT is illustrated in the high-resolution Ti 2p XPS spectra in Figure A13 (a). As a reference, the Ti 2p spectra of the commercial TiO₂ anatase nanopowder can be deconvoluted into a pair of peaks at 458.23 eV and 463.98 eV, respectively, corresponding to the Ti 2p_{3/2} and Ti 2p_{1/2} doublet of Ti⁴⁺ ions in TiO₂. Whereas for TiO₂/ONCNT, another pair of peaks (about 12.2 at%) at lower BE needs to be included to fit the Ti 2p spectra, which is due to the Ti³⁺ ions in TiO₂. Some of the Ti⁴⁺ was reduced into Ti³⁺ during the microwave-assisted deposition. In TiO₂/ONCNT-400, the Ti³⁺ composition increased to ~16.7 at% (see Figure A13 (b)) due to H₂ reduction during the thermal annealing, reflecting the formation

of defective hydrogenated TiO_2 .¹¹⁹⁻¹²¹ It is noteworthy that, for electrocatalysis, the defective hydrogenated TiO_2 is beneficial due to the higher electronic conductivity than the pristine TiO_2 anatase.^{96, 122, 123}

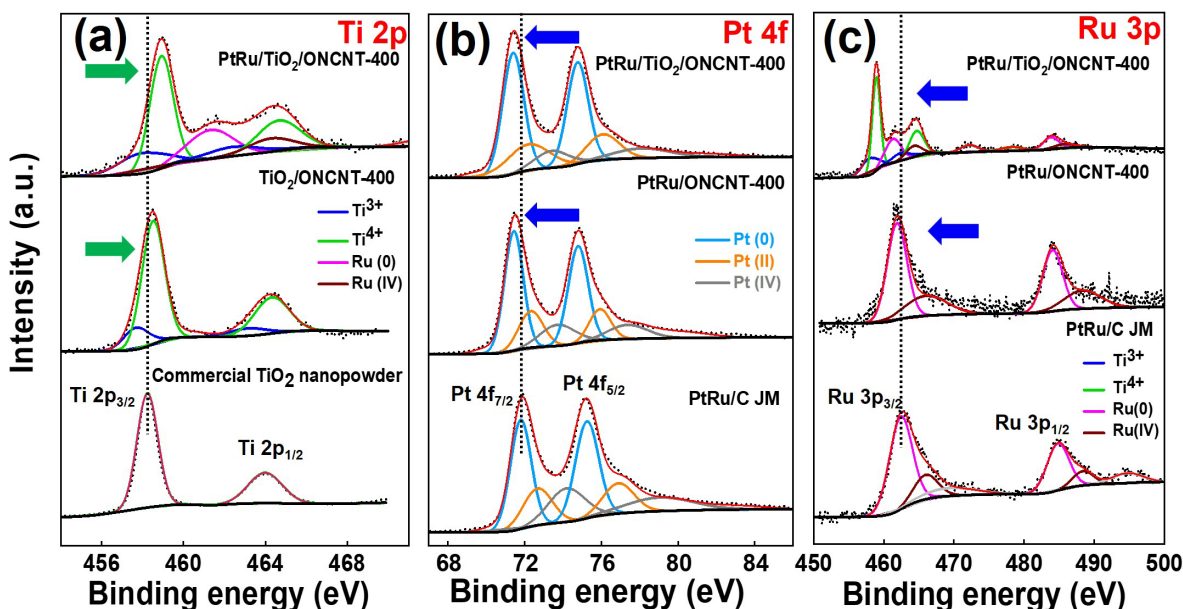


Figure 2.3. XPS analysis of (a) Ti 2p spectra of commercial TiO_2 nano powder, $\text{TiO}_2/\text{ONCNT-400}$ and $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$; (b) Pt 4f spectra of commercial $\text{PtRu}/\text{C JM}$, $\text{PtRu}/\text{ONCNT-400}$ and $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$; (c) Ru 3p spectra of commercial $\text{PtRu}/\text{C JM}$, $\text{PtRu}/\text{ONCNT-400}$ and $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$. The legends in each panel apply to all three curves in that panel. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

The interaction of PtRu catalyst with the TiO_2 support can be derived by comparing the high-resolution XPS spectra of Ti 2p, Pt 4f, and Ru 3p peaks of $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$ with those of $\text{PtRu}/\text{ONCNT-400}$ and other control samples including $\text{TiO}_2/\text{ONCNT-400}$, commercial TiO_2 anatase nanopowder and $\text{PtRu}/\text{C JM}$ catalyst, as shown in Figure 2.3. The BE and relative at% of each deconvoluted peak are shown in Table A3. Figure 2.3 (a) shows that the Ti^{3+} content in $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$ further increases to ~27.0 at% from ~16.7 at% in $\text{TiO}_2/\text{ONCNT-400}$. In addition, the BE of $2p_{3/2}$ peak of Ti^{4+} in $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$ shifts up to 458.92 eV compared

to that in TiO₂/ONCNTs-400 (458.50 eV) and commercial TiO₂ anatase nanopowder (458.32 eV), suggesting a lower electron density at Ti⁴⁺ sites likely due to electron transfer from Ti⁴⁺ to PtRu in PtRu/TiO₂/ONCNT-400 catalyst. It is to be noted that the Ti 2p doublets of Ti⁴⁺ and Ti³⁺ states in PtRu/TiO₂/ONCNT-400 partially overlap with the Ru 3p_{3/2} peaks (at BE of 458.92 eV and 458.02 eV). Nevertheless, they can be separated by deconvolution.

Figure 2.3 (b) shows that the Pt 4f spectra of PtRu/TiO₂/ONCNT-400, PtRu/ONCNT-400 (the control w/o TiO₂) and the commercial PtRu/C JM catalyst can all be deconvoluted into three pairs of Pt 4f_{7/2} and Pt 4f_{5/2} doublets attributing to Pt(0), Pt²⁺ and Pt⁴⁺ states in metallic, PtO & Pt(OH)₂, and PtO₂ species,¹²⁴ respectively. Pt (0) is the dominant species consisting of ~61% of Pt atoms, which is higher than ~51% in PtRu/C JM catalyst. The BE of Pt 4f_{7/2} of metallic Pt in PtRu/TiO₂/ONCNT-400 downshifted to 71.41 eV from 71.47 eV in PtRu/ONCNT-400 and 71.82 eV in the commercial PtRu/C JM catalyst. This trend is opposite to that of the Ti 2p peaks, indicating a higher electron density at Pt atomic sites in PtRu/TiO₂/ONCNT-400 due to partial electron transfer from Ti⁴⁺ to Pt. In Figure 2.3 (c), the Ru 3p peak of PtRu/TiO₂/ONCNT-400, PtRu/ONCNT-400 and commercial PtRu/C JM catalysts can all be deconvoluted into two pairs of doublets, corresponding to Ru(0) and Ru⁴⁺ in metallic and RuO₂ species,¹²⁵ respectively. Ru(0) comprises of as high as ~69% of all Ru atoms in PtRu/TiO₂/ONCNT-400, again higher than ~64% in PtRu/C JM catalyst. The BE of Ru 3p_{3/2} of metallic Ru in the three samples shows the similar downshift trend as Pt 4f peaks in Figure 2.3 (b), with the lowest value in PtRu/TiO₂/ONCNT-400 (461.32 eV) comparing to PtRu/ONCNT-400 (461.87 eV) and PtRu/C JM (462.43 eV). This indicates that electron transfer also occurs from Ti⁴⁺ to Ru sites. Overall, the XPS spectra in Figure 2.3 depict that there is likely a partial electron transfer from Ti⁴⁺ sites to the metallic Pt and Ru sites, resulting in a SMSI between the PtRu NP and TiO₂ support. This downshift in Pt 4f BE will

give a stronger Pt-CO binding, but it has an even bigger effect in increasing the OH⁻ binding on Pt which was found to accelerate the oxidation of CO to CO₂ and enhance C-H cleavage on Pt sites to improve MOR kinetics.²³

2.3.5. Assessment of CO oxidation with anodic CO stripping

As CO is a strong intermediate which poisons the Pt sites during MOR, it is important to investigate the anti-CO poisoning ability of a prepared catalyst. Linear CO stripping voltammograms and the consequent CV curves are present in Figures 2.4 (a) – (d) to evaluate the ability of CO oxidation and derive the ECSA of the optimal PtRu/TiO₂/ONCNT-400 catalyst in comparison with PtRu/ONCNT-400 and the commercial PtRu/C catalysts from JM and TKK. All measurements were done in 0.50 M H₂SO₄ at a PGM catalyst loading of 54 µg/cm². All catalysts show a clear anodic stripping peak in the first positive scan due to electro-oxidation of the pre-adsorbed CO on the Pt surface. All subsequent CV curves except the JM PtRu/C catalyst show only the flat baseline confirming the complete stripping of adsorbed CO. Figure 2.4 (e) compares the first anodic CO stripping curve of the four catalysts. The CO oxidation onset potential for all catalysts is determined when the oxidation current reaches 0.150 mA/cm²_{geo} and summarized in Table A4. The obtained CO oxidation onset potential increases in the order of PtRu/TiO₂/ONCNT-400 (~ 0.170 V), PtRu/C TKK (~ 0.170 V), PtRu/C JM (~ 0.190 V) and PtRu/ONCNT-400 (~ 0.205 V), versus an Ag/AgCl (1.0 M KCl) reference electrode. The CO oxidation peak potential appears in a different increasing order of PtRu/TiO₂/ONCNT-400 (~ 0.214 V), PtRu/C JM (~ 0.228 V), PtRu/ONCNT-400 (~ 0.234 V), and PtRu/C TKK (0.302 V), versus an Ag/AgCl (1.0 M KCl) reference electrode, respectively. This illustrates that the ultrathin defective hydrogenated TiO₂ shell in PtRu/TiO₂/ONCNT-400 indeed improves CO oxidation to surpass the state-of-the-art commercial PtRu/C catalysts, possibly by providing more -OH species near the Pt sites.

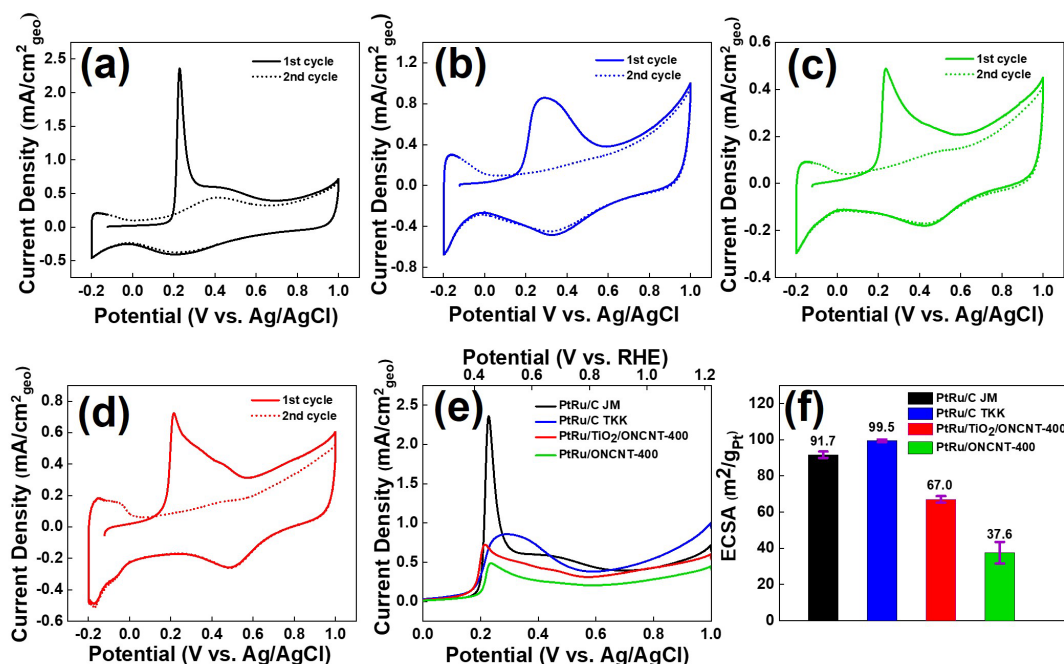


Figure 2.4. CO stripping voltammograms of (a) commercial PtRu/C JM; (b) commercial PtRu/C TKK; (c) PtRu/ONCNT-400; and (d) PtRu/TiO₂/ONCNT-400 catalysts recorded in Ar-purged 0.5 M H₂SO₄ solution at a scan rate of 10 mV/s. (e) Comparison of first anodic scan of CO stripping curves of PtRu/ONCNT-400 and PtRu/TiO₂/ONCNT-400 in comparison with the commercial PtRu/C catalysts from TKK and JM. (f) Bar plot of ECSA of different catalysts derived from the CO stripping measurements. The filling solution of Ag/AgCl reference electrode is 1.0 M KCl. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

The critical role of TiO₂ in PtRu/TiO₂/ONCNT-400 can be clearly observed by the earlier CO oxidation onset potential (by 35 mV lower) relative to PtRu/ONCNT-400 (without TiO₂). In addition, the SMSI illustrated by XPS, between PtRu and defective hydrogenated TiO₂/ONCNT support also contributes to enhancing the OH⁻ adsorption over the CO adsorption and thus lowers the CO oxidation potentials.

The ECSA of the catalysts was derived from the charge associated with the CO oxidation peak and mass of Pt on the electrode surface. Figure 2.4 (f) presents the derived ECSA values of the four catalysts, which are 67.0 m²/g_{Pt} for PtRu/TiO₂/ONCNT-400, 37.6 m²/g_{Pt} for PtRu/ONCNT-400, 129.6 m²/g_{Pt} for PtRu/C JM and 99.5 m²/g_{Pt} for PtRu/C TKK. The high ECSA

of PtRu/C JM included an additional peak area associated with the oxidation of Pt or Ru catalysts in the subsequent CV (2nd) cycle as shown in Figure 2.4 (a). Subtracting this contribution gives a corrected ECSA of 91.7 m²/g_{Pt} for PtRu/C JM. The ECSA of PtRu/TiO₂/ONCNT-400 is higher than the PtRu/ONCNT-400, depicting better PtRu NP dispersion on the TiO₂ shell. However, it is still lower than the commercial catalysts. As shown in Figure A14 (a), the CO oxidation peak potential of PtRu/TiO₂/ONCNT-400 (annealed at 400 °C) shifts by over -200 mV comparing to PtRu/TiO₂/ONCNT (un-annealed). This re-iterates the necessity of thermal annealing to improve the catalytic activity by forming PtRu alloy NPs and generating SMSI between PtRu and TiO₂. However, the ECSA of the PtRu/TiO₂/ONCNT-400 (67.0 m²/g_{Pt}) is lower than the PtRu/TiO₂/ONCNT (un-annealed), 75.0 m²/g_{Pt}, due to the slight increase in the particle size during alloy formation by thermal annealing in 3% H₂/97% Ar atmosphere. The effect of nitrogen doping and oxygen functionalization in enhancing the CO oxidation kinetics are shown in Figure A14b. The earlier CO oxidation onset potential for PtRu/ONCNT when compared to PtRu/NCNT and PtRu/OCNT illustrates the synergistic of nitrogen doping and oxygen functionalization in improving the CO oxidation kinetics. The ECSA values of PtRu/ONCNT (55.5 m²/g_{Pt}) is found to be higher than PtRu/OCNT (46.5 m²/g_{Pt}) showing the better PtRu nanoparticle dispersion on NCNT support due to nitrogen anchoring sites. The critical role of Ru is further illustrated in Figure A15. For the catalysts without Ru, the CO stripping properties of Pt/TiO₂/ONCNT-400 are very similar to the commercial Pt/C JM catalyst, with the peak potential of 0.522 V vs. 0.528 V (relative to Ag/AgCl (1.0 M KCl)), both are more than 300 mV higher than their PtRu counterparts. The ECSA values of these two Pt catalysts (58.7 m²/g_{Pt} vs. 56.6 m²/g_{Pt}) are also very similar. This clearly illustrates the critical role of Ru in providing OH species at much lower potential which significantly enhances the CO oxidation kinetics of PtRu/TiO₂/ONCNT-400.

2.3.6. Assessment of the catalytic activity of MOR

The electrocatalytic performance in MOR was investigated by CV in Ar-saturated 0.5 M H₂SO₄ containing 0.75 M methanol solution at a PGM catalyst loading of 54 µg/cm². As shown in Figure 2.5 (a), a typical CV curve of MOR consists of two irreversible oxidation peaks, one in the forward anodic scan and the other in the backward cathodic scan. The forward peak current density (I_f) is attributed to the methanol oxidation on the Pt surface whereas the backward peak current density (I_b) is commonly attributed to the oxidation of carbonaceous intermediate species formed in the previous anodic scan.¹²⁶ However, some recent literature attributes the I_b to the methanol oxidation on regenerated Pt surface by reducing PtO_x formed in the high potential region (> 0.6 V vs. Ag/AgCl (1.0 M KCl) or 0.8 V vs. RHE) of the previous forward scan, based on the fact that the I_b peak potential is strongly dependent on the upper potential in the CV.^{23, 60, 127, 128} Hence, the I_f/I_b ratio is associated with the degree of oxophilicity of the catalyst.²³

Since the NCNTs were oxygenated before TiO₂ deposition, its effect on catalyst oxophilicity was first studied by comparing the MOR curves of Pt deposited on oxygenated and pristine NCNT support, i.e., Pt/ONCNT and Pt/NCNT, relative to the commercial Pt/C JM catalyst. To make it consistent, all CVs are from the 100th cycle after the catalyst is stabilized. As shown in Figure A16 (a), Pt/ONCNT has a higher I_f (9.17 mA/cm²_{geo}) than Pt/NCNT (6.39 mA/cm²_{geo}) but a similar I_f/I_b ratio of 1.1), both higher than those of commercial Pt/C JM catalyst ($I_f = 6.19$ mA/cm²_{geo} and $I_f/I_b = 0.6$). This suggests that the additional oxygen functional groups in ONCNT and the intrinsic N-doping in pristine NCNT supports are effective in facilitating facile oxidation of carbonaceous species on the Pt surface and thereby improving the MOR kinetics.^{23, 73, 81} Similarly, the MOR curves of PtRu/NCNT and PtRu/ONCNT are compared to study the contribution of Ru and ONCNTs in MOR, as shown in Figure A16 (b).

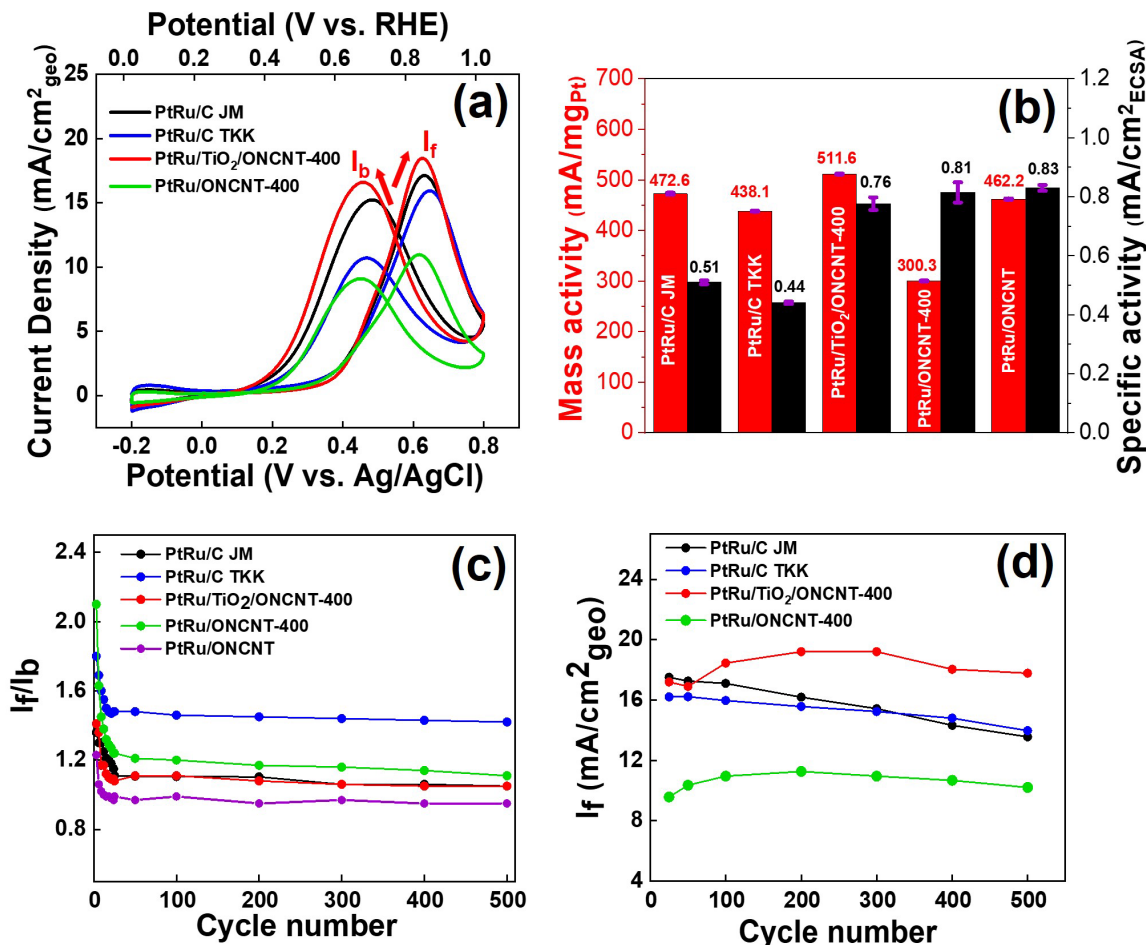


Figure 2.5. (a) Cyclic voltammetry curves (in the 100th cycle) of PtRu/ONCNT-400 and PtRu/TiO₂/ONCNT-400 in comparison with the two commercial PtRu/C catalyst from TKK and JM, with all PGM loading at 54 $\mu\text{g}/\text{cm}^2$, recorded in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s. (b) The bar plot showing the mass activity and ECSA-normalized specific activity derived from CVs of the four catalysts in panel (a). (c) Plot of I_f/I_b ratio and (d) plot of I_f of the four catalysts in panel (a) versus the cycle number recorded in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s. The filling solution in Ag/AgCl reference electrode is 1.0 M KCl. Reprinted (adapted) with permission from ACS Appl. Nano Mater. 2022, 5, 3, 3275–3288. Copyright 2022 American Chemical Society.

The I_f values are 17.20 $\text{mA}/\text{cm}^2_{\text{geo}}$ for PtRu/C JM, 16.64 $\text{mA}/\text{cm}^2_{\text{geo}}$ for PtRu/ONCNT and 12.58 $\text{mA}/\text{cm}^2_{\text{geo}}$ for PtRu/NCNT, which are substantially higher than the counterparts without Ru, while the I_f/I_b ratios maintain at about 1.1, 1.1 and 1.0. These results agree well with the recent

reports that the oxygen functional groups in the carbon support improves the oxophilicity of the catalyst.^{23, 81} The catalytic MOR after TiO₂ deposition on ONCNT was then studied following the same protocol. Figure 2.5 (a) presents the MOR curves from the 100th CV cycle for the PtRu/TiO₂/ONCNT-400 and PtRu/ONCNT-400 in comparison with the commercial PtRu/C catalysts from JM and TKK. The PtRu/TiO₂/ONCNT-400 catalyst exhibits the highest I_f (18.61 mA/cm²_{geo}) that outperforms not only PtRu/ONCNT-400 (10.90 mA/cm²_{geo}) but also commercial PtRu/C JM (17.20 mA/cm²_{geo}) and PtRu/C TKK (15.91 mA/cm²_{geo}). These trends corroborate with the corresponding CO stripping voltammetry. It is noteworthy that thermal annealing of PtRu/ONCNT causes significant drop in the I_f value from 16.64 mA/cm²_{geo} in Figure S16 (b) to 10.90 mA/cm²_{geo} for PtRu/ONCNT-400 in Figure 2.5 (a), mainly due to PGM agglomeration without the defective hydrogenated TiO₂ shell as we discussed above.

It is to be noted that the I_f/I_b ratio is much higher in the first few CV cycles but decreases fast within the initial 25 CV cycles (as shown in Figure 2.5 (c)). Most studies in literature only report the CVs in the early cycles. For comparison with literature, the MOR curves recorded at the 3rd CV cycle of the above catalysts are shown in Figure A17. The I_f/I_b ratio is found to be 1.4 for PtRu/TiO₂/ONCNT-400, 2.1 for PtRu/ONCNT-400, 1.4 for PtRu/C JM, and 1.8 for PtRu/C TKK, respectively. The PtRu/TiO₂/ONCNT-400 shows an I_f/I_b of 1.4 in the initial cycles and maintains $I_f/I_b > 1$ till 500 cycles (shown in Figure 2.5 (c)). Typically in literature, only PtRu/C catalysts having high oxophilicity show an $I_f/I_b > 1$, is attributed to the tendency to form more oxygenated species that enhance oxidization of the poisonous CO intermediate.¹²⁸ The MOR activity of PtRu/TiO₂/ONCNT (un-annealed) catalyst is compared with PtRu/TiO₂/ONCNT-400 in Figure A18 (a). The I_f of PtRu/TiO₂/ONCNT-400 (18.61 mA/cm²_{geo}) is slightly higher than that of the un-annealed PtRu/TiO₂/ONCNT (18.54 mA/cm²_{geo}), but the I_f/I_b of PtRu/TiO₂/ONCNT-400

(1.1) is significantly higher than that of PtRu/TiO₂/ONCNT (0.9). Thermal annealing the catalyst in 3% H₂/97% Ar is critical in enhancing the oxophilicity of the catalyst, likely by the combined effects of forming defective hydrogenated ultrathin TiO₂ shell and crystalline PtRu alloy. Interestingly, if Ru is not included, the Pt catalyst Pt/TiO₂/ONCNT-400 produces a substantially higher I_f (8.73 mA/cm²_{geo}) than the commercial Pt/C JM catalyst (6.20 mA/cm²_{geo}), as shown in Figure A18 (b). Additional insights into the catalysts are illustrated in Figure 2.5 (b), which summarizes the mass activity, defined by the measured geometric current density I_f (mA/cm²) divided by the mass loading of Pt (mg_{Pt}/cm²), and the ECSA-normalized specific activity, defined by I_f (mA/cm²) divided by the product of ECSA (m²/g_{Pt}) and Pt loading (mg_{Pt}/cm²) on the electrode surface. PtRu/TiO₂/ONCNT-400 showed the highest mass activity of 511.6 mA/mg_{Pt}, which surpasses the two state-of-the-art commercial PtRu/C catalysts from JM (472.6 mA/mg_{Pt}), TKK (438.1 mA/mg_{Pt}) and PtRu/ONCNTs-400 (300.3 mA/mg_{Pt}). In terms of ECSA-normalized specific activity, PtRu/TiO₂/ONCNT-400 exceeds the commercial PtRu/C catalysts even more, giving a value of 0.76 mA/cm²_{ECSA}, which is about 1.5-fold of the commercial PtRu/C JM catalyst (0.51 mA/cm²_{ECSA}) and 1.7-fold of PtRu/C TKK catalyst (0.44 mA/cm²_{ECSA}). This is largely due to its ability to present a slightly higher mass activity at the much lower ECSA. The PtRu/ONCNT-400 catalyst (without the TiO₂ coating) shows an even higher ECSA-normalized specific activity but suffers with a low mass activity due to its very low ECSA. Balancing all the trading factors, PtRu/TiO₂/ONCNT-400 shows enhanced MOR catalytic activity. The mass activity of PtRu/TiO₂/ONCNT-400 can be further enhanced by increasing its ECSA in the future.

The long-term stability is another important characteristic to evaluate the MOR catalysts for DMFC applications. In this study, the long-term stability of the in-house prepared PtRu/TiO₂/ONCNT-400, PtRu/ONCNT and PtRu/ONCNT-400 catalysts were evaluated and

compared with the two commercial PtRu/C catalysts from JM and TKK by monitoring the I_f/I_b ratio and I_f values over 500 consecutive CV cycles, as shown in Figure 2.5 (c) and Figure 2.5 (d). In Figure 2.5 (c), all five catalysts show rapid decrease in I_f/I_b ratio in the initial 25 cycles but get stabilized after 25th cycle, being able to retain 97.3%, 96.0%, 89.5%, 94.6% and 95.9% till the 500th cycle, indicating that the degree of oxophilicity of the catalysts did not have significant change from 25th cycle to 500th cycle. PtRu/TiO₂/ONCNT-400 and PtRu/ONCNT-400 have the similar I_f/I_b values as PtRu/C JM while that of PtRu/C TKK is somehow much higher though it did not lead to higher MOR mass activity in Figure 2.5 (b). In Figure 2.5 (d), the I_f value of the two commercial PtRu/C catalysts steadily decreases over time during the 500 cycles, giving a 20.7% drop for PtRu/C JM and 12.5% drop for PtRu/C TKK. In contrast, the two in-house prepared catalysts PtRu/TiO₂/ONCNT-400 and PtRu/ONCNT-400 show drastically different behaviors. Their I_f values increase in the first 100 to 200 cycles (due to catalyst activation) and then become relatively stable in the rest cycles, giving only 3.6% and 6.8% drop from the highest point in the 500th cycle. More importantly, the I_f value of PtRu/TiO₂/ONCNT-400 is about 20% higher than the two state-of-the-art PtRu/C catalysts from 200th to 500th cycles. In addition, MOR stability of the PtRu/TiO₂/ONCNT-400, commercial PtRu/C JM, and PtRu/C TKK catalyst was also evaluated by chronoamperometric measurements at a constant potential of 0.62 V vs Ag/AgCl (1.0 M KCl), as shown in Figure A19 (a). The rapid loss in the initial MOR current was observed for all catalysts, which is due to the formation and poisoning of catalyst surface by the intermediate carbonaceous species. The PtRu/TiO₂/ONCNT-400 showed a slower loss in initial current when compared to commercial PtRu/C JM and PtRu/C TKK.

Electrochemical impedance spectroscopy (EIS) measurements (see more details in ESI) of PtRu/TiO₂/ONCNT-400, PtRu/ONCNT-400, commercial PtRu/C JM, and PtRu/C TKK are shown

in Figures A19 (b) and A19 (c). The corresponding equivalent circuit for fitting the EIS is shown in Figure A19 (c) and fitted values are shown in Table A5. The main electronic charge transfer resistance (R_1) for PtRu/TiO₂/ONCNT-400 was found to be 4.45 Ω , which is lower than the PtRu/ONCNT-400 without TiO₂ (32.5 Ω), commercial PtRu/C JM (21.8 Ω) and PtRu/C TKK (18.3 Ω). This reveals that PtRu NPS in PtRu/TiO₂/ONCNT-400 have superior charge transfer kinetics owing to its SMSI and increased charge density provided by the hydrogenated TiO₂ shell (as evidenced in XPS). The small increase in the serial resistance (R_s) may be due to the inclusion of ultrathin TiO₂ shell on ONCNT. But the value is very small, and its effect is negligible.

These studies display that PtRu/TiO₂/ONCNT-400 shows an excellent stability and a higher electrocatalytic activity towards MOR which can be attributed to the strong attachment of PtRu on the ultrathin defective hydrogenated TiO₂ shell on ONCNT support and the SMSI due to chemical interaction and electron transfer from hydrogenated TiO₂ to the PGM NPs.

2.4. Conclusion

We have demonstrated the synthesis of a multifunctional hybrid catalyst support for PtRu-based MOR catalysts. A thin disordered hydrogenated TiO₂ shell is deposited on the oxygenated N-doped carbon nanotube by rapid microwave-assisted synthesis based on specific heating of the carbon core. PtRu nanoparticles are further deposited on the exterior surface of the hydrogenated TiO₂ shell by another microwave-assisted synthesis step. The hydrogenated TiO₂ shell is found to exhibit a strong interaction with the PtRu nanoparticles and is effective in retaining them in place and avoid agglomeration during the thermal annealing at 400 °C. The optimal catalyst consists of crystalline PtRu alloy nanoparticles of ~3.8 nm in diameter anchored on the amorphous defective hydrogenated TiO₂ shell, denoted as PtRu/TiO₂/ONCNT-400. XPS spectra reveal that there is a partial electron transfer from defective hydrogenated TiO₂ support to PtRu catalyst which is

consistent with the observed lower CO stripping onset potential. The synergistic effects of electron transfer and the increased oxophilicity provided by the defective hydrogenated TiO_2 support help to accelerate the CO oxidation and lead to higher mass activity and higher ECSA-specific activity in methanol oxidation than the two state-of-the-art commercial PtRu/C catalysts from JM and TKK. Furthermore, the PtRu/ TiO_2 /ONCNT-400 catalyst is much more stable than the commercial catalysts in the long cycles. It is a very promising anode catalyst for future direct methanol fuel cell.

Chapter 3 - Investigation of Hydrogenated TiO₂ Shell Modified on Different Carbon Supports on the Activity and Durability of PtRu Catalysts for Methanol Oxidation

3.1. Introduction

The direct methanol fuel cells (DMFC) have driven tremendous research interests to deploy as alternative renewable energy conversion device. The main advantage of DMFC comes from the low cost, high energy density (6.08 kWh/kg) and environmental friendliness of methanol fuel.¹¹ The anode and cathode reactions of DMFC are methanol oxidation reaction (MOR) and oxygen reduction reaction (ORR) which result in the formation of carbon dioxide (CO₂), water and electricity.¹¹ Among the anode and cathode electrocatalytic reactions, the anode MOR kinetics is sluggish and limits DMFC performance. Platinum (Pt) metal is the active electrocatalyst for MOR.¹²⁹ But the Pt active sites are prone to intermediate carbon monoxide (CO) poisoning during MOR. Hence, oxophilic nanostructured Pt-M (M = Ru, Fe, Ir, Co, etc.) alloy catalysts were developed to improve the MOR electro kinetics by suppressing the CO poisoning at Pt surface by bifunctional mechanism.¹²⁹ The state-of-the-art electrocatalyst for MOR is PtRu alloy nanoparticles dispersed on carbon.⁸ Generally, Pt based alloy catalyst nanoparticles are dispersed on carbon catalysts supports to enable efficient utilization of the active sites.¹³⁰

One of the major hurdles for DMFC commercialization is the methanol crossover.⁶⁴ The crossover of methanol is the phenomenon where methanol pass from anode through cathode via the polymer electrolyte membrane (PEM).¹³¹ This causes serious efficiency loss owing to the mixed potential and poisoning of cathode catalysts by CO from MOR at cathode.^{132, 133} The methanol crossover happens due to electro-osmotic drag and diffusion, and hence using pure

methanol completely degrades the performance.^{131, 134} For this reason, dilute methanol solutions are employed in DMFC. So, it is essential to identify strategies to reduce or withstand the methanol crossover in DMFC in order to utilize the high energy density that pure methanol may offer. Approaches such as modification of membranes and catalyst layers,^{135, 136} optimizing water management,^{134, 137} developing methanol tolerant PGM-free cathodes¹³⁸ and highly selective anodes⁶⁴ were developed to operate DMFC at high concentrations of methanol. Choi et.al. reported the concept of sputtering palladium on the plasma-etched Nafion™ (a polymer electrolyte membrane – PEM) to decrease the permeability and methanol cross-over from anode to cathode.¹³⁵ Whereas Babora et.al. and Bonies et.al. formed TiO₂ composite Nafion membrane to reduce methanol and ethanol permeability.¹³⁹ Nam et.al. developed hydrophilic SiO₂ based catalysts supports for PtRu to mitigate methanol crossover compared to carbon black supports. In all the above cases, the hydrophilicity of the anode catalyst layer is improved with metal or metal oxide modification of membrane to maintain a higher water content. Because the diffusion rate of methanol through membrane is determined by the methanol concentration gradient, a high-water content at the anode catalyst layer can locally dilute methanol to reduce the concentration to some extent at the anode catalyst layer-membrane interface. This can reduce methanol crossover to the cathode. The peak power density ($P_{\max}$) of 90 mW/cm² and 60 mW/cm² was achieved at 5 M and 10 M methanol feed.¹³² Yang et.al. applied a double layer sulfonated poly(ether ether ketone) (SPEEK) based membrane to show reduced methanol crossover owing to the reduced water uptake in SPEEK membranes. Shi et.al developed methanol tolerant PGM-free cathodes to accomplish high power density with high concentration methanol.^{137, 138} Xia et.al reported the development of ultrathin anode gas diffusion layers (GDL) based on carbon nanotube composite materials in enhancing the methanol transport at anode to improve the DMFC performance with PGM-free

cathodes. The CNTs-based GDLs are reported to provide enhanced mass transport properties.¹³³ Feng et.al. reported the development of highly selective core-shell Au@Ag₂S@Pt based anode electrocatalyst which operated well with 15 M methanol. Among these, engineering selective anode electrocatalyst and anode catalyst support architecture shows promising results to mitigate/withstand methanol crossover to operate DMFC using high concentrations methanol.

Catalyst supports play a crucial role in designing highly active and selective electrocatalysts, as they impact several important characteristics such as the (a) catalyst nanoparticle size, morphology and dispersion, (b) degree of alloying, (c) electrocatalytic activity and stability due to strong-metal-support interaction (SMSI), (d) catalyst layer conductivity, (e) catalyst layer porosity and thickness and (f) methanol crossover.¹³⁰ Hence, it is essential to optimize the catalyst supports to achieve a high-performance DMFC. There are several studies reporting different carbon catalyst support architectures such as carbon black, Vulcan, acetylene black, carbon nanotubes (CNTs), carbon nanofibers (CNFs), vertically aligned carbon nanofibers (VACNFs) and reduced graphene oxide (rGO) in enhancing the methanol oxidation activity of Pt based electrocatalysts.^{23, 73, 79, 130} Nevertheless, it is still unclear which carbon support is advantageous for DMFCs despite these major efforts. This is due to the fact that it is challenging to comprehend and compare the activity between various works due to the different electrocatalyst synthesis used in each investigation. However, there are a few systematic studies reported on studying the effects of different carbon catalyst supports with electrocatalysts deposited in same fashion.¹⁴⁰⁻¹⁴² However, the results of studies do not agree with each other, making it necessary for further studies.

On the other hand, the PtRu electrocatalysts directly deposited on carbon supports suffer from poor durability in MOR environments owing to catalyst nanoparticle agglomeration or

dissolution due to carbon corrosion. Several researchers reported the use of metal oxides such as TiO_2 , SnO_2 , CeO_2 , RuO_2 , etc. as hybrid catalysts supports or co-catalysts to enhance the stability and MOR activity of Pt-based alloy electrocatalysts.^{72, 143} Among them, TiO_2 is a promising metal oxide support due to its low cost and superior corrosion resistance properties in harsh acidic fuel cell environments.⁸ However, titania has a wide band gap resulting in poor electronic conductivity. Several studies show the enhancement of electrical conductivity of TiO_2 by forming reduced or hydrogenated titania. Recently, we reported a unique multifunctional core-shell catalyst support based on oxygenated nitrogen doped carbon nanotubes (ONCNTs) modified with a defective hydrogenated ultra-thin TiO_2 shell ($\text{TiO}_2/\text{ONCNT}$) using a simple microwave-assisted synthesis method.⁸ Enhanced stability and MOR activity of Pt and PtRu nanoparticles were achieved while using the hydrogenated TiO_2 modified carbon supports owing to the SMSI provided by the defective hydrogenated TiO_2 . A partial electron transfer between PGM catalysts and defective TiO_2 was revealed from in-depth XPS analyses. The beneficial role of hydrogenated TiO_2 in enhancing the CO oxidation kinetics were illustrated by the lower onset potential in the anodic CO stripping voltammetry studies. However, choosing a right carbon support is essential to make effective use of the highly active PtRu catalyst and hydrogenated TiO_2 as co-catalysts.

Herein, we systematically studied the effect of various carbon materials, in the core-shell catalyst supports consisting of a defective hydrogenated TiO_2 ultra-thin shell, on the activity and durability of PtRu electrocatalysts. We followed the same microwave-assisted two-step synthesis protocol developed in Chapter 2 report to modify the carbon supports with TiO_2 and to deposit PtRu nanoparticles. Carbon catalyst supports such as ONCNTs, Vulcan and Ketjen black were investigated in this study, which present different carbon support structures, morphology, degree of graphitization, nitrogen dopants, BET specific surface area (SSA) and porosity. Systematic

materials and electrochemical characterization were done for different carbon supported electrocatalysts to understand the critical effect of carbon in PtRu MOR electrocatalysis. Accelerated stress tests (ASTs) were carried to understand the degradation mechanism of electrocatalysts on hydrogenated TiO₂ modified different carbon supports by conducting CO stripping experiments at various stages of ASTs. To the best of our knowledge, this is the first report showing the structural evolution of PtRu electrocatalysts for MOR during AST by CO stripping studies. Full DMFC evaluation incorporating these anode catalysts against the commercial Pt/C cathode and PGM-free Fe-N-C based cathodes were performed to understand the kinetic and mass transport effects of various anode carbon support structures in the peak power density ($P_{\max}$). Preliminary tests of the anode electrocatalysts on TiO₂-modified carbon supports show high selectivity towards high methanol concentrations and reduced of methanol crossover may be due to TiO₂ modification on carbon supports.

3.2. Experimental Section

3.2.1. Chemical and Materials

The titanium tetraisopropoxide (TTIP), ethylene glycol (EG), sulfuric acid (H₂SO₄), nitric acid (HNO₃), pure ethanol 200 proof, and methanol (ACS grade) were purchased from Fisher Scientific (Hampton, NH). The potassium hexachloroplatinate (K₂PtCl₆), ruthenium chloride (RuCl₃.xH₂O), and Nafion[®] solution (5 wt% in lower aliphatic alcohols) were purchased from Sigma-Aldrich (St. Louis, MO). Commercial Vulcan and Ketjen black 600JD (KB 600JD) carbon supports were purchased from Fuel Cell Store (Bryan, TX) and HM Royal Materials Distribution (Trenton, NJ). The commercial Pt/C catalyst (20 wt% Pt on carbon, HiSPEC[®] 3000) and PtRu/C catalyst (48.0 wt% Pt and 23.1 wt% Ru on carbon, HiSPEC[®] 12100) by Johnson Matthey (JM) were purchased from Alfa Aesar (Tewksbury, MA) as the benchmark reference. Two more

benchmark commercial PtRu/C catalyst 50% (TEC 66E50 – 32.8 wt% Pt and 16.9 wt% Ru on carbon) and PtRu/C 77% were purchased from Tanaka Kikinzoku International (America) Inc. (Schaumburg, IL), referred as PtRu/C TKK 50% and PtRu/C TKK 77%. Ultrapure water (18.2 M Ω .cm at 25 °C) purified from a Millipore water system (EASYPURE II, Thermo Scientific, Waltham, MA) was used to prepare all aqueous solutions for the experiments.

3.2.2. Material Synthesis

N-doped CNTs (NCNTs) were synthesized from the pristine CNTs (obtained from Zhongshan CNM Plastic Co., Ltd., Zhongshan, China) by chemical vapor deposition of pyridine on the cleaned pristine CNTs. Briefly, CNT was placed into a quartz tube and heated from room temperature to 760 °C at a rate of 10 °C/min under N₂ atmosphere. Pyridine solution was charged into the quartz tube at 2 mL/min for 4 h. After that, the furnace was cooled down in N₂ atmosphere and NCNT was obtained.

3.2.2.1. Preparation of TiO₂/C

Three different carbon supports such as NCNT, Vulcan and KB 600JD are used in this study. All the carbon supports are first oxygenated by refluxing 1.0 g of each carbon separately in an aqueous mixture of 2.0 M H₂SO₄ and 4.0 M HNO₃ at 120 °C for 12 h under constant stirring. The obtained oxygenated carbon was washed with ultrapure water till the pH reached 7.0, filtered, and dried at 80 °C in a vacuum oven. Then, 10.0 mg of carbon was dispersed in 6.0 ml of ethanol by ultrasonication for 30 min. Further, 10.0 mg of TTIP was added to this dispersion and sonicated in a water bath. After 30 min sonication, this mixture was transferred to a 10 ml Pyrex glass microwave vessel and put into Discover[®] SP microwave synthesizer (CEM Corporation., Matthews, NC). A microwave irradiation was applied in the standard mode with the power up to 300 W to maintain a reaction temperature of 150 °C for 5 min. The reaction pressure rose to ~

19 bar during the process. After reaction, the naturally cooled product mixture was washed 2-3 times using ethanol to remove the unreacted precursors and dried at 80 °C in a vacuum oven to obtain the TiO₂ coated C, referred as TiO₂/ONCNT or TiO₂/Vulcan or TiO₂/KB 600JD.

3.2.2.2. Preparation of PtRu/TiO₂/C-400

To deposit PtRu catalysts, 12.5 mg of K₂PtCl₆, 5.1 mg of RuCl₃.xH₂O, and 16.0 mg of different TiO₂/C were dispersed in 20 ml of mixture of ethylene glycol and water (at 4:1 volume ratio) by ultrasonication for 1 hour. The solution was then transferred to 35 ml Pyrex glass microwave vessel. The weight ratio of Pt and Ru is maintained at 2:1 in the precursors. Ethylene glycol serves as a reducing agent and solvent in this reaction. The mixture was irradiated with a 300 W microwave under the standard mode to maintain a reaction temperature of 190 °C for 20 min in Discover[®] SP microwave synthesizer to deposit Pt and Ru NPs onto TiO₂/C. The reaction pressure rose to ~8 bar during this process. The cooled product mixture was washed several times using acetone to remove residual ethylene glycol and then dried at 80 °C in a vacuum oven to obtain PtRu/TiO₂/C. The dried catalyst material was annealed in a tube furnace at 400 °C for 2 h in 3% H₂/97% Ar atmosphere at a ramp rate of 10 °C/min, to form crystalline PtRu alloyed NPs and defective hydrogenated TiO₂ shell on the carbon support. The as-prepared catalyst is named as PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB 600JD-400 depending on the carbon support used. Synthesis of control samples was carried out using the same reaction conditions as mentioned above with appropriate precursors but skipping some specific intermediate steps.

3.2.3. Materials Characterization

The structure of the catalysts was characterized using three transmission electron microscopes (TEM) at different stages of the project, including: a Tecnai Osiris

Scanning/Transmission Electron Microscope (S/TEM, FEI, Hillsboro, OR) at a 200 kV acceleration voltage, located at University of Nebraska, Lincoln; a Hitachi H-8100 TEM (Hitachi, Krefeld, Germany) at a 200 kV acceleration voltage, located at University of Kansas, Lawrence and a Philips CM 100 TEM at a 100 kV acceleration voltage, located at Department of Biology, KState. The crystal structure of the catalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 1 mm, located at Department of Chemistry, KState. XRD reference spectra are used from Joint Committee on Powder Diffraction Standards (JCPDS). The composition of the catalysts was determined using a Thermogravimetric Analyzer (TGA) Q50 system (TA instruments - Waters LLC, New Castle, DC) from the room temperature to 900 °C in a compressed air atmosphere located at Department of Chemistry, KState. The surface chemical composition of the catalysts was characterized using a PHI 5000 Versa XPS system (Chanhassen, MN) with a monochromatized Al K α source (1486.7 eV), located at Department of Chemistry, KState. All the XPS spectra were obtained using a 400 μ m spot size. Shirley background was used in the curve fitting. The binding energy (B.E.) of all XPS data was calibrated vs. the standard sp² C 1s peak at 284.60 eV. The BET specific surface area and pore size distribution of the prepared samples were tested by N₂ adsorption at 77 K in a Quantichrome Autosorp IQ (Anton Paar - Ashland, VA), located at Department of Physics, KState.

3.2.4. Electrochemical Characterization

All the half-cell electrochemical experiments were performed in a standard three-electrode setup using a CHI 760D electrochemical workstation (CH Instruments, Austin, TX) at room temperature. A silver-silver chloride (Ag/AgCl in 1.0 M KCl) reference electrode and a coiled Pt counter electrode (0.55 mm in diameter and 23 cm in length) were used. The working electrode

was prepared by drop-casting the catalyst ink onto a glassy carbon electrode (GCE) encased in a PEEK rod. Before drop-casting the catalyst ink, the GCE was polished using 0.05 μm alumina slurry. The catalyst ink was prepared by dispersing the required amount of catalyst powder in 1.0 ml of mixture of ethanol and ultrapure water (at 3:1 volume ratio) with addition of the 30 μl of Nafion[®] solution (5 wt% in lower aliphatic alcohols). The loading of the platinum group metal (PGM, specifically Pt and Ru in this study) was maintained at 54 $\mu\text{g}/\text{cm}^2$ for all catalysts in the half-cell studies. The MOR experiments were performed by recording CV in the potential range of 0 V to 1 V vs. RHE at a scan rate of 50 mV/s in Ar-purged 0.5 M H_2SO_4 solution containing 0.75 M methanol. For direct comparison of the potentials with literature, the measured electrode potential vs. the Ag/AgCl (1.0 M KCl) reference electrode is converted to the value vs. the reversible hydrogen electrode (RHE) using the following equation:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Ag/AgCl})} + E_{(\text{Ag/AgCl vs. SHE})} + 0.059\text{pH} = E_{(\text{vs. Ag/AgCl})} + 0.222 \text{ V} \quad (3.1)$$

where $E_{(\text{vs. Ag/AgCl})}$ is the measured potential vs. the Ag/AgCl (1.0 M KCl) reference electrode, $E_{(\text{Ag/AgCl vs. SHE})} = 0.222 \text{ V}$ is the Ag/AgCl (1.0 M KCl) reference electrode potential vs. SHE, and $\text{pH} = 0$ for 0.50 M H_2SO_4 .

The CO stripping voltammetry experiments were performed in 0.50 M H_2SO_4 to evaluate the catalyst activity towards CO oxidation and to determine the active electrochemical surface area (ECSA) of the catalyst. In CO stripping experiments, the electrolyte was first purged with Ar gas to remove any dissolved oxygen species in the electrolyte. Then, a pure CO gas was used to purge the electrolyte for 10 min while the potential of the working electrode was held at 0.10 V vs. RHE. After 10 min, the purging gas was switched back to pure Ar to purge for 30 min to remove the dissolved CO gas from the electrolyte, while the potential of the working electrode was still held at 0.10 V vs RHE which retained the adsorbed CO monolayer on the Pt surface. Subsequently, the

CO monolayer on the Pt surface was stripped off with a linear anodic sweep at 10 mV/s from 0.10 V to 1.222 V vs. RHE. A few CV cycles were taken following CO stripping to evaluate the baseline of the electrode.

The ECSA of Pt in the catalysts was determined using the following equation:

$$\text{ECSA} = \frac{Q_a}{Q_{\text{CO}}^0 \times m_{\text{Pt}}} \quad (3.2)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of CO oxidation peak; $Q_{\text{CO}}^0 = 420 \mu\text{C}/\text{cm}^2$ is the charge required to oxidize a monolayer of CO adsorbed on 1 cm^2 of flat Pt surface and m_{Pt} ($\text{g}_{\text{Pt}}/\text{cm}^2$) is the mass loading of Pt on the working electrode surface.

AST of all the electrocatalysts was investigated by two protocols. **Protocol 1:** Continuous CV cycling of electrocatalysts were performed in the potential range of 0 to 1.0 V vs. RHE at 50 mV/s scan rate for 500 cycles CO stripping voltammogram were obtained on fresh catalysts surface, after CV activation in 0.50 M H_2SO_4 , after 25th, 50th, 100th, 200th, 300th, 400th and 500th MOR cycle to understand the PtRu structural evolution over MOR cycles. **Protocol 2:** Continuous CV cycling of electrocatalysts were performed in the potential range of 0 to 0.5 V vs. RHE at 500 mV/s scan rate for 1000 cycles CO stripping voltammogram were obtained on fresh catalysts surface, after CV activation in 0.50 M H_2SO_4 , after 25th, 50th, 100th, 200th, 300th, 400th, 500th, 750th and 1000th MOR cycle to understand the PtRu structural evolution over MOR cycles.

3.2.5. Full DMFC Characterization

Major part of the full DMFC tests with various anodes and commercial Pt/C cathodes were carried out by our collaborators Dr. Xianglin Li and Nathaniel Metzger from Department of Mechanical Engineering, the University of Kansas (KU). The PGM-free cathode synthesis and full DMFC tests of MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG (PGM-free) cathode

was done by our collaborators Dr. Yachao Zeng and Dr. Gang Wu of Department of Chemical and Biological Engineering, University at Buffalo (UB), State University of New York.

Fabrication of the GDEs (for DMFC tests done at KU) were performed by KSU in the following way. Appropriate quantity of catalysts was dispersed in ethanol and Nafion[®] for achieving a PGM loading of $\sim 4.5 \text{ mg/cm}^2$ and $\sim 1.5 \text{ mg/cm}^2$ for anode and cathode GDEs, respectively. The anode and cathode were maintained an ionomer to carbon ratio of 1.0 and 0.2, respectively. Each of the catalysts were air-brush spray coated onto Toray carbon paper 060 (190 μm) on a 70 °C hotplate. Our collaborators at KU then performed fabrication of the MEAs using Nafion[®] 212 as a proton exchange membrane (PEM). The MEAs were heated at 275 °F for five minutes and then compressed at 50 psi in 275 °F for one minute. Each MEA followed an activation procedure using 0.25M methanol solution as a fuel at 0.5 mL/min with humidified air at 90 °C and 0.1 L/min with a stack temperature of 80 °C. The MEA was allowed to rest at open circuit voltage for 3 minutes then holding at 0.4 V or 0.3 V volts for one hour. A voltage scan was performed between each cycle and activation was completed once the current density and resistance stabilized.

3.3. Results and Discussion

3.3.1. Morphological and Structural Characterization

Various carbon supports such as nitrogen doped carbon nanotubes (NCNTs), Vulcan, and Ketjen black 600JD (KB 600JD) with different morphology, nanostructure, BET specific surface area (SSA), and pore size distribution are studied as catalyst supports in this work. Figure B1 (in Appendix B) shows the TEM images of the bare catalyst supports. As discussed in Chapter 2, the NCNTs possess unique conical stacks of graphitic layers along the fiber axis with a diameter ranging from 20 to 50 nm and length ranging from 2 – 10 μm (see Figure B1 (a)). High resolution TEM (HRTEM) in the inset of Figure B1 (a) shows the graphitic planes present with lattice fringes ($d = 0.34 \text{ nm}$) at the edges. Figure B1 (b) and (c) shows the TEM images of the conventional commercially available amorphous Vulcan and KB 600JD carbon supports. Vulcan carbon and KB 600JD possess disordered and amorphous irregular shaped carbon particles whose average diameter ranges from 50 to 80 nm. The carbon nanostructure of amorphous Vulcan and KB 600JD are quite different from that of tubular graphitic nanostructure of NCNTs. This study will focus on studying the effect of different carbon support nanostructure with different density of micropores in the methanol oxidation reaction (MOR) activity of PtRu nanoparticles. The BET N_2 adsorption/desorption isotherm and pore size distribution of ONCNT, Vulcan and KB 600JD are shown in Figure B2. The BET SSA was found to be $149 \text{ m}^2/\text{g}$, $280 \text{ m}^2/\text{g}$ and $1447 \text{ m}^2/\text{g}$ for ONCNT, Vulcan and KB 600JD respectively. KB 600JD carbon support is found to have abundant micropores. Firstly, all the bare carbon supports are functionalized with oxygen functional groups to enhance the hydrophilicity.

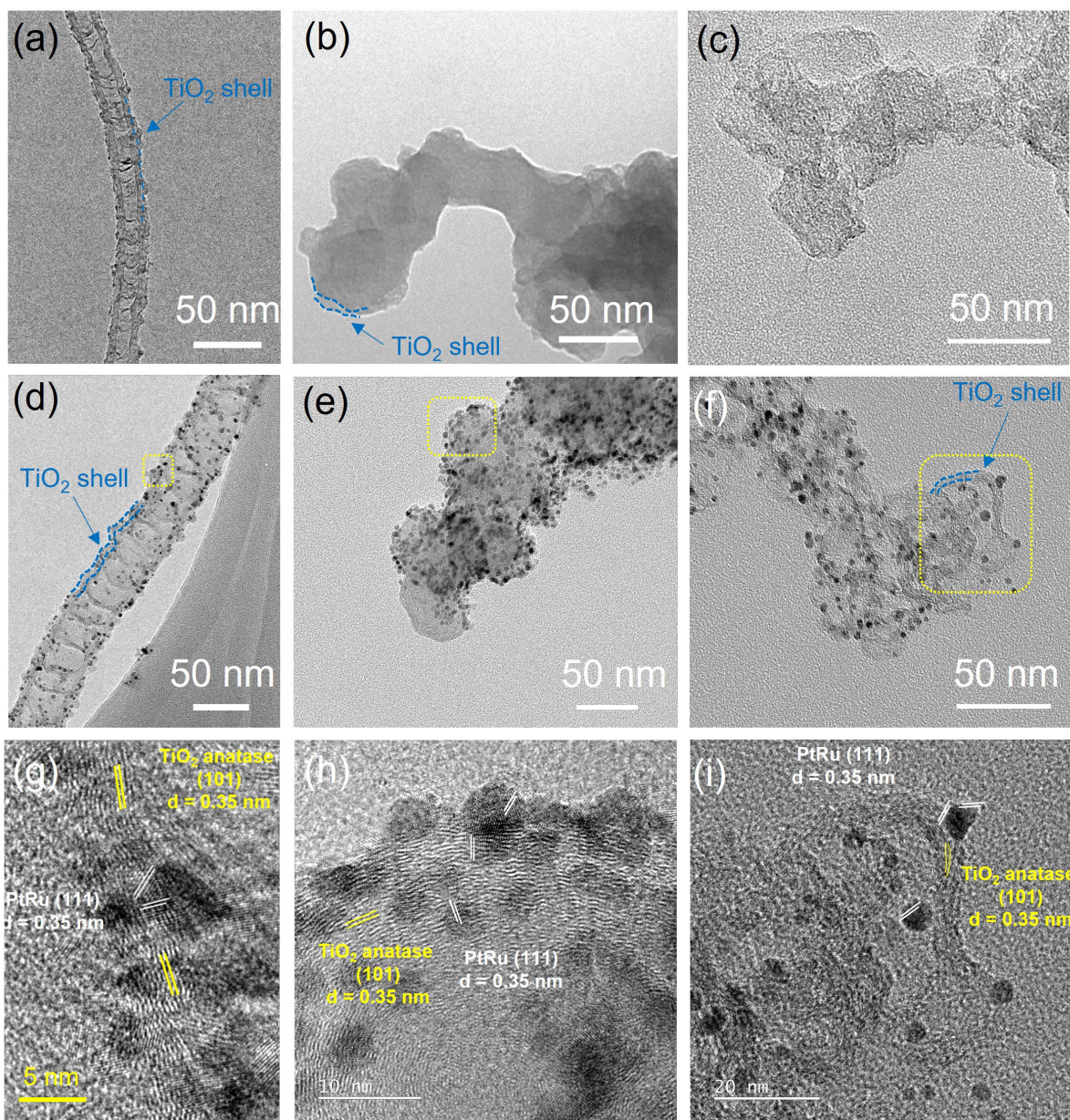


Figure 3.1. TEM images of (a) TiO₂/ONCNT, (b) TiO₂/Vulcan, (c) TiO₂/KB600JD, (d) PtRu/TiO₂/ONCNT-400, (e) PtRu/TiO₂/Vulcan-400 and (f) PtRu/TiO₂/KB 600JD-400. HRTEM images of (g) PtRu/TiO₂/ONCNT-400 from the rectangle highlighted in (d); (h) PtRu/TiO₂/Vulcan-400 from the rectangle highlighted in (e); and (i) PtRu/TiO₂/KB 600JD-400 from the rectangle highlighted in (f).

As discussed in the Chapter 2, the oxygen functionalization not only enables better nanoparticle dispersion but also participates in the MOR to enhance the kinetics.^{8, 81} It is to be noted that, the BET SSA of carbon supports improved with acid functionalization due to the

formation of more micropores and removal of impurities. For instance, the SSA of KB 600JD increased to 2081 m²/g from 1447 m²/g, after acid functionalization treatment as shown in Figure 3.2.

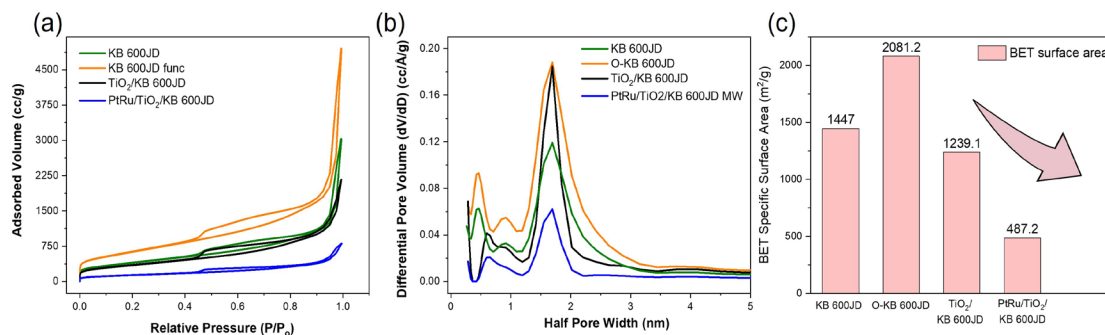


Figure 3.2. (a) BET N₂ adsorption-desorption isotherms and (b) corresponding pore size distribution curves of KB 600JD, KB 600JD after acid functionalization, TiO₂/KB 600JD, PtRu/TiO₂/KB 600JD and PtRu/TiO₂/KB 600JD-400. (c) Bar plot comparing the BET specific surface area of catalysts at different stages synthesis of PtRu/TiO₂/KB 600JD-400.

From our previous studies, XPS analysis of carbon supports after strong acid functionalization revealed increase in COOH, CO and C=O functional groups.⁸ Experimental section shows the detailed procedure of acid functionalization step. Briefly, each carbon support is refluxed in 4.0 M HNO₃ and 2.0 M H₂SO₄ at 120 °C for 12 hours. As-functionalized carbon supports are used for further TiO₂ modification. Ultrathin shell of TiO₂ was deposited on each of the carbon support using a simple and rapid 5 min of microwave-assisted synthesis (in ethanol solvent) reported in Chapter 2.⁸ The high tangent loss value of the carbon supports ($\tan\delta \sim 1.0$) compared to ethanol solvent (< 0.9), enabled preferential deposition of TiO₂ as ultrathin shells on carbon supports.¹⁴⁴ Figure 3.1 (a) to (c) shows the TEM images of TiO₂ deposited on ONCNT, Vulcan and KB 600JD, denoted as TiO₂/ONCNT, TiO₂/Vulcan and TiO₂/KB 600JD. As shown in Figure 3.1 (a), a clear conformal TiO₂ shell is deposited on ONCNT forming a core-shell catalyst support. As reported in previous chapter,⁸ the TiO₂ shell thickness was found to be ~ 5 nm from

STEM/EDX elemental mapping. It was quite difficult to observe the clear TiO₂ interface on TiO₂/Vulcan and TiO₂/KB 600JD owing to the very low contrast difference. Hence, STEM-EDX elemental mapping was done (see Figure B3) on TiO₂/KB 600JD to show the deposition of ultra-thin TiO₂ shells. Clearly, uniform distribution of Ti and O was seen throughout the carbon support. Moreover, the BET SSA decreased to 1239.1 m²/g after TiO₂ shell modification on carbon support, indirectly revealing the presence of thin shell of TiO₂. From the pore-size distribution curve (see Figure 3.2 (b)), the TiO₂ shells have not completely filled the micropores of the high surface area KB 600JD and the KB 600JD support remains porous enough to provide high surface for PtRu nanoparticle deposition.

As shown in Figure 3.1 (d) – (f), uniform and well dispersed PtRu nanoparticles are present on the surface of different TiO₂ modified carbon supports after microwave and post thermal annealing at 400 °C for 2h in 3% H₂/ 97% Ar atmosphere. The TiO₂ and carbon interface was clearly observed in the PtRu/TiO₂/ONCNT-400. The blue arrow highlights the TiO₂ ultra-thin conformal shell on NCNT in Figure 3.1 (d) of PtRu/TiO₂/ONCNT-400 sample. The TiO₂ conformal shell thickness was found to be ~ 5 nm. The HRTEM image of PtRu/TiO₂/ONCNT-400 showing the lattice fringes of C (002), Ti anatase (101) and PtRu (111) is shown in Figure 3.1 (g). From this, a few TiO₂ anatase nanocrystals are found to be embedded in the TiO₂ shell. The average PtRu nanoparticle size was found to be 3.8 nm ± 0.6 nm (see Figure B4 for particle size distribution histogram). PtRu nanoparticles dispersion on PtRu/TiO₂/Vulcan-400 was better than PtRu/TiO₂/ONCNT-400 (see Figure 3.1 (h)) with an average nanoparticle size of about 3.3 nm ± 1.0 nm owing to the slightly higher SSA of Vulcan than NCNT. The particle size distribution and dispersion (Figure B4-particle size distribution histogram) were even better when KB600JD was used as carbon support in PtRu/TiO₂/KB600JD-400 resulting in an average nanoparticle size of

3.1 nm $\pm$ 0.6 nm. In Figure 3.1 (f) and (i), the blue arrow indicates the clear ultra-thin TiO₂ shell and carbon interface with TiO₂ shell thickness of about $\sim$ 3 to 4 nm. The HRTEM images of PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB 600JD-400 are shown in Figure 3.1. (h) to (i), respectively. The lattice fringes of TiO₂ (101) were observed around the edge of the carbon supports with PtRu nanoparticles, PtRu (111), embedded on them.

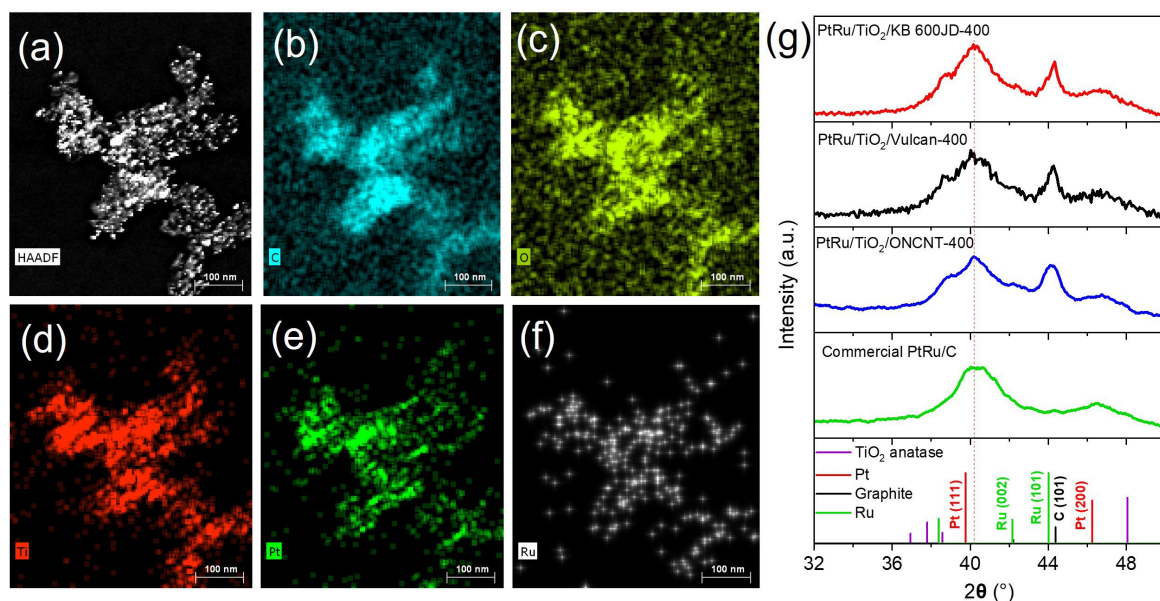


Figure 3.3. (a) HAADF-STEM image and (b–f) STEM-EDX elemental mapping of C, Ti, O, Pt and Ru of PtRu/TiO₂/KB 600Jd-400. XRD patterns in the 2 θ range of 30° to 50° of Ru reference (JCPDS # 06-0663), graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), TiO₂ anatase reference (JCPDS# 21-1272) compared with commercial PtRu/C, PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400.

Figure 3.3 (a) to (f) shows the STEM-EDX elemental mapping of C, O, Ti, Pt and Ru of PtRu/TiO₂/KB 600JD-400. The uniform distribution of TiO₂ was observed on carbon surface with Pt and Ru nanoparticles sparsely present on the surface. The BET SSA of PtRu/TiO₂/KB 600JD-MW further reduced to 487.2 m²/g after PtRu deposition on TiO₂/KB 600JD indicating nucleation and nanoparticle formation in the micropores (see Figure 3.2 (b)). Figure B5 shows the STEM-EDX mapping for PtRu/TiO₂/Vulcan-400 with uniform distribution of TiO₂, Pt and Ru

nanoparticles. Overall, the nanoparticle size distribution was precisely controlled by using high surface carbon supports. The smallest size of PtRu alloy nanoparticle was obtained when KB 600JD carbon support was used. Nevertheless, it is important to reiterate the critical role of TiO₂ in controlling the nanoparticle size. Figure B6 (a) to (f) shows the TEM images and its corresponding particle size distribution of control samples of PtRu deposited on bare carbon supports such as ONCNT, Vulcan and KB 600JD without TiO₂ modification. The average PtRu nanoparticle size in this case was much larger by ~ 2 to 3 nm. Hence, this shows that nanoparticle size and agglomeration during annealing was reduced with TiO₂ modification on carbon support owing to the strong interaction of metal nanoparticle with metal oxide supports.

TGA experiments and analysis were done to determine the elemental composition of each of the catalysts as shown in Figure B7. The PtRu (PGM) wt% in PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB 600JD was found to be 35.7%, 27.5% and 32.6%, respectively. XRD was done to understand the crystal structure of the catalysts. Figure 3.3 (g) shows the XRD patterns of PtRu deposited on various TiO₂ modified carbon structures such as ONCNT, Vulcan and KB600JD compared with commercial PtRu/C. The diffraction peaks at 2 θ angle of 40.2° and 46.72°, was observed, corresponding to fcc Pt (111) and fcc Pt (200) for all the catalysts revealing the crystalline nature of Pt catalysts. The PtRu alloy formation was uncovered from the peak shift in Pt (111) and Pt (200) peak to higher 2 θ angles, when compared to Pt reference spectrum (JCPDS: 04-0802). These peak shifts reveal the introduction of Ru atoms into Pt lattice resulting in shrinking of lattice constant of Pt. These peak shifts are consistent with the commercial PtRu/C catalysts. The atomic fraction of Pt and Ru was calculated to be ~ 1.6:1, for all the catalysts, by Vegard's law. The diffraction peak corresponding to hcp Ru (101) at 2 θ angle of 44.2° was observed for PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB

600JD, indicating the presence of some individual Ru nanoparticles along with PtRu alloy nanoparticles.¹⁴⁵ Such Ru (101) peak was not observed for commercial PtRu/C and PtRu/C-400 depicting the complete PtRu alloy formation. Scherrer's formula was used to calculate the crystallite size of PtRu nanoparticle to be 3.16 nm, 2.93 nm, and 2.90 nm in PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400, respectively. The PtRu crystallite size calculated from XRD and the decreasing trend in particle size with increasing BET SSA of carbon are consistent with TEM particle size analysis. Diffraction peaks (see Figure B8 (a)) for anatase TiO₂ (101) was observed at 2 θ angle of 25.6° indicating the crystalline nature of TiO₂ shell deposited on carbon supports for PtRu/TiO₂/C samples. This supports the HRTEM images (Figure 3.1 (g) – (i)) showing TiO₂ anatase nanocrystals embedded into TiO₂ shell.

3.3.2. Materials Compositional Analysis

XPS analysis was done to understand the surface elemental composition of all the catalysts. Figure B8 (b) and (c) shows the XPS survey spectra of all catalysts. The chemical composition of the amorphous TiO₂ deposited on different carbon supports such as ONCNT, Vulcan and KB 600JD is illustrated in the high-resolution Ti 2p XPS spectra in Figure B9. For comparison, Ti 2p spectrum of TiO₂ anatase nanopowder was deconvoluted into a pair of Ti 2p_{3/2} and Ti 2p_{1/2} doublet at 458.17 eV and 463.88 eV corresponding to Ti⁴⁺ of TiO₂.¹²² However, another pair of doublet corresponding to Ti³⁺, in addition to Ti⁴⁺ was required to fit the Ti 2p spectra of the amorphous TiO₂ on TiO₂/ONCNT, TiO₂/Vulcan and TiO₂/KB 600JD. This is indicative of partial reduction of Ti⁴⁺ of TiO₂ to form hydrogenated TiO₂ with Ti³⁺ states with oxygen vacancies while annealing in 3% H₂/ 97% Ar reducing atmosphere.^{8, 122} It is worth to note that the defective hydrogenated TiO₂ enhances the electronic conductivity when compared to pristine TiO₂ anatase.^{82, 88, 89} The BE of Ti⁴⁺ and Ti³⁺ states were shifted to higher BE for all the TiO₂ modified carbon supports when

compared to commercial TiO₂ anatase, revealing a strong metal-support interaction between TiO₂ shell and carbon supports.

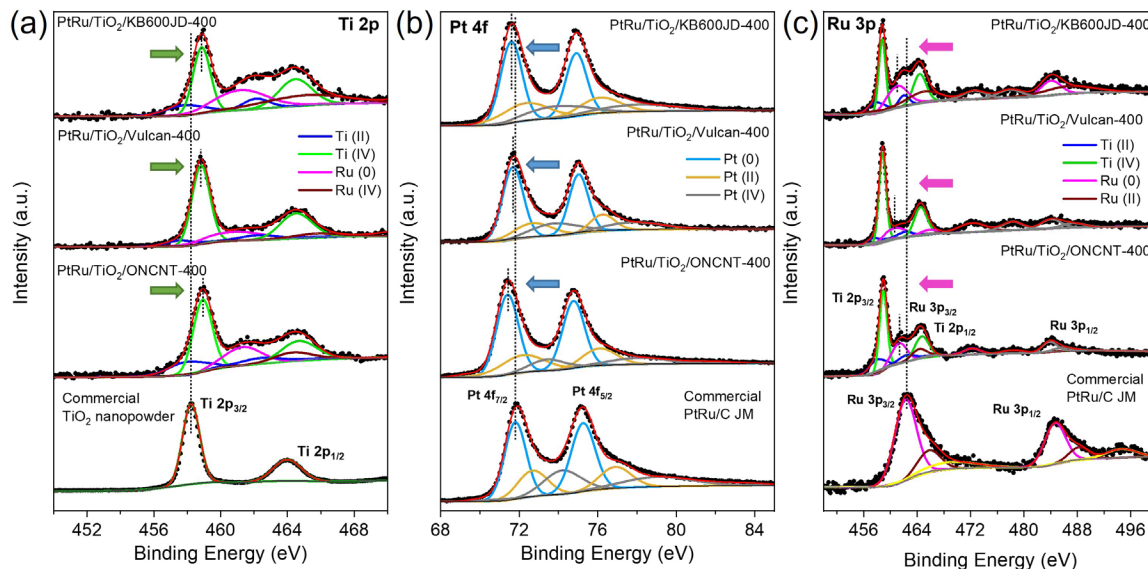


Figure 3.4. XPS analysis of (a) Ti 2p spectra of commercial TiO₂ nano powder, PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400; (b) Pt 4f spectra and (c) Ru 3p spectra of commercial PtRu/C JM, PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400; The legends in each panel apply to all three curves in that panel.

The interaction of PtRu catalyst with TiO₂ support was understood by comparing the XPS spectra of Ti 2p, Pt 4f and Ru 3p for various catalysts as shown in Figure 3.4. Following the deposition of PtRu on TiO₂-modified carbon supports, the Ti 2p spectra were investigated (Figure 3.4 (a)). It is to be noted that, the Ti 2p spectra overlapped with the Ru 3p_{3/2} peaks (at BE of 458.92 eV and 458.02V) spectra for all the PtRu/TiO₂ modified carbon supports. Hence, careful peak fitting was done to deconvolute the Ti 2p and Ru 3p peaks. The Ti 2p spectra of PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB 600JD-400 were deconvoluted in to two pairs of 2p_{3/2} and 2p_{1/2} doublets corresponding to Ti⁴⁺ and Ti³⁺ of TiO₂ and hydrogenated TiO₂, respectively. The binding energy positions are summarized in Table B1 and

B2. There was a significant upshift in BE of Ti^{4+} peak was observed for all the catalysts when compared to the commercial TiO_2 nanopowder and their corresponding TiO_2 modified carbon without PtRu (see Figure B10) suggesting a lower electron density at Ti^{4+} sites likely due to partial electron transfer from Ti^{4+} to PtRu. The Ti $2p_{3/2}$ spectra of PtRu/ TiO_2 /ONCNT-400, PtRu/ TiO_2 /Vulcan-400 and PtRu/ TiO_2 /KB 600JD-400 was shifted to 458.92 eV, 458.80 eV and 458.85 eV, respectively. In addition, the amount of Ti^{3+} states increased in PtRu/ TiO_2 /ONCNT-400, PtRu/ TiO_2 /Vulcan-400 and PtRu/ TiO_2 /KB 600JD-400 when compared to their corresponding TiO_2 modified carbon supports without PtRu (see Figure B10). This reveals that the Pt and Ru nanoparticles catalyzes the reduction process of Ti^{4+} to Ti^{3+} . Table B1 summarizes the relative at% of Ti^{4+} and Ti^{3+} states among different catalysts.

Figure 3.4 (b) shows the Pt 4f spectra of PtRu/ TiO_2 /KB 600JD-400, PtRu/ TiO_2 /Vulcan-400, PtRu/ TiO_2 /ONCNT-400 and commercial PtRu/C JM. The Pt 4f spectra of all the catalysts were deconvoluted into three pairs of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ doublets attributed to Pt(0), Pt^{2+} and Pt^{4+} states in metallic, PtO & $\text{Pt}(\text{OH})_2$, and PtO_2 species, respectively.¹²⁴ The BE of Pt $4f_{7/2}$ of metallic Pt in PtRu/ TiO_2 /ONCNT downshifted to 71.43 eV compared to 71.80 eV in commercial PtRu/C catalyst. This trend was opposite to the trend observed for Ti 2p peaks, indicating a higher electron density at Pt atomic sites in PtRu/ TiO_2 /ONCNT-400 due to partial electron transfer from Ti^{4+} to Pt resulting in strong-metal support interaction (SMSI). Similar peak shifts in Pt 4f to lower BE and Ti 2p to higher BE was reflected in PtRu/ TiO_2 /Vulcan-400 and PtRu/ TiO_2 /KB 600JD-400 revealing the SMSI between TiO_2 and Pt in both catalysts. The peak positions are summarized in Table B2. In Figure 3.4 (c), the Ru 3p spectra of all catalysts were deconvoluted into two pairs of doublets corresponding to Ru(0) and Ru^{4+} in metallic and RuO_2 species, respectively.¹²⁵ The BE of Ru $3p_{3/2}$ of metallic Ru in the three samples shows the similar downshift trend as in Pt 4f peaks

in Figure 3.4 (b), with the lowest value in PtRu/TiO₂/ONCNT-400 (461.02 eV), followed by PtRu/TiO₂/KB 600JD-400 at 461.06 eV and PtRu/TiO₂/Vulcan-400 at 461.25 eV , indicating partial electron transfer from Ti⁴⁺ sites to metallic Ru sites, resulting in SMSI between TiO₂ support and PtRu nanoparticles. Overall, compared to all the PtRu catalysts on TiO₂ modified carbon supports, a greater upshift and downshift in the BE of the Ti 2p and Pt 4f & Ru 3p spectra, respectively, was reported for PtRu/TiO₂/ONCNT-400, indicating higher SMSI in this catalyst.

3.3.3. Assessment of CO oxidation with Anodic CO stripping

As CO is a poisonous intermediate formed during MOR, it is important to investigate the CO oxidation properties of PtRu catalysts deposited on various TiO₂ modified carbon supports. CO stripping studies not only provides the information on kinetics but also provides the electrochemical active surface area (ECSA) of the catalyst by integrating the charge under the CO oxidation curve. The CO oxidation onset potential is assessed when the oxidation current reaches 0.150 mA/cm². We have studied three different commercial catalysts namely PtRu/C JM (71%), PtRu/C TKK (50%) and PtRu/C TKK (77%) with 71%, 50% and 77% of PGM, purchased from Johnson Matthey and Tanaka Kikinzoku International, respectively. Figure 3.5 (a) shows the CO oxidation curves of commercial catalysts. The CO oxidation onset potential of commercial PtRu/C JM, PtRu/C TKK 50% and PtRu/C TKK 77% was found to be present at 0.435 V, 0.415 V and 0.415 V vs. RHE, respectively. The ECSA was found to be 91.7 m²/g, 99.5 m²/g and 82.3 m²/g for PtRu/C JM, PtRu/C TKK 50% and PtRu/C TKK 77%, respectively. Chapter 2 clearly illustrated the beneficial oxophilic nature of the defective hydrogenated TiO₂ in enhancing the CO oxidation kinetics. Hence, we study the effect of TiO₂ shells on different carbon supports in this chapter.

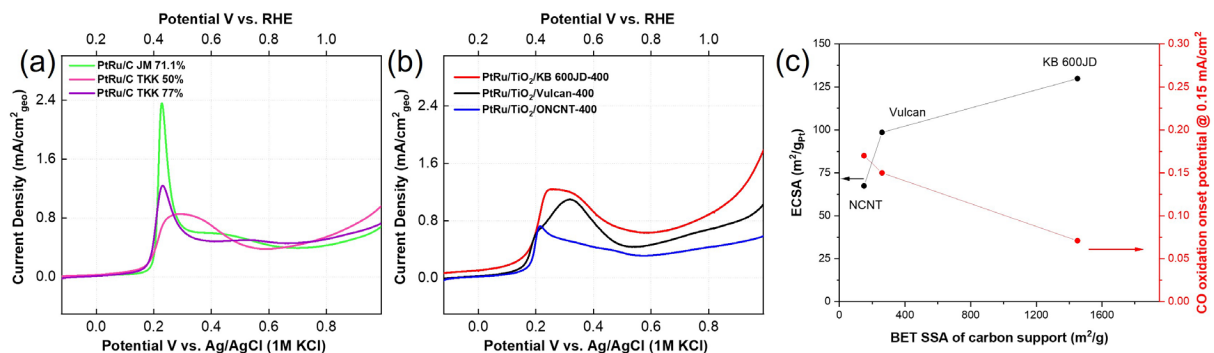


Figure 3.5. First anodic scan of CO stripping voltametric curves of (a) PtRu/C TKK 77%, PtRu/C TKK 50%, PtRu/C JM 71%, (b) PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400 catalysts recorded in Ar-purged 0.5 M H₂SO₄ solution at a scan rate of 10 mV/s. (c) Plot of BET SSA of carbon support vs. ECSA and CO oxidation onset potential at 0.15 mA/cm².

Figure 3.5 (b) shows the first anodic scan of CO stripping voltammetry curve of the PtRu catalysts deposited on various TiO₂ modified carbon supports. Among those, the PtRu/TiO₂/KB 600JD-400 showed the lowest CO oxidation onset potential at 0.319 V vs. RHE. This can be attributed to the smaller and active PtRu alloy nanoparticles obtained due to the high surface area KB 600JD support. This in fact provided a high ECSA of about 133.8 m²/g for the PtRu/TiO₂/KB 600JD-400, owing the abundant exposed PtRu sites for electrocatalytic reaction. The lowest CO oxidation potential and highest ECSA is the desired property of a good electrocatalyst to have high MOR performance. The next best catalysts were PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/ONCNT-400 which had a CO oxidation onset potential at 0.394 V vs. RHE and 0.414 V vs. RHE, respectively. The ECSA was found to be 98.5 m²/g and 67 m²/g, respectively. The ECSA comparison of all catalysts are shown in Figure B11. The CO oxidation onset potential and ECSA had a linear relationship with porosity and BET SSA of the TiO₂ modified carbon supports as shown in Figure 3.5 (c). All of the PtRu catalysts deposited on TiO₂ modified carbon supports

showed enhanced CO oxidation kinetics with lower CO oxidation onset potential when compared to commercial catalysts illustrating the oxophilic effect of TiO_2 .

3.3.4. Assessment of MOR Electrocatalytic Activity

The MOR performance evaluation for all the catalysts were investigated using CV in Ar-saturated 0.50 M H_2SO_4 containing 0.75 M methanol solution at a PGM catalyst loading of 54 $\mu\text{g}/\text{cm}^2$. The MOR onset potential is assessed when the oxidation current reaches 1.50 mA/cm^2 . It is important to mention which cycle of MOR CV curve is chosen to compare different catalysts. Most of the literatures do not provide that information. As will be discussed later in detail, MOR reaction condition is very harsh, and few CV cycles of catalysts in methanol containing electrolyte suffers drastic changes in the surface PtRu composition. Here in, we have used the first MOR CV curve obtained for all the catalysts in Figure 3.6 to investigate the MOR characteristics of the fresh electrocatalyst.

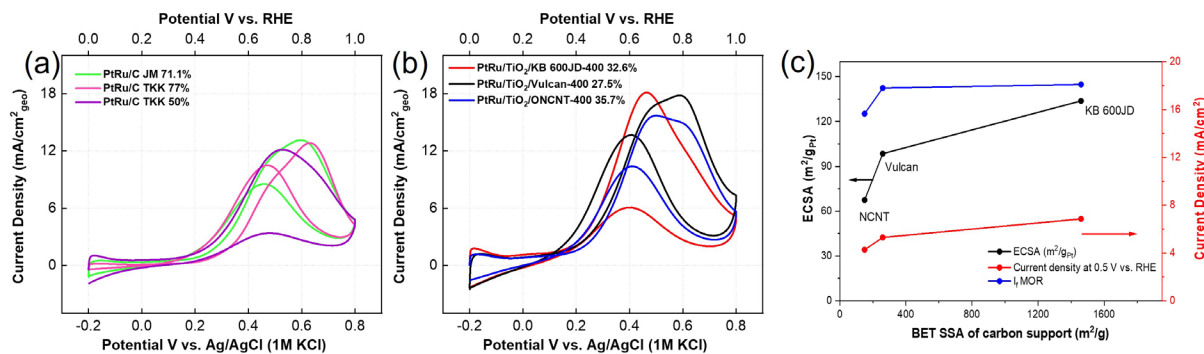


Figure 3.6. First MOR CV curves of (a) PtRu/C TTK 77%, PtRu/C TTK 50%, PtRu/C JM 71%, (b) PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400 catalysts recorded in Ar-purged 0.5 M H_2SO_4 solution containing 0.75M methanol at a scan rate of 50 mV/s. (c) Plot of BET SSA of carbon support vs. ECSA and MOR current density.

Firstly, the MOR performance of commercial catalysts was investigated as shown in Figure 3.6 (a). The PtRu/C JM, PtRu/C TTK 50% and PtRu/C TTK 77% catalysts showed the MOR onset potential of 0.50 V vs. RHE, 0.465 V vs. RHE, and 0.556 V vs. RHE with MOR forward

peak current density (I_f) of 13.1 mA/cm², 12.2 mA/cm², and 12.8 mA/cm², respectively. As mentioned in previous works and chapters, the forward peak current density and backward peak current density is attributed to the methanol oxidation. The I_f/I_b ratio can provide the oxophilicity of the catalyst. The I_f/I_b ratio was found to be 1.54, 1.23 and 3.57 for PtRu/C JM, PtRu/C TKK 77% and PtRu/C TKK 50%, respectively. Among the three commercial catalysts, the PtRu/C TKK 50% showed the lowest MOR onset potential and PtRu/C JM showed the highest I_f . Among the in-house prepared PtRu deposited on various TiO₂ modified carbon supports, the PtRu/TiO₂/KB 600JD-400 showed the lowest MOR onset potential of about 0.375 V vs. RHE and a MOR forward peak current density (I_f) of $\sim$ 18.1 mA/cm². This high performance can be attributed to the high ECSA, and low CO oxidation potential of the catalysts obtained due to the use of highly porous carbon support (KB 600JD) along with the beneficial role of TiO₂. The MOR activity trend was followed by PtRu/TiO₂/Vulcan-400 with an onset potential of 0.40 V vs. RHE with I_f of 17.8 mA/cm². The PtRu/TiO₂/ONCNT-400 had an onset potential of 0.442 vs. RHE with an I_f of 15.7 mA/cm². The I_f/I_b ratio was found to be 2.98, 1.31 and 1.51 for PtRu/TiO₂/KB 600JD-400, PtRu/TiO₂/Vulcan-400, and PtRu/TiO₂/ONCNT-400, respectively. The MOR performance (onset potential and I_f) of all the PtRu deposited on TiO₂ modified carbon supports outperformed the commercial PtRu/C catalysts. This suggests that the better MOR and CO oxidation properties of the catalysts depend directly on the ECSA (PtRu nanoparticle size) and TiO₂ modification which is dependent on the porosity and SSA of the carbon support employed as shown in Figure 3.6 (c). Nevertheless, the TiO₂ modification is quite important as the oxophilic effect was much required for enhancing MOR activity. Figure 3.7 shows the MOR performance of the catalysts at 100th MOR CV curve. The trend in MOR activity and performance of all the catalysts remained the same, however, the MOR onset potential moved to more positive potential with I_f increasing to a

much higher value at 100th cycle. And the MOR I_b peak increased for all catalysts resulting in I_f/I_b ratio of 1.00, 0.97 and 1.11 for PtRu/TiO₂/KB 600JD-400 PtRu/TiO₂/Vulcan-400, PtRu/TiO₂/ONCNT-400, respectively. This is owing to the dissolution of Ru from the alloy and exposing more Pt sites for MOR, respectively, during cycling of catalyst in MOR electrolyte.

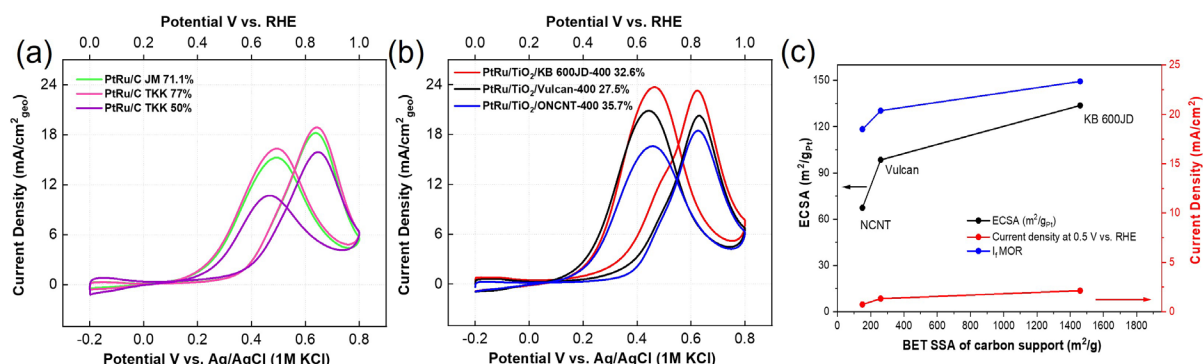


Figure 3.7. 100th MOR CV curves of (a) PtRu/C TKK 77%, PtRu/C TKK 50%, PtRu/C JM 71%, (b) PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400 catalysts recorded in Ar-purged 0.5 M H₂SO₄ solution containing 0.75M methanol at a scan rate of 50 mV/s. (c) Plot of BET SSA of carbon support vs. ECSA and MOR current density.

3.3.5. Understanding the Degradation Mechanism

As MOR is a harsh environment due to the involvement of poisonous CO as intermediate, most of the PtRu catalysts have poor stability over time. Hence, it is important to subject the catalysts for accelerated stress tests (AST). Here in, we performed AST by continuous CV cycling of electrocatalysts in the potential range of 0 to 1.0 V vs. RHE at 50 mV/s scan rate for 500 cycles. In addition to that, we obtained CO stripping voltammogram at different stages of AST CV cycling to study the degradation mechanism of the PtRu catalysts as shown in Figure 3.8 (a). The CO stripping curve provided plethora of information. The CO stripping curves obtained at different stages of AST tests of PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD-400 are compared with commercial PtRu/C JM and PtRu/C TKK catalysts.

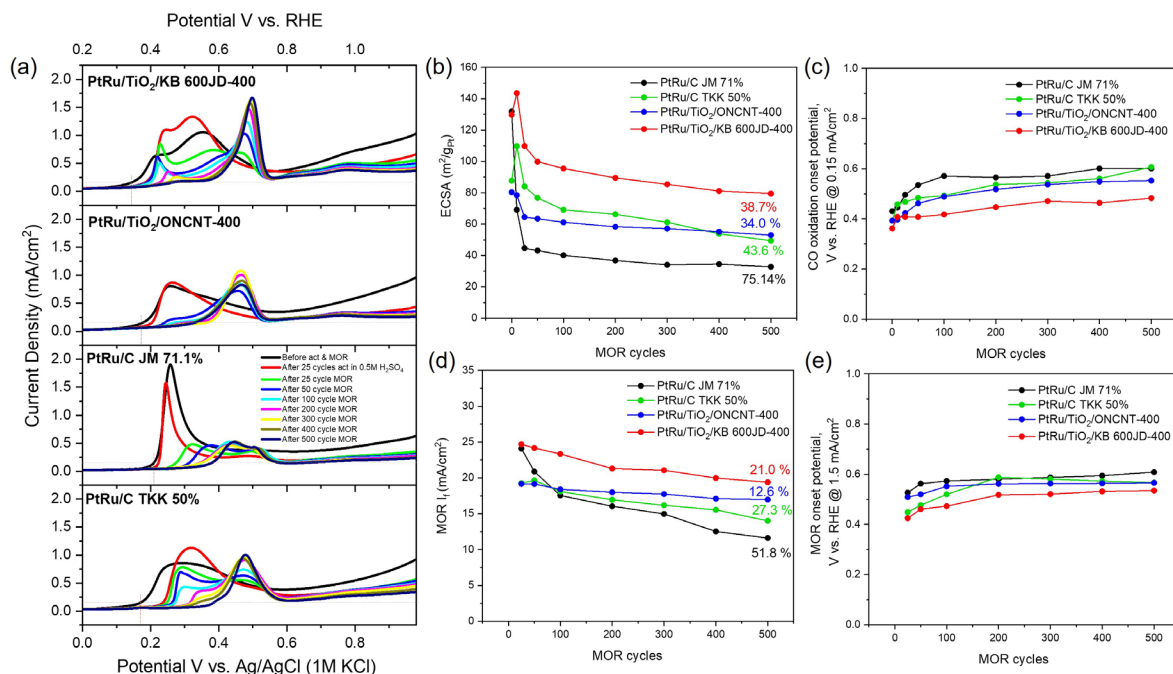


Figure 3.8. (a) CO stripping LSV curves collected at different stages of MOR AST CV cycles for PtRu/C TKK 50%, PtRu/C JM 71%, PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD-400 catalysts. (b) Plot of change in ECSA, (c) plot of change in CO oxidation onset potential, (d) plot of change in MOR I_r and (e) plot of change in MOR onset potential at different stages of the MOR AST CV cycling for PtRu/C TKK 50%, PtRu/C JM 71%, PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD-400 catalysts. AST protocol: CV curves were collected in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s in a potential window from 0V to 1.0 V vs. RHE for 500 cycles. The CO stripping LSV curves were collected in Ar-purged 0.50 M H₂SO₄ at a scan rate of 10 mV/s. All the catalysts were tested at 54 μg/cm² at I/carbon ratio of 0.4.

The first CO stripping curve provides understandings about the fresh catalyst surface before methanol oxidation as shown in Figure 3.5. (a) and (b). From Figure 3.8 (a) (see red curve), after CV activation in 0.50 M H₂SO₄, the ECSA increased by 10.5% and 25% for PtRu/TiO₂/KB 600JD-400 and PtRu/C TKK 50%, respectively owing to more exposed Pt sites due to Ru dissolution or activation of Pt catalysts. However, for PtRu/TiO₂/ONCNT-400 and PtRu/C JM, the ECSA decreased by 2.5% and 47.9%, respectively. By performing just 25 CV cycles in MOR containing electrolytes caused ~24.5%, 35.4%, 23.5% and 17.7% loss in ECSA for PtRu/C TKK 50%, PtRu/C JM, PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400, respectively (see green

curve in Figure 3.8 (a)). Relatively lower ECSA loss was observed for PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400 after first 25 MOR CV cycles, depicting the efficacy of TiO₂ in strongly anchoring the PtRu nanoparticles compared to the commercial catalysts. In addition, CO oxidation onset potential starts to shift to positive potentials for all catalysts with changes in peak shape indicating change in surface PtRu composition (see green curve for all catalysts in Figure 3.8 (a)). In all the catalysts, the CO oxidation peak shape changed from a single sharp/broad peak to two broad peaks after 25 MOR CV cycles. The CO oxidation peak at low potential can be attributed to the exposed PtRu alloy lattices and the peak at the higher potentials can be attributed to the exposed Pt lattice.¹⁴⁶ Looking at the shift in CO oxidation onset potential, it is likely that Ru metal dissolution starts as soon as the electrode is cycled in methanol containing electrolyte. It is to be noted that after 25 MOR CV cycles, the shift in CO oxidation onset potential was lower for PtRu/TiO₂/KB 600JD-400 (0.408 V vs. RHE) and PtRu/TiO₂/ONCNT-400 (0.423 V vs. RHE) when compared to PtRu/C JM (0.496 V vs. RHE) and PtRu/C TKK 50% (0.468 V vs. RHE), depicting the SMSI provided by defective hydrogenated TiO₂ to PtRu nanoparticles.

By further AST MOR CV cycling till 500 cycles, the CO oxidation onset potential further shifted to positive potentials. And the intensity of current density of CO oxidation peak at low potential (corresponding to PtRu lattice) decreases and the intensity of current density of CO oxidation peak at high potential (corresponding to Pt lattices) increases from 25th to 500th MOR CV cycles. This indicates the slow dissolution of Ru atoms and exposure of more Pt sites. Towards the end of MOR CV cycling ~ 400th and 500th cycle, the ECSA loss started to decrease owing to the agglomeration of Pt nanoparticles. Interestingly, except for PtRu/C JM, other three catalysts PtRu/C TKK, PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400 had their CO stripping curves at different stages of AST crossing a common point at ~0.43 V, similar to an isosbestic

point. This shows the degradation of the catalysts begins with dissolution of unstable Ru metal and eventually leading to exposure of more Pt sites and agglomeration at higher MOR CV cycle numbers.

The changes in the ECSA and CO oxidation onset potential during the 500 MOR CV cycles for KSU made catalysts and commercial catalysts are shown in Figure 3.8 (b) and (c), respectively. At the end of AST studies, the commercial PtRu/C JM and PtRu/C TKK catalysts showed 75.1% and 43.6% loss in ECSA with 170 mV and 214 mV shift in CO oxidation onset potential at 0.15 mA/cm², respectively, indicating severe Ru dissolution during MOR CV cycling. At similar AST condition, the PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD-400 showed a 34.0% and 38.7% loss in ECSA with 160 mV and 121 mV shift in CO oxidation onset potential, respectively. With carbon support changing from graphitic (ONCNT) to amorphous (KB 600JD) the loss in ECSA slightly increased. But it is interesting to note that the rate of Ru atom dissolution was slow in PtRu/TiO₂/KB 600JD-400 when compared to PtRu/TiO₂/ONCNT-400, while looking at the green, blue, cyan and pink colors of CO stripping curves in Figure 3.8 (a). It is critical to have high ECSA and less shift in CO oxidation peak potential to have enhanced CO and MOR oxidation kinetics for longer period of time. The TiO₂ modified carbon supported catalysts showed less loss in ECSA and less shift in CO oxidation onset potential when compared to commercial PtRu/C catalysts, showing the critical role of TiO₂ in providing SMSI revealed by XPS studies, in enhancing the durability of electrocatalysts.

Such dissolution of Ru evidenced in CO stripping curves affects the MOR reaction parameters such as MOR onset potential and MOR I_f as shown in Figure 3.8 (d) and (e). The PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD showed a 12.6% and 21.0% loss in I_f when compared to PtRu/C JM (51.8% loss) and PtRu/C TKK (27.3% loss), respectively. Overall stability

performance of these four catalysts are compared in bar graph in Figure 3.9 (a). Even when comparing the CO stripping curve obtained after the AST study (Figure 3.9 (b)), the PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400 possess low CO oxidation onset potential when compared to commercial PtRu/C catalysts. The PtRu nanoparticle size and morphology after 500 AST CV cycles were examined by TEM. Figure 3.10 and Figure B12 compares the TEM images of commercial PtRu/C JM and PtRu/C TKK catalysts at fresh and after AST cycles. It is clearly seen that after 500 AST cycle, more bare carbon support was exposed while some PtRu nanoparticles agglomerated into larger nanoparticles. The average agglomerated nanoparticle size was found to be 7.1 nm $\pm$ 3.3 nm and 5.5 nm $\pm$ 2.2 nm for PtRu/C JM and PtRu/C TKK 50% with 162.9% and $\sim$ 22.2% increase in size, respectively. The TEM imaging of in-house PtRu catalysts deposited on TiO₂ modified carbon supports after AST cycles are in progress.

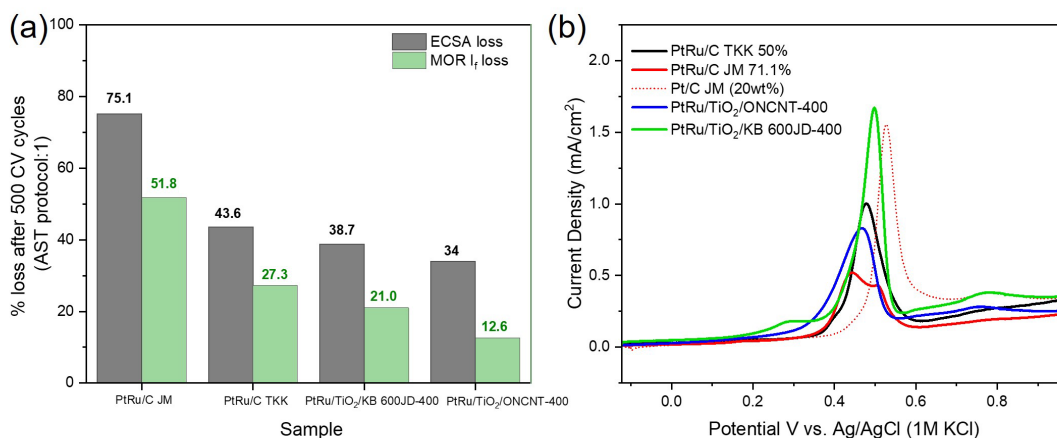


Figure 3.9. (a) Bar graph comparison of % loss of ECSA and MOR I_f for PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/KB600JD-400, PtRu/C TKK and PtRu/C JM after 500 MOR AST CV cycles in protocol 1. (b) Comparison of anodic scan of CO stripping voltammetric curves of (a) PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/KB600JD-400, PtRu/C JM and PtRu/C TKK after 500 MOR AST CV cycles in protocol 1.

It is to be noted that, the AST CV protocol used in Figure 3.9 was performed at much wider potential window with higher upper potential of 1.0 V vs. RHE in CV which is a very harsh

condition for an anode electrocatalyst. Anode in DMFC is anticipated to reach a maximum of 0.5V vs. SHE during normal operation.¹⁴⁷ Testing the anode electrocatalysts at high potentials results in dissolution of unstable Ru which may exaggerate the losses reported in performance. Hence, the AST protocol was revised to use a low upper potential (0.5 V vs. RHE) in CV to translate the typical DMFC operation. New AST protocol: CV cycling was done in 0V to 0.5 V vs. RHE window at 0.5 V/s scan rate for 1000 cycles, was followed from literature.¹⁴⁷ Durability studies for one of the best catalysts PtRu/TiO₂/KB 600JD-400 and one commercial catalysts, PtRu/C JM, were done using the new revised AST protocol. Similar CO stripping curves were collected at different stages of MOR AST CV cycling to understand the degradation mechanism of the catalysts as shown in Figure 3.11 (a).

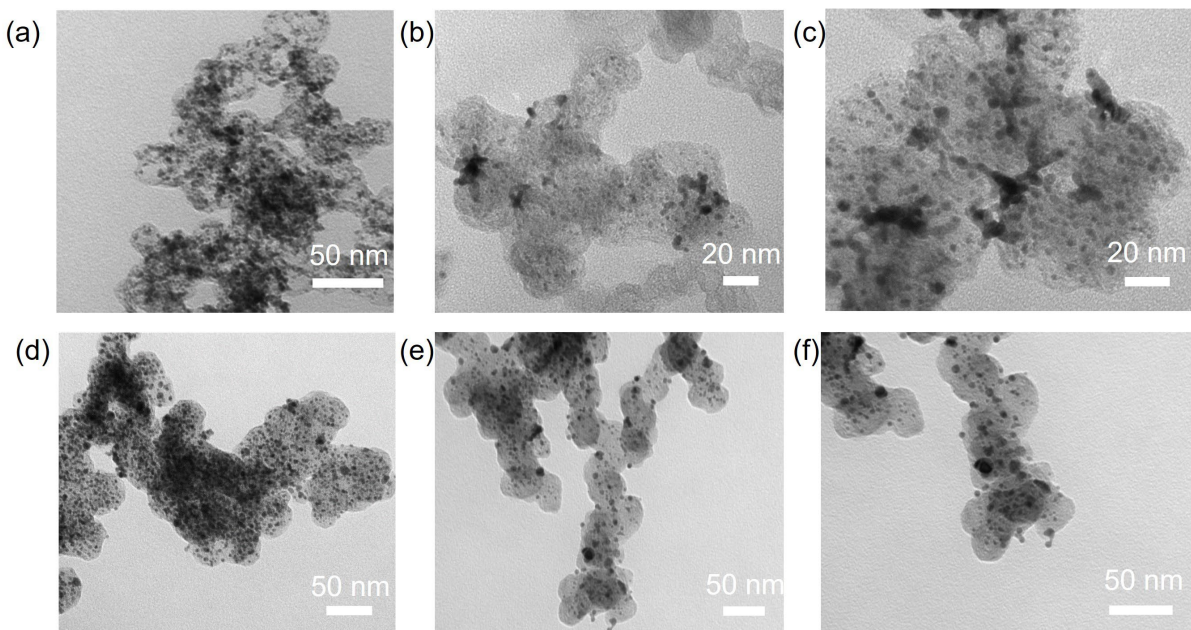


Figure 3.10. TEM image of (a) fresh PtRu/C JM, (b) and (c) PtRu/C JM after 500 MOR AST CV cycles. TEM image of (d) fresh PtRu/C TTK 50%, (e) and (f) PtRu/C TTK 50% after 500 MOR AST CV cycles.

Figure 3.11 (b) and (c) shows the change in ECSA and shift in CO oxidation onset potential by continuous AST CV cycles. Similar to previous AST protocol, a steep drop in ECSA was observed for PtRu/C JM catalyst during the initial MOR CV cycling showing the dissolution of

unstable Ru. Unlike previous AST protocol, the rate of dissolution of Ru was further decreased in PtRu/TiO₂/KB 600JD-400 (see green, blue, cyan and pink CO stripping curves in Figure 3.11 (a)). Compared to PtRu/C JM (63.5% ECSA loss and 113 mV shift in CO oxidation onset potential), PtRu/TiO₂/KB 600JD-400 demonstrated lower ECSA loss (35.4%) and lower shift in CO oxidation onset potential (52 mV) as shown in Figure 3.11 (b)-(c) and Figure 3.12 (b).

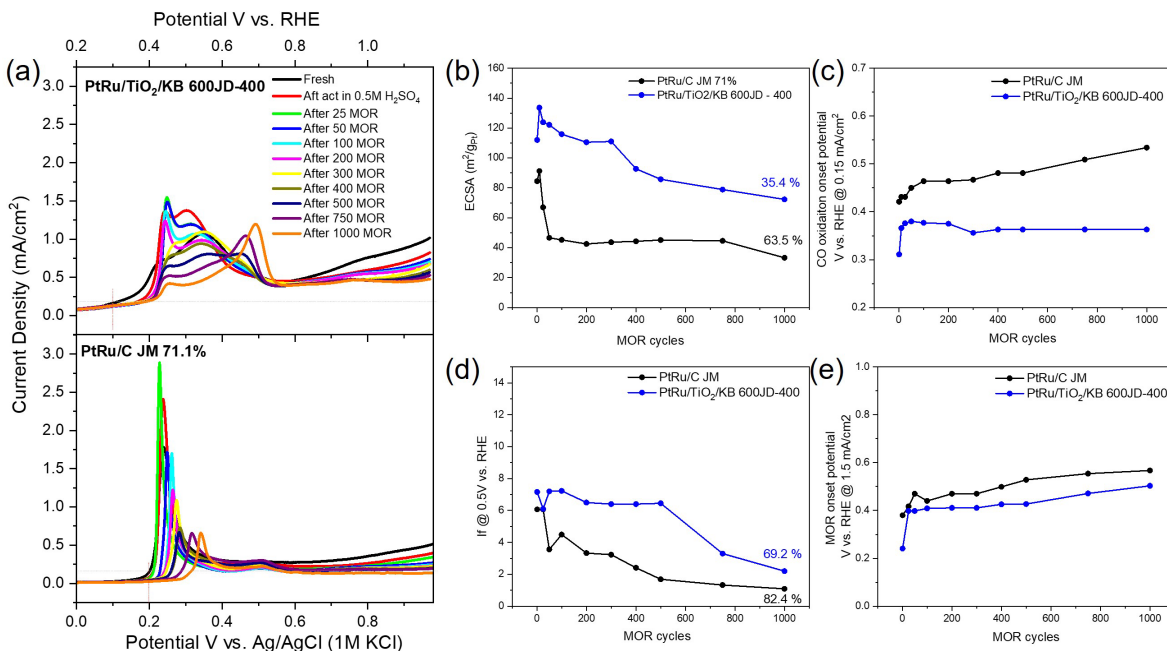


Figure 3.11. (a) CO stripping LSV curves collected at different stages of MOR AST CV cycles for PtRu/C JM 71% and PtRu/TiO₂/KB 600JD-400 catalysts. (b) Plot of change in ECSA, (c) plot of change in CO oxidation onset potential, (d) plot of change in MOR I_r and (e) plot of change in MOR onset potential at different stages of the MOR AST CV cycling for PtRu/C JM 71% and PtRu/TiO₂/KB 600JD-400 catalysts. AST protocol: CV curves were collected in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 500 mV/s in a potential window from 0V to 0.50 V vs. RHE for 1000 cycles. The CO stripping LSV curves were collected in Ar-purged 0.50 M H₂SO₄ at a scan rate of 10 mV/s. All the catalysts were tested at 54 μg/cm² at I/carbon ratio of 0.4.

The rate of degradation of electrocatalysts in new AST protocol has significantly reduced due to the reduction in upper potential. However, the trend in catalyst durability losses remained the same. The changes in MOR current at 0.5V vs. RHE (I_{at 0.5V vs. RHE}) was monitored, as that

translates the maximum current that can be obtained in typical DMFC. The changes in MOR $I_{\text{at } 0.5 \text{ V vs. RHE}}$ and change in MOR onset potential over 1000 CV cycles is shown in Figure 3.11 (d) and (e). There was 82.4% loss in MOR $I_{\text{(at } 0.5 \text{ V vs. RHE)}}$ for PtRu/C JM and 69.2% loss in MOR $I_{\text{(at } 0.5 \text{ V vs. RHE)}}$ for PtRu/TiO₂/KB 600JD-400. After the 1000 AST cycles, the CO oxidation kinetics and ECSA was higher for PtRu/TiO₂/KB 60JD-400 when compared to PtRu/C JM (see Figure 3.12 (a)). Unlike the first AST protocol where the MOR I_f kept on decreasing over MOR CV cycling, in the new AST protocol the MOR I_f showed significant increase in current values accompanied by > 200 mV positive shift in MOR onset potential after 1000 AST CV cycles (see Figure 3.12 (c) and (d)).

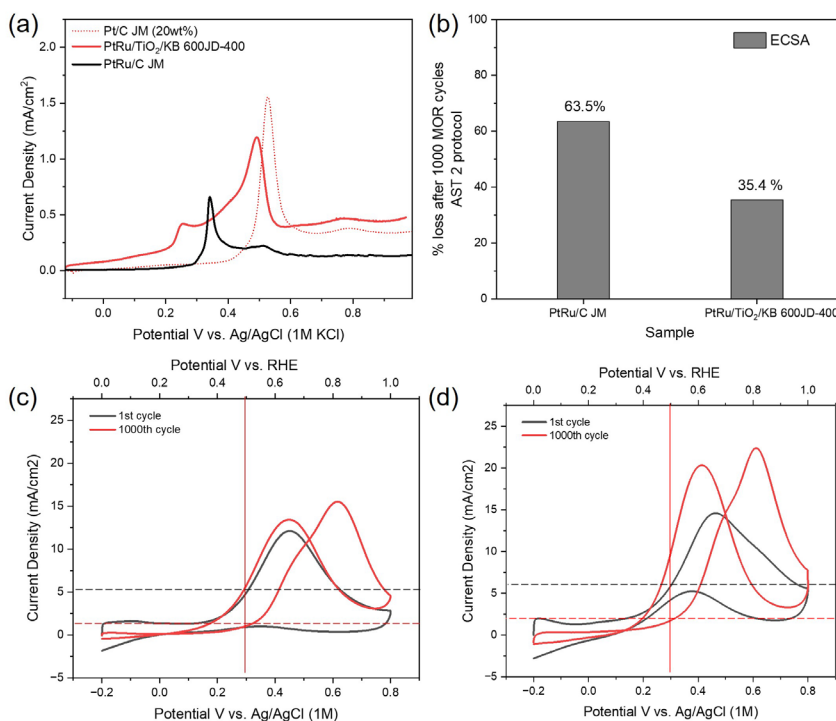


Figure 3.12. Comparison of anodic scan of CO stripping voltametric curves of (a) PtRu/TiO₂/KB600JD-400, PtRu/C JM and Pt/C catalysts recorded in Ar-purged 0.5 M H₂SO₄ solution at a scan rate of 10 mV/s after 1000 MOR AST CV cycles in protocol 2. (b) Bar graph comparison of % loss of ECSA for PtRu/TiO₂/KB600JD-400 and PtRu/C JM. Comparison of 1st and 1000th MOR CV cycle of (c) PtRu/C JM and (d) PtRu/TiO₂/KB600JD-400.

Overall, the TiO₂ modified carbon supported catalysts were able to show enhanced durability and MOR kinetics when compared to commercial catalysts owing to SMSI provided by TiO₂.

3.3.6. Full DMFC Performance Evaluation

Inspired by the enhanced MOR activity and stability of the in-house prepared anode in the half-cell tests, the methanol-air DMFC full cells were conducted for the same. The best performing anode catalysts with different carbon support nanostructures such as PtRu/TiO₂/KB600JD-400 and PtRu/TiO₂/ONCNT-400 were tested with various methanol feed concentrations. Both the anode and cathode were spray-coated on to Toray H060 gas diffusion layer (GDL) at ionomer to carbon ratio of 1.0 and 0.2, respectively. The PGM loading of anode and cathode were maintained at 4.5 mg/cm² and 1.5 mg/cm², respectively. Nafion 212 membrane with 50 µm thickness was used in this study. The anode and cathode GDEs were sandwiched between Nafion 212 membrane and hot-pressed at 275 °F for five minutes to form a membrane electrode assembly (MEA). Figure B14 shows the schematic of MEA and its components. The DMFC was fed with various concentrations of methanol feed as fuel at a flow rate of 0.5 mL/min at the anode and oxygen or air as fuel at 0.1 L/min at the cathode. The DMFC stack temperature was maintained at 80 °C, 90 °C and 100 °C. The performance always increases with increasing temperature owing to the enhanced kinetics at high temperatures.

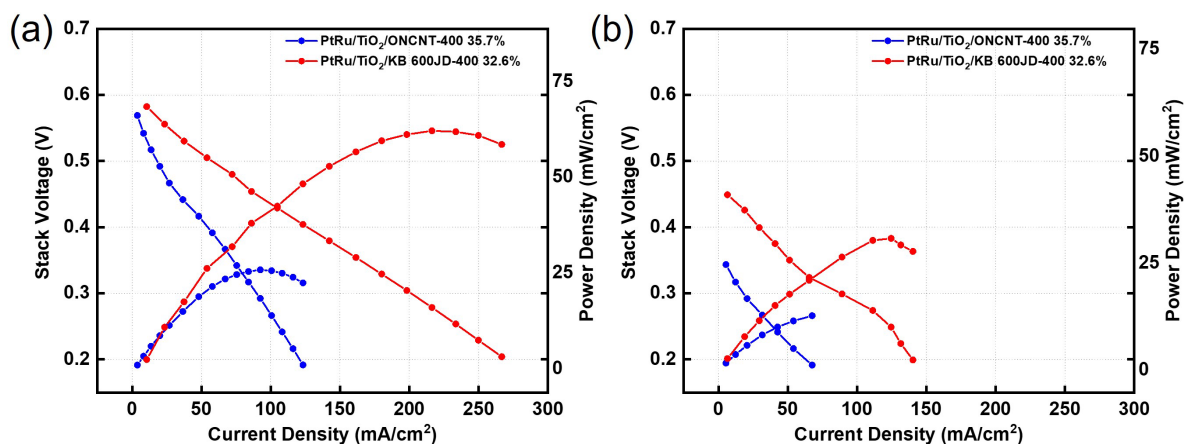


Figure 3.13. DMFC performance curves of PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/KB 600JD-400 catalysts in (a) 1.0 M methanol solution and (b) 3.0 M methanol solution with Pt/C JM 60% cathode. The anode and cathode catalyst loadings were 4.5 mg_{PtRu}/cm² and 1.5 mg_{Pt}/cm², respectively. Test conditions: cell temperature at 80.0 °C, at 1 mL/min methanol and 0.1 L/min air flow rate with 0.5 bar back pressure. Nafion 212 membrane was used and ionomer/carbon ratio of 1.0 and ionomer/Pt of 0.2 was maintained at anode and cathode, respectively. Credit: DMFC tests were done by Nathan in Dr. Xianglin Li's lab at KU.

Figure 3.13 (a) and (b) shows the polarization plots of DMFC using in-house prepared anodes and commercial Pt/C (60 wt%) catalyst at 1.0 M methanol and 3.0 M methanol feed, respectively, obtained at 80 °C with 50 kPa back pressure. The MEA with PtRu/TiO₂/KB 600JD-400 anode and commercial Pt/C cathode showed the highest $P_{\max}$ of 63.3 mW/cm² when compared to the MEA with PtRu/TiO₂/ONCNT-400 anode (27.2 mW/cm² of PPD) at 1.0 M methanol concentration. An OCV of about 0.58 V and 0.57 V was achieved for PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400, respectively, indicating similar methanol crossover effects in both MEAs at 1.0 M methanol feed. The major degradation was observed in the ohmic (see mid current density region) and mass transport region (see high current density region) of PtRu/TiO₂/ONCNT-400's polarization curve. This directly correlates to the anode catalyst support architecture, which governs the mass transport of fuel in DMFC. The nanofibrous structure of NCNTs may be beneficial for better transport, however, at an optimum anode catalyst layer thickness. If the anode

catalyst layer thickness becomes large, then the DMFC may suffer from severe ohmic and mass transport resistance. In the case of PtRu/TiO₂/ONCNT-400, the anode catalyst loading of 4.5 mg/cm² is quite massive (compared to anodes of conventional hydrogen fuel cell) and has a thickness ~ 50 to 60 µm with the 32% PGM and 57% carbon support composition. As DMFC has poor anode and cathode reaction kinetics due to CO poisoning, higher loading of PGM catalyst is used to achieve decent performances. In addition, the catalyst layer requires an optimum amount of ionomer dispersed around the catalyst layer to provide proton transfer and enough binding for improved stability. But the ionomer is not electrically conductive, hence requires careful optimization to avoid ohmic resistance caused by ionomer on the catalyst layer. There is a tradeoff between the ionomer to carbon ratio and catalyst layer thickness to achieve a low ohmic resistance and a low mass transport resistance from the catalyst layer. In addition, efficient removal to CO₂ produced during the MOR is necessary which may cause severe mass transport losses, which is further complicates the DMFC study. Hence, the high performance of PtRu/TiO₂/KB 600JD-400, compared to PtRu/TiO₂/ONCNT-400, can be attributed to the high intrinsic catalytic activity with optimum PtRu catalyst morphology and the favorable porosity and catalyst layer thickness provided by the TiO₂ modified KB 600JD.

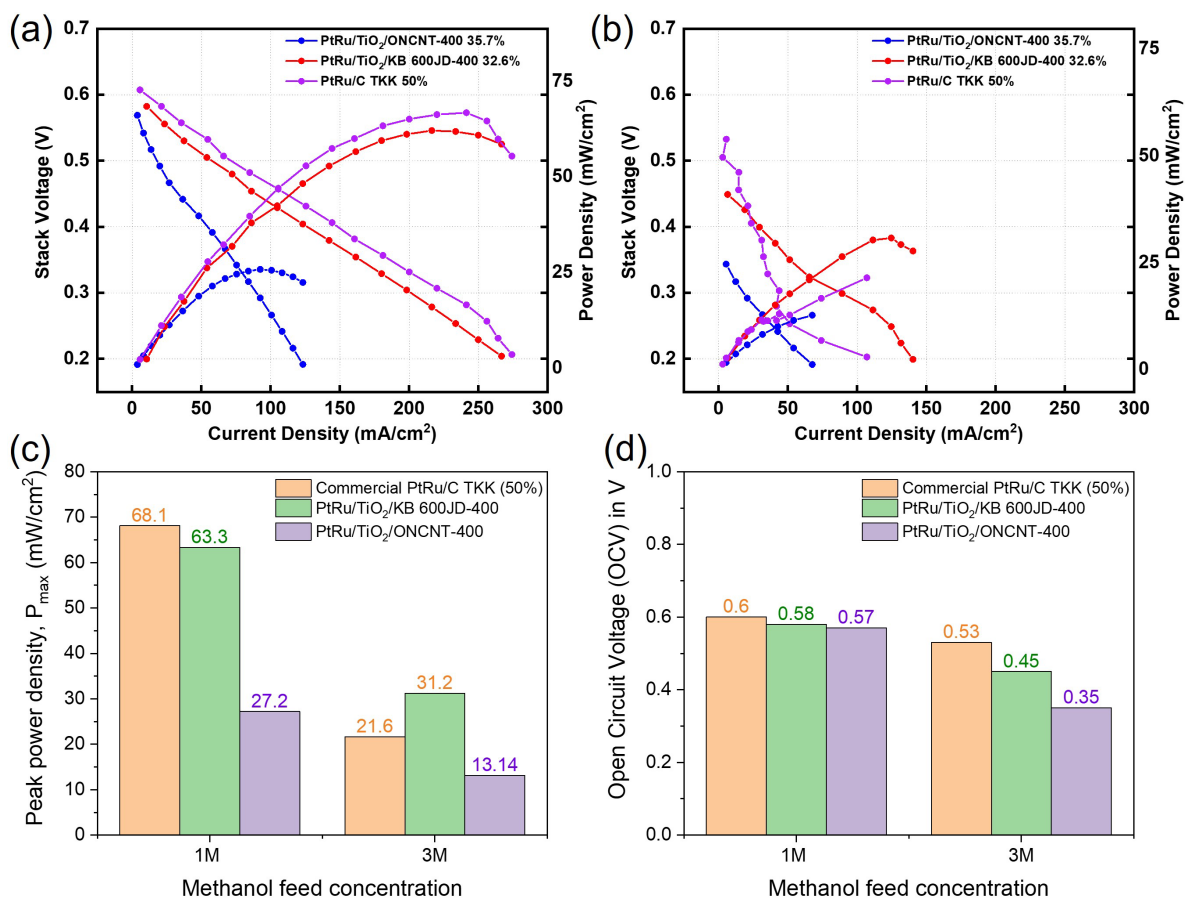


Figure 3.14. DMFC performance curves of PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/KB 600JD-400 and PtRu/C TTK 50% catalysts in (a) 1.0 M methanol solution and (b) 3.0 M methanol solution with Pt/C JM 60% cathode. (c) Bar graph comparing the P_{max} of various catalysts at different methanol feed concentration. (d) Bar graph comparing the OCV of various catalysts at different methanol feed concentration. The anode and cathode catalyst loadings were 4.5 mg_{PtRu}/cm² and 1.5 mg_{Pt}/cm², respectively. Test conditions: cell temperature at 80.0 °C, at 1 mL/min methanol and 0.1 L/min air flow rate with 0.5 bar back pressure. Nafion 212 membrane was used and ionomer/carbon ratio of 1.0 and ionomer/Pt of 0.2 was maintained at anode and cathode, respectively, in all the fuel cell tests. Credit: DMFC tests were done by Nathan in Dr. Xianglin Li's lab at KU.

When the methanol feed concentration was increased to 3.0 M, the DMFC performance was reduced owing to the methanol crossover from anode to cathode. Because the cathode used in these studies is commercial Pt/C, it suffers from significant voltage loss due to the mixed potential from the ORR and the MOR at the cathode. This is reflected in the OCV drop in the MEAs (see

Figure 3.14 (c) and (d)). The OCV of MEA with PtRu/TiO₂/KB 600JD-400 anode and MEA with PtRu/TiO₂/ONCNT-400 anode dropped from 0.58 V to 0.45 V and 0.57 V to 0.34 V, respectively, when the methanol feed concentration increased to 3.0 M. Similarly, the $P_{\max}$ of PtRu/TiO₂/KB 600JD-400 and PtRu/TiO₂/ONCNT-400 reduced from 63.3 mW/cm² to 31.2 mW/cm² and 27.2 mW/cm² to 13.1 mW/cm², respectively, when the methanol feed concentration increased (see Figure 3.14). Both the MEAs with in-house prepared anode catalysts showed ~ 50% drop in performance. The obtained performances of in-house prepared anodes were compared with the MEA prepared with commercial PtRu/C anode (TKK 50%) and commercial Pt/C cathode, as shown in Figure 3.14 (a) and (b). The commercial PtRu/C anode showed a slightly higher $P_{\max}$ of 68.1 mW/cm² and OCV of 0.60 V at 1.0 M methanol feed concentration when compared to PtRu/TiO₂/KB 600JD-400. However, when the methanol feed concentration increased to 3.0 M, the $P_{\max}$ significantly reduced from 68.1 mW/cm² to 20 mW/cm², translating to a performance loss of about ~ 70% in MEA with commercial PtRu/C anode. Figure 3.14 (c) and (d) shows the comparison of changes in $P_{\max}$ and OCV of different catalysts at various methanol concentration feed. The relatively high performance of PtRu/TiO₂/KB 600JD-400 (32.6%) at higher concentration methanol feed indicates the selectivity of the catalyst to methanol and the efficacy of hydrogenated defective TiO₂ modification on carbon supports in providing oxophilic and hydrophilic property in reducing methanol crossover. The hydrophilic properties of TiO₂ are found to reduce methanol permeability and crossover in TiO₂ composite Nafion membranes.^{139, 148, 149}

The hydrophilic catalyst layers with metal oxides would remain with higher water content. Such high-water content at the catalyst layer can locally dilute methanol to lower the concentration to some extent at the interface of the anode catalyst layer-membrane, which can result in mitigating methanol crossover to the cathode, as the methanol concentration gradient will be reduced.¹³²

Similar principle has been used by Wu et.al to improve the passive DMFC performance using neat methanol through applying silica nanoparticles coated membrane to sustain high water retention at the interface of catalyst layer-membrane.¹⁵⁰

The reason for the slightly lower performance of MEA with PtRu/TiO₂/KB 600JD-400 anode compared to MEA with commercial PtRu/C anode at 1.0 M methanol feed can be attributed to the mass transport loss in the anode compartment of KB 600JD MEA. As mentioned previously, the catalyst layer thickness and porosity play a major role in governing the mass transport resistance. It should be noted that commercial PtRu/C TTK 50% and PtRu/TiO₂/KB 600JD-400 contain roughly 57% and 49% carbon, respectively. Catalysts with a higher carbon content will have a thicker catalyst layer, which would compromise mass transfer. Considering all these factors, it is critical to have lower catalyst layer thickness with high micropores and optimum PtRu morphology with high intrinsic catalytic activity to achieve high performance in DMFC. In order to have thin catalyst layer thickness, one of the best ways is to increase the PGM to carbon ratio in the catalyst. Hence, we prepared another catalyst using same synthesis procedure but with ~50% PGM and ~35% carbon denoted as PtRu/TiO₂/KB 600JD-400 (47.5%). The materials and electrochemical characterization of PtRu/TiO₂/KB 600JD-400 (47.5%) is shown in Figure B13. The average PtRu particle size increased to 3.5 ± 0.8 nm compared to PtRu/TiO₂/KB 600JD-400 (32.6%). This is because of increased agglomeration of PtRu during annealing with the excess 20% PGM present on carbon. The half-cell MOR activity was slightly lower than PtRu/TiO₂/KB 600JD-400 (32.6%) in terms of MOR onset potential and I_f (see Figure B13 (c)). However, the MOR activity in half-cell of PtRu/TiO₂/KB 600JD-400 (47.5%) was better than PtRu/TiO₂/Vulcan-400, PtRu/TiO₂/ONCNT-400 and other commercial PtRu/C catalysts, hence we tested this catalyst in DMFC.

Figure B15 shows the DMFC polarization curves for the MEA with PtRu/TiO₂/KB 600JD-400 (47.5%) anode compared to other in-house prepared anode MEAs and commercial MEAs. P_{max} of about 44.8 mW/cm² was achieved at 80 °C with 1.0 M methanol feed concentration for the PtRu/TiO₂/KB 600JD-400 (47.5%) anode. However, the P_{max} was lower than PtRu/TiO₂/KB 600JD-400 (32.6%). When the methanol feed concentration was increased to 3.0 M, the P_{max} was reduced to 24.1 mW/cm² translating to a P_{max} loss of ~ 46%. This further indicates the high selectivity or reduced methanol crossover at 3.0 M methanol concentration when PtRu/TiO₂/KB 600JD-400 was employed as anode when compared to commercial PtRu/C TTK anode. Due to the complication of methanol crossover, it is difficult to study the effect of anode catalyst support in DMFC performance at high methanol concentration using Pt/C cathodes. To clearly understand the effects of anode catalyst support structure in DMFC and to take advantage of the high energy density that pure methanol may offer, strategies to limit the impacts of methanol crossover must be developed. This is because methanol crossover at high methanol concentration compromises the achievable high-power density of DMFC. Several studies have been reported on developing methanol tolerant cathode or membranes which can reduce the diffusion of methanol from anode to cathode.^{138, 148} On this line, we have employed PGM-free methanol tolerant cathodes prepared by one of our collaborators (Dr. Gang Wu group at SUNY, Buffalo) to be paired with the in-house prepared PtRu/TiO₂/C anode catalysts.

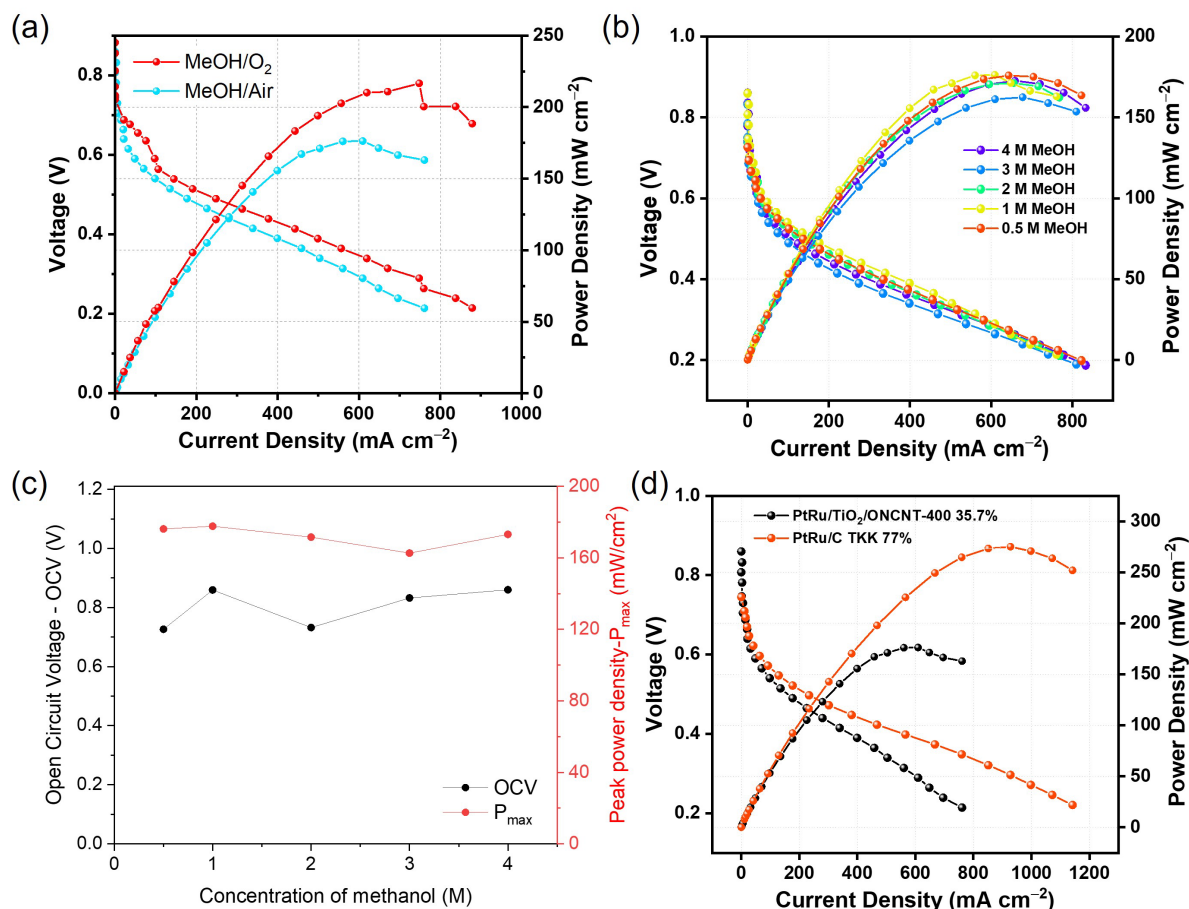


Figure 3.15. DMFC polarization curve MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode (a) at 1.0 M methanol feed concentration with oxygen and dry air as cathode feed. (b) in different methanol feed concentrations at dry air as cathode feed (c) Comparison of OCV and P_{max} of PtRu/TiO₂/ONCNT-400 anode at different methanol feed concentration from (b). (d) Comparison of DMFC polarization curves of MEA with PtRu/C TKK 77% anode and MEA with PtRu/TiO₂/ONCNT-400 anode with Fe-N-C-FG cathode. Fuel cell test conditions: The anode and cathode catalyst loadings were 4.0 mg_{PtRu}/cm² and 4.2 mg/cm², respectively. Cell temperature at 100.0 °C, at 0.5 mL/min methanol and 0.5 L/min air or oxygen flow rate with 2.5 bar back pressure. Nafion 212 membrane was used and ionomer/carbon ratio of 0.8 was maintained for anode and cathode in all the fuel cell tests. Credit: DMFC tests were done by Dr. Yachao in Dr. Gang Wu's lab at UB.

Atomically dispersed single metal atom coordinated with nitrogen atoms in carbon matrix, i.e., are called M-N-C catalysts (M=Fe, Co, Mn, etc). These M-N-C catalysts have been found to provide promising ORR activity and are successful cathodes in PEM based fuel cells such as hydrogen PEMFC and DMFC. Researchers from Los Alamos National Laboratory developed the

first M-N-C catalysts, based on iron salt and polyaniline (PANI) to derive Fe-N-C ORR catalyst by pyrolysis.¹⁵¹ The Fe-N-C and Co-N-C catalysts are reported to have methanol tolerance to employ as cathodes in DMFC to overcome the effects of methanol crossover. Shi et. al, reported the use Co-N-C as cathode in DMFC to show the reduced performance loss with increasing methanol concentration compared to Pt based cathodes.¹³⁸ Here in, we have employed a state-of-the-art M-N-C based on Fe-N-C-FG prepared by Dr. Gang Wu's group as cathode to test the effects of in-house anode catalyst support architecture in DMFC performance.

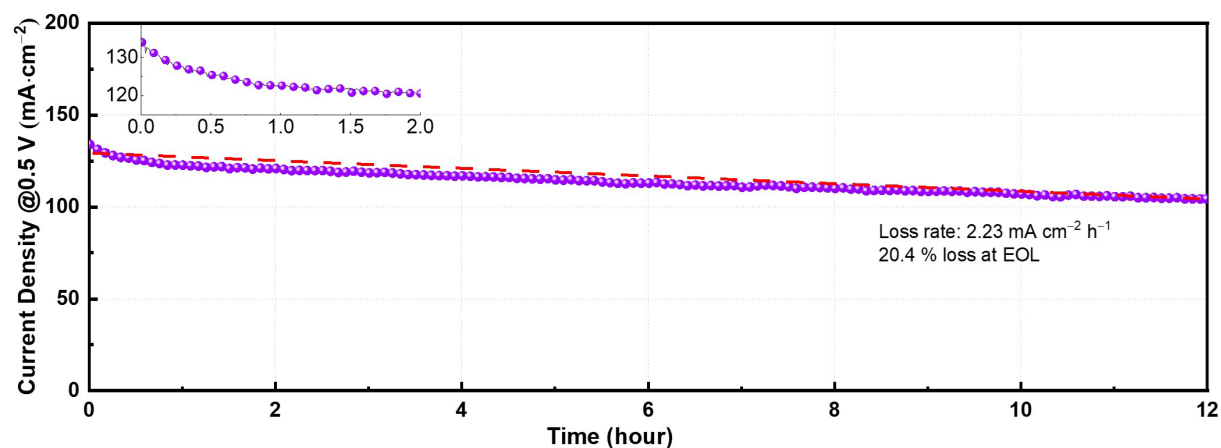


Figure 3.16. DMFC stability data at a constant voltage of 0.5 V for PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode. The anode and cathode catalyst loadings were 4.0 mg_{PtRu}/cm² and 4.2 mg/cm², respectively. Test conditions: cell temperature at 100.0 °C, at 0.5 mL/min methanol and 0.5 L/min air flow rate with 2.5 bar back pressure. Nafion 212 membrane was used and ionomer/carbon ratio of 0.8 was maintained for anode and cathode in all the fuel cell tests. Credit: DMFC tests were done by Dr. Yachao in Dr. Gang Wu's lab at UB.

Figure 3.15 (a) shows the DMFC polarization curve of MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG (PGM-free) cathode at 100 °C with 1.0 M methanol feed and different cathode feed (dry air or oxygen). Both the anode and cathode were prepared by spray coating catalysts on membrane (otherwise called as catalyst coated membrane (CCM) technique). As electrodes (anode/cathode) prepared using CCM technique have lower ohmic resistance than the catalysts coated on GDL, the MEA was prepared utilizing the CCM approach. This MEA achieved

a $P_{\max}$ of about 216.7 mW/cm² and 176.8 mW/cm² when oxygen and dry air was used as cathode fuel, respectively, at 1.0 M methanol anode feed. It is expected that the $P_{\max}$ would increase when pure oxygen is fed as cathode fuel compared to the dry air fuel which comprise of only 21% of oxygen. The high performance of the MEA can be attributed to the effect of electrode preparation methods, ionomer to carbon ratio, improved anode and cathode kinetics, optimum porosity and morphology of anode and cathode catalyst layer and the effect of TiO₂ modification on the carbon supports. Figure 3.15 (b) shows the polarization curves of MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode collected at various methanol feed concentrations and dry air cathode feed. Negligible loss in $P_{\max}$ was observed when methanol feed concentration was increased from 0.50 M to 4.0 M. This clearly shows that the PtRu/TiO₂/ONCNT-400 anode is either highly selective to high-concentration methanol solutions or the TiO₂ modification reduces methanol permeability at the anode catalyst layer and thus reduces methanol crossover to the cathode. In any case, the cathode being methanol-tolerant helps to mitigate the loss in cathode performance due to crossover which is reflected in OCV. Figure 3.15 (c) shows the change OCV and $P_{\max}$ vs. concentration of methanol feed. There was only a slight fluctuation in OCV indicating the cathode was pretty methanol tolerant. To the best of our knowledge, this is one of the best performances obtained in DMFC with excellent $P_{\max}$ retention with varied methanol feed concentrations. The negligible change in $P_{\max}$ indicates that the anode is limiting the performance of DMFC. It is necessary to increase the number of Pt active sites of anode to further improve the DMFC performance. Figure 3.15 (d) shows the DMFC polarization curve of the MEA with commercial PtRu/C TKK 77% as the anode with Fe-N-C-FG as the cathode. A $P_{\max}$ of 275 mW/cm² was achieved with dry air as the cathode feed, depicting one of the highest DMFC performances at 1 M methanol feed at the anode. It is in progress to collect data to show the effect

of different concentrations of methanol on the DMFC performance with commercial PtRu/C anode. The data for the MEA with commercial PtRu/C anode and Fe-N-C-FG cathode with varying methanol concentrations will reveal a plethora of information regarding whether the anode architecture/support structure or the TiO₂ modification on carbon support controls the $P_{\max}$ retention. There is a high possibility that the PtRu deposited on TiO₂-modified carbon supports may have high selectivity to high concentration methanol and also reduce methanol crossover. Further tests with PtRu/TiO₂/KB 600JD-400 are also in progress to understand the effect of the morphology of the anode catalyst support in DMFC using the same PGM-free cathode.

Figure 3.16 shows the DMFC stability data at a constant voltage of 0.5 V for PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode. The MEA produced an initial current density of $\sim 135 \text{ mA/cm}^2$ at 0.5V and showed a promising stability over 12 h with 20.4% loss in current density. Figure B16 shows additional DMFC polarization curves and high frequency resistance data of MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode at different backpressures, anode feed concentrations and cathode feed. This study will help to design and engineer novel modified carbon support architectures for MOR electrocatalysts to improve the activity, durability, and the ability to use higher concentrations of methanol in DMFCs, where methanol crossover limits the power output. Overall, we have developed a simple and facile synthesis based on microwave-assisted methods to prepare highly active and stable PtRu alloy nanoparticles deposited on defective hydrogenated TiO₂ modified carbon supports as anode for DMFC.

3.4. Conclusion

We have studied the effect of modification of various carbon catalyst supports such as ONCNT, Vulcan and KB 600JD, with defective hydrogenated TiO₂ ultra-thin shells in the activity

and durability of PtRu electrocatalysts. Microwave-assisted synthesis method was used to modify the carbon supports with hydrogenated TiO₂ shells and to deposit PtRu nanoparticles. The half-cell evaluation and XPS characterization of these electrocatalysts revealed improved MOR electrocatalytic activity and durability with the presence of hydrogenated TiO₂ shell due to its ability to provide strong-metal support interaction (SMSI) and higher degree of oxophilicity. The MOR electrocatalytic activity and ECSA of PtRu electrocatalysts improved with greater BET SSA of carbon supports, demonstrating the importance of carbon support structures. Systematic ASTs were carried to understand the degradation mechanism of electrocatalysts on hydrogenated TiO₂ modified different carbon supports by conducting CO stripping experiments at various stages of ASTs. PtRu/TiO₂/KB 600JD-400 with high BET SSA carbon support exhibited the highest MOR activity (620 mA/mg_{Pt}) whereas PtRu/TiO₂/ONCNT-400 with abundant N-dopants, oxygen functional groups and graphitic nature exhibited excellent stability (35.4% ECSA loss) in MOR DMFC conditions. Full DMFC evaluation incorporating these anode catalysts against the commercial Pt/C cathode and PGM-free Fe-N-C based cathodes were performed to understand the kinetic and mass transport effects of various anode carbon support structures in $P_{\max}$. The PtRu/TiO₂/KB 600JD-400 catalysts presented high selectivity to high concentration methanol solutions. Preliminary results on TiO₂ modified ONCNT-supported anode tested with PGM-free cathode catalysts revealed the insignificant dependence of $P_{\max}$ with increasing methanol feed concentration from 1.0 M to 4.0 M further illustrating either the high selectivity of anode catalysts towards high methanol concentrations or reduction of methanol crossover due to TiO₂ modification on carbon supports. This study provides new directions to design and engineer novel modified carbon support architectures for MOR electrocatalysts to improve the activity, durability, and selectivity to use higher concentrations of methanol in DMFCs.

Chapter 4 - Enhancing the Stability of PtRu Electrocatalysts with SnO₂ Modified Carbon Support for Methanol Oxidation Reaction

4.1. Introduction

Direct methanol fuel cells (DMFC) are one of the prime candidates to consider as alternate renewable energy conversion device owing to the low cost and high energy density (6.08 kWh/kg) of liquid methanol fuel.^{8, 11} As discussed in previous chapter 2 and 3, the major hurdles limiting the commercialization of this technology is due to the high cost, low stability of PtRu based MOR electrocatalysts and methanol crossover in the DMFC. Hence, it is necessary to develop highly active, selective, and stable electrocatalysts to overcome the issues to commercialize DMFC. In previous chapters, we developed a novel hydrogenated TiO₂ modified carbon support as multifunctional catalyst support to enhance the activity, selectivity, and durability of PtRu electrocatalyst.⁸ However, from the systematic AST studies, it was evident that even the TiO₂ modified carbon supports had poor stability towards Ru dissolution in harsh MOR conditions. Hence, in this chapter we focused on employing alternate metal oxide as co-catalyst and hybrid catalyst support for PtRu nanoparticles to enhance the stability towards reducing the Ru dissolution.

On this note, tin oxide (SnO₂) is a viable candidate for co-catalysts or hybrid catalyst support owing to its excellent chemical properties. It has superior ability to produce OH species at low potentials and provide strong-metal support interaction (SMSI) which can cause electronic effects on Pt based catalysts to reduce the Pt-CO binding energy.^{129, 152} In addition to excellent oxophilic properties of SnO₂, it has reasonable corrosion resistance properties in acid environment.¹⁵² However, the SnO₂ has relatively low electronic conductivity of SnO₂ owing to its wide band gap of 3.6 eV, hence hybrid structures with electrically conductive carbon are formed

to overcome the conductivity issues to utilize as catalyst supports.^{152, 153} Several researchers developed various methods to synthesis SnO₂ based catalyst supports for MOR electrocatalyst in DMFC. For example, Huang et.al. reported thioglycolic acid assisted sol-gel synthesis of densely coated SnO₂ on MWCNTs as hybrid catalyst support for Pt to achieve high electrocatalytic activity and stability for methanol oxidation.¹⁵³ The enhanced activity and stability were attributed to the synergistic effect of SMSI between Pt and SnO₂. Similarly, Cui et.al. and Ribeiro et.al. reported the synthesis of SnO₂ nanoparticles deposited on mesoporous carbon by a 12h wet-chemical synthesis method to use a hybrid catalyst support for Pt to enhance the stability of catalysts for MOR.^{154, 155} The above works reported the nanoparticle morphology of SnO₂ on carbon supports as catalyst supports.

The morphology of metal oxide in hybrid catalyst support plays crucial role in electrochemical performance of catalysts. Among the various morphologies of metal oxides, thin shell deposition on carbon support received considerable attention owing to the maximal SMSI and -OH groups that metal oxide can provide to Pt based catalysts.⁸ In addition, the metal oxide thin shells can represent the morphology and surface area of the carbon support beneath and can protect them from corrosion. Zhang et.al. reported deposition of 2 nm thick SnO₂ coating on CNTs by wet-chemical synthesis at room temperature for 2h. The as obtained core-shell SnO₂/CNT provided excellent ethanol oxidation activity and stability of Pt nanoparticles.¹⁵⁶ Lee et.al. showed deposition of atomically controlled thin SnO₂ layers on a carbon-supported Pt nanoparticle (Pt/C) surface using the atomic layer deposition (ALD) technique. The SnO₂ shell coated on Pt/C showed improved the catalytic stability for the glycerol-oxidation-reaction, preventing sintering of Pt nanoparticle catalysts.¹⁵⁷ So far metal oxide thin shell depositions are widely done using ALD^{100, 157}, chemical vapor deposition (CVD)¹⁰¹ or wet chemical synthesis¹⁰², which is either time

consuming or energy intensive. On this line microwave-assisted synthesis is a promising, low cost, rapid, and facile method to deposit thin shells of metal oxides on carbon supports.⁸ Carbon materials have a higher microwave absorptivity than the solvent (as reflected in its high dielectric tangent loss values), the “specific heating” by microwave irradiation can be used to enable preferential metal oxide nucleation and thin film growth on the carbon support, unlike the conventional synthesis methods where heat transfer happens from solvent to substrate.^{8, 105} Recently, we reported a simple five min microwave-assisted synthesis to deposit 5 nm ultra-thin shell of TiO₂ on NCNTs to use as multifunctional catalyst support to enhance the MOR activity and stability of PtRu catalysts.⁸

Inspired by our recent work, we extended the same synthesis methodology to use tin isopropoxide precursor to deposit different thicknesses of ultra-thin shell of SnO₂ on high surface area carbon supports, to form a core-shell hybrid support for PtRu alloy nanoparticles. The PtRu nanoparticles were deposited on SnO₂/C by microwave-assisted synthesis and were subjected to thermal annealing at 400 °C for 2h to enable PtRu alloy formation and to improve the crystallinity. The effect of different annealing atmosphere (such as nitrogen and hydrogen) and different ratio of SnO₂ and carbon were investigated to optimize the MOR activity of PtRu catalyst alloy nanoparticles. By increasing the amount of SnO₂ precursor, the SnO₂ thin shell thickness was increased. Systematic CO stripping studies at different stages of accelerated stress tests (AST) were done to reveal the excellent MOR stability exhibited by the as-prepared SnO₂ modified carbon support (nitrogen annealed) towards strongly anchoring Ru nanoparticles when compared to the TiO₂ modified carbon supports. Moreover, the PtRu/h-SnO₂/C-N₂ showed enhanced CO oxidation kinetics and comparable MOR activity when compared to the three types of benchmark commercial PtRu/C catalysts from Johnson Matthey (JM) and Tanaka KiKinzoku (TKK),

respectively. The enhanced stability of these catalysts may be attributed to the SMSI provided by SnO_2 to the PtRu nanoparticles, which can be revealed by XPS analysis. The superior CO oxidation kinetics is contributed to the abundant hydroxyl groups provided by the ultrathin SnO_2 shell. This work provides a scalable and simple metal oxide deposition technique to prepare multifunctional catalyst supports to improve the stability of MOR electrocatalysts for DMFCs.

4.2. Experimental Section

4.2.1. Chemical and Materials

Tin (IV) isopropoxide, ethylene glycol (EG), sulfuric acid (H_2SO_4), nitric acid (HNO_3), pure ethanol 200 proof, and methanol (ACS grade) were purchased from Fisher Scientific (Hampton, NH). The potassium hexachloroplatinate (K_2PtCl_6), ruthenium chloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), and Nafion[®] solution (5 wt% in lower aliphatic alcohols) were purchased from Sigma-Aldrich (St. Louis, MO). The Ketjen black 600JD (KB 600JD) carbon support were purchased from HM Royal Materials Distribution (Trenton, NJ). The commercial Pt/C catalyst (20 wt% Pt on carbon, HiSPEC[®] 3000) and PtRu/C catalyst (48.0 wt% Pt and 23.1 wt% Ru on carbon, HiSPEC[®] 12100) by Johnson Matthey (JM) were purchased from Alfa Aesar (Tewksbury, MA) as the benchmark reference. Two more benchmark commercial PtRu/C catalyst 50% (TEC 66E50 – 32.8 wt% Pt and 16.9 wt% Ru on carbon) and PtRu/C 77% were purchased from Tanaka Kikinzoku International (America) Inc. (Schaumburg, IL), referred as PtRu/C TTK 50% and PtRu/C TTK 77%. Ultrapure water (18.2 M Ω .cm at 25 °C) purified from a Millipore water system (EASYPURE II, Thermo Scientific, Waltham, MA) was used to prepare all aqueous solutions for the experiments.

4.2.2. Material Synthesis

4.2.2.1. Preparation of SnO_2/C

High surface area Ketjen Black 600JD (KB 600JD) carbon support was used in this study. The KB 600JD was first oxygenated by refluxing 1.0 g of carbon in an aqueous mixture of 2.0 M H_2SO_4 and 4.0 M HNO_3 at 120 °C for 12 h under constant stirring. The obtained oxygenated carbon was washed with ultrapure water till the pH reached 7.0, filtered, and dried at 80 °C in a vacuum oven. Then, 10.0 mg of carbon was dispersed in 6.0 ml of ethanol by ultrasonication for 30 min. Further, 10.0 μL of tin isopropoxide was added to this dispersion and sonicated in a water bath. After 30 min sonication, this mixture was transferred to a 10 ml Pyrex glass microwave vessel and put into Discover®SP microwave synthesizer (CEM Corporation., Matthews, NC). A microwave irradiation was applied in the standard mode with the power up to 300 W to maintain a reaction temperature of 150 °C for 5 min. The reaction pressure rose to ~19 bar during the process. After reaction, the naturally cooled product mixture was washed 2-3 times using ethanol to remove the unreacted precursors and dried at 80 °C in a vacuum oven to obtain the SnO_2 coated C, referred as $\text{SnO}_2/\text{C-MW}$. The higher ratio of SnO_2 deposited carbon support was prepared by adding more tin isopropoxide precursor in the synthesis procedure mentioned before. Three times higher weight% of SnO_2 was deposited on KB 600JD by adding 30 μL of tin isopropoxide precursor and 10.0 mg of KB 600JD. The same microwave-assisted synthesis procedure was carried out to form higher wt% SnO_2 deposited on KB600JD and was denoted as h- $\text{SnO}_2/\text{C-MW}$.

4.2.2.2. Preparation of PtRu deposition on SnO_2/C

To deposit PtRu catalysts, 12.5 mg of K_2PtCl_6 , 5.1 mg of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and 16.0 mg of $\text{SnO}_2/\text{C-MW}$ were dispersed in 20 ml of mixture of ethylene glycol and water (at 4:1 volume ratio) by ultrasonication for 1 hour. The solution was then transferred to 35 ml Pyrex glass microwave vessel. The weight ratio of Pt and Ru is maintained at 2:1 in the precursors. Ethylene glycol serves as a reducing agent and solvent in this reaction. The mixture was irradiated with a 300 W

microwave under the standard mode to maintain a reaction temperature of 190 °C for 20 min in Discover®SP microwave synthesizer to deposit Pt and Ru NPs onto SnO₂/C. The reaction pressure rose to ~8 bar during this process. The cooled product mixture was washed several times using acetone to remove residual ethylene glycol and then dried at 80 °C in a vacuum oven to obtain PtRu/SnO₂/C-MW. The dried catalyst material was annealed in a tube furnace at 400 °C for 2 h in 3% H₂/97% Ar at a ramp rate of 10 °C/min, to form crystalline PtRu alloyed NPs and defective SnO₂ shell on the carbon support. The as-prepared catalyst is named as PtRu/SnO₂/C-400 H₂. The PtRu/h-SnO₂/C-MW as also annealed in 3% H₂/97% Ar at 400 °C for 2 h to form PtRu/h-SnO₂/C-H₂. The effect of different annealing atmosphere was studied in this work. Hence the PtRu/h-SnO₂/C-MW was annealed in nitrogen atmosphere at 400 °C for 2 h to form PtRu/h-SnO₂/C-N₂. Synthesis of control samples was carried out using the same reaction conditions as mentioned above with appropriate precursors but skipping some specific intermediate steps. For instance, the control sample SnO₂/C-MW annealed at 400 °C for 2 h in 3% H₂/97% Ar or nitrogen atmosphere is denoted as SnO₂/C-H₂ or SnO₂/C-N₂.

4.2.3. Materials Characterization

The structure of the catalysts was characterized using two transmission electron microscopes (TEM), including a Tecnai Osiris Scanning/Transmission Electron Microscope (S/TEM, FEI, Hillsboro, OR) at a 200 kV acceleration voltage, located at University of Nebraska, Lincoln; and a Philips CM 100 TEM at a 100 kV acceleration voltage, located at Department of Biology, KState. The crystal structure of the catalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 1 mm, located at Department of Chemistry, KState. XRD reference spectra are used from Joint Committee on Powder Diffraction

Standards (JCPDS). The composition of the catalysts was determined using a Thermogravimetric Analyzer (TGA) Q50 system (TA instruments - Waters LLC, New Castle, DC) from the room temperature to 900 °C in a compressed air atmosphere. The surface chemical composition of the catalysts was characterized using a PHI 5000 Versa XPS system (Chanhasen, MN) with a monochromatized Al K α source (1486.7 eV), located at University of Nebraska, Lincoln. All the XPS spectra were obtained using a 400 μ m spot size. Shirley background was used in the curve fitting. The binding energy (B.E.) of all XPS data was calibrated vs. the standard sp² C 1s peak at 284.60 eV.

4.2.4. Electrochemical Characterization

All the half-cell electrochemical experiments were performed in a standard three-electrode setup using a CHI 760D electrochemical workstation (CH Instruments, Austin, TX) at room temperature. A silver-silver chloride (Ag/AgCl in 1.0 M KCl) reference electrode and a coiled Pt counter electrode (0.55 mm in diameter and 23 cm in length) were used. The working electrode was prepared by drop-casting the catalyst ink onto a glassy carbon electrode (GCE) encased in a PEEK rod. Before drop-casting the catalyst ink, the GCE was polished using 0.05 μ m alumina slurry. The catalyst ink was prepared by dispersing the required amount of catalyst powder in 1.0 ml of mixture of ethanol and ultrapure water (at 3:1 volume ratio) with addition of the 30 μ l of Nafion[®] solution (5 wt% in lower aliphatic alcohols). The loading of the platinum group metal (PGM, specifically Pt and Ru in this study) was maintained at 54 μ g/cm² for all catalysts in the half-cell studies. The MOR experiments were performed by recording CV in the potential range of 0 V to 1 V vs. RHE at a scan rate of 50 mV/s in Ar-purged 0.5 M H₂SO₄ solution containing 0.75 M methanol. For direct comparison of the potentials with literature, the measured electrode

potential vs. the Ag/AgCl (1.0 M KCl) reference electrode is converted to the value vs. the reversible hydrogen electrode (RHE) using the following equation:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Ag/AgCl})} + E_{(\text{Ag/AgCl vs. SHE})} + 0.059\text{pH} = E_{(\text{vs. Ag/AgCl})} + 0.222 \text{ V} \quad (4.1)$$

where $E_{(\text{vs. Ag/AgCl})}$ is the measured potential vs. the Ag/AgCl (1.0 M KCl) reference electrode, $E_{(\text{Ag/AgCl vs. SHE})} = 0.222 \text{ V}$ is the Ag/AgCl (1.0 M KCl) reference electrode potential vs. SHE, and $\text{pH} = 0$ for 0.50 M H_2SO_4 .

The CO stripping voltammetry experiments were performed in 0.50 M H_2SO_4 to evaluate the catalyst activity towards CO oxidation and to determine the active electrochemical surface area (ECSA) of the catalyst. In CO stripping experiments, the electrolyte was first purged with Ar gas to remove any dissolved oxygen species in the electrolyte. Then, a pure CO gas was used to purge the electrolyte for 10 min while the potential of the working electrode was held at 0.10 V vs. RHE. After 10 min, the purging gas was switched back to pure Ar to purge for 30 min to remove the dissolved CO gas from the electrolyte, while the potential of the working electrode was still held at 0.10 V vs RHE which retained the adsorbed CO monolayer on the Pt surface. Subsequently, the CO monolayer on the Pt surface was stripped off with a linear anodic sweep at 10 mV/s from 0.10 V to 1.222 V vs. RHE. A few CV cycles were taken following CO stripping to evaluate the baseline of the electrode.

The ECSA of Pt in the catalysts was determined using the following equation:

$$\text{ECSA} = \frac{Q_a}{Q_{\text{CO}}^0 \times m_{\text{Pt}}} \quad (4.2)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of CO oxidation peak; $Q_{\text{CO}}^0 = 420 \mu\text{C}/\text{cm}^2$ is the charge required to oxidize a monolayer of CO adsorbed on 1 cm^2 of flat Pt surface and m_{Pt} (g/cm^2) is the mass loading of Pt on the working electrode surface.

Durability of all the electrocatalysts was investigated by the following accelerated stress test (AST) protocol: Continuous CV cycling of electrocatalysts were performed in the potential range of 0 to 0.5 V vs. RHE at 500 mV/s scan rate for 1000 cycles. At certain intervals, one MOR CV curve in the potential range of 0 to 1.0 V vs. RHE at 50 mV/s scan rate is collected. CO stripping voltammogram were collected at different stages of AST studies such as on fresh catalysts surface, after CV activation in 0.50 M H₂SO₄, after 25th, 50th, 100th, 200th, 300th, 400th, 500th, 750th and 1000th MOR cycle to understand the PtRu structural evolution over MOR cycles.

4.3. Results and Discussion

4.3.1. Morphological and Structural Characterization

High surface area KB 600JD was used as carbon support. The BET SSA of KB 600JD was found to be $\sim 1447 \text{ m}^2/\text{g}$. A rapid microwave-assisted deposition of ultra-thin shell of SnO₂ on carbon support is presented. Figure 4.1 (a) shows the TEM image of microwave deposited SnO₂ on KB 600JD. It was difficult to observe the SnO₂ and carbon interface, hence STEM-EDX elemental mapping was done. Figure 4.1 (b) shows the HAADF-STEM image of SnO₂/C-MW and Figure 4.1 (c) – (e) shows the elemental mapping of C, Sn and O, depicting the uniform distribution of SnO₂ on the carbon support. This was confirmed by TGA experiments (Figure C1 (a)), which revealed that after heating at 900 °C, there was $\sim 4.4\%$ of the material remained in SnO₂/C-MW, which may be attributed to the SnO₂. The earlier carbon decomposition temperature (at $\sim 500 \text{ }^\circ\text{C}$) in TGA curves of SnO₂/C-MW, when compared to bare C, further indicates the evidence of presence of SnO₂, as metal oxides are said to catalyze carbothermal reaction.^{8, 158} When the SnO₂/C-MW was annealed at 400 °C in 3% H₂/ 97% Ar, the contrast of SnO₂ improved showing a clear interface of SnO₂ shell covering the carbon support (see at the edge of carbon support in Figure 4.1 (f)).

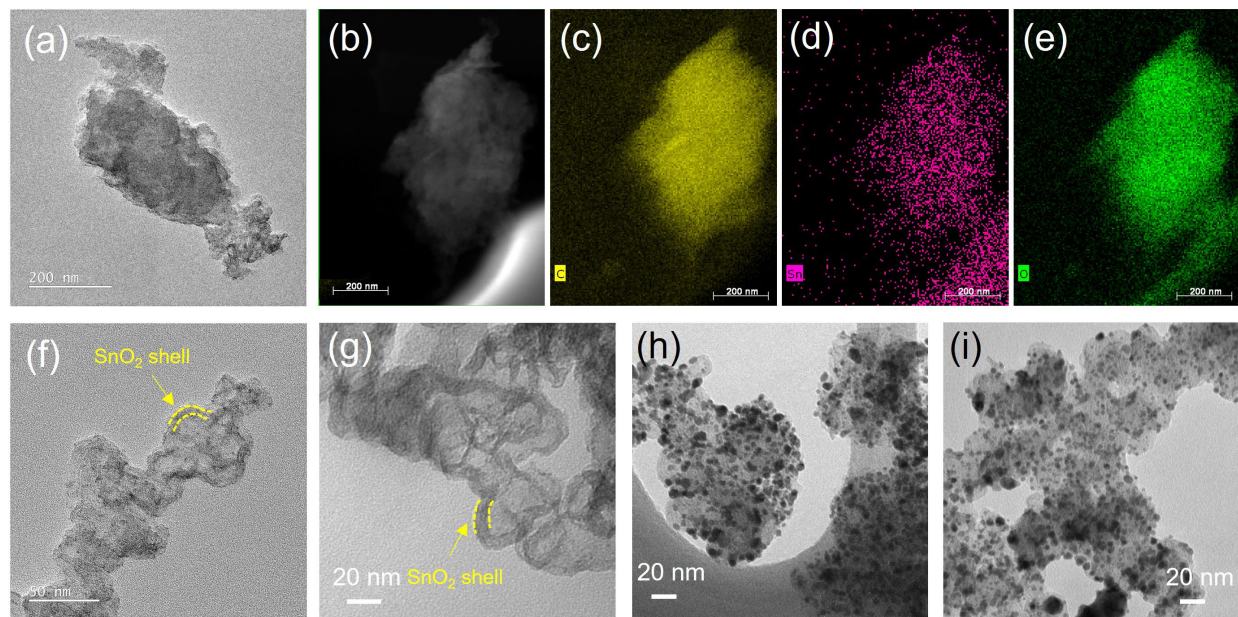


Figure 4.1. TEM image of (a) SnO₂/C-MW, (b) HAADF-STEM image (c–e) STEM-EDX elemental mapping of C, Sn, and O of SnO₂/C-MW, (f) TEM image of SnO₂/C-H₂, (g) TEM image of h-SnO₂/C-H₂, (h) TEM image of PtRu/SnO₂/C-H₂ and (i) TEM image of PtRu/h-SnO₂/C-H₂.

The thickness of SnO₂ shell was found to be ~ 6 to 7 nm. When the amount of SnO₂ was increased by three times, to form h-SnO₂/C, the SnO₂ shell thickness increased to ~ 8 to 9 nm as shown in Figure 4.1 (g). There was about $\sim 9.7\%$ of SnO₂ present in the h-SnO₂/C sample as per TGA experiments shown in Figure C1 (a). A second microwave-assisted synthesis method developed in our previous work was used to deposit uniform PtRu nanoparticles on different thicknesses of SnO₂ coated C to form PtRu/SnO₂/C-MW as shown in Figure C2. The PtRu nanoparticles are found to be well distributed on the surface of SnO₂/C with an average nanoparticle size of 2.6 ± 0.5 nm. This sample was further annealed in 3% H₂/97% Ar at 400°C for 2h to obtain the active catalyst, PtRu/SnO₂/C-H₂. After annealing the PtRu alloy nanoparticle size was found to be increased to 5.4 ± 1.2 nm, as shown in Figure 4.1 (h) and Figure C3 (a), owing to the agglomeration of nanoparticles to form PtRu alloys. Similarly, Figure 4.1 (i) shows the PtRu alloy nanoparticle distribution on higher wt% SnO₂ coated carbon support, denoted as PtRu/h-

SnO₂/C-H₂. The average PtRu nanoparticle size was found to be decreased 4.3 ± 1.4 nm when h-SnO₂/C was used as catalyst support as shown in Figure C3 (b).

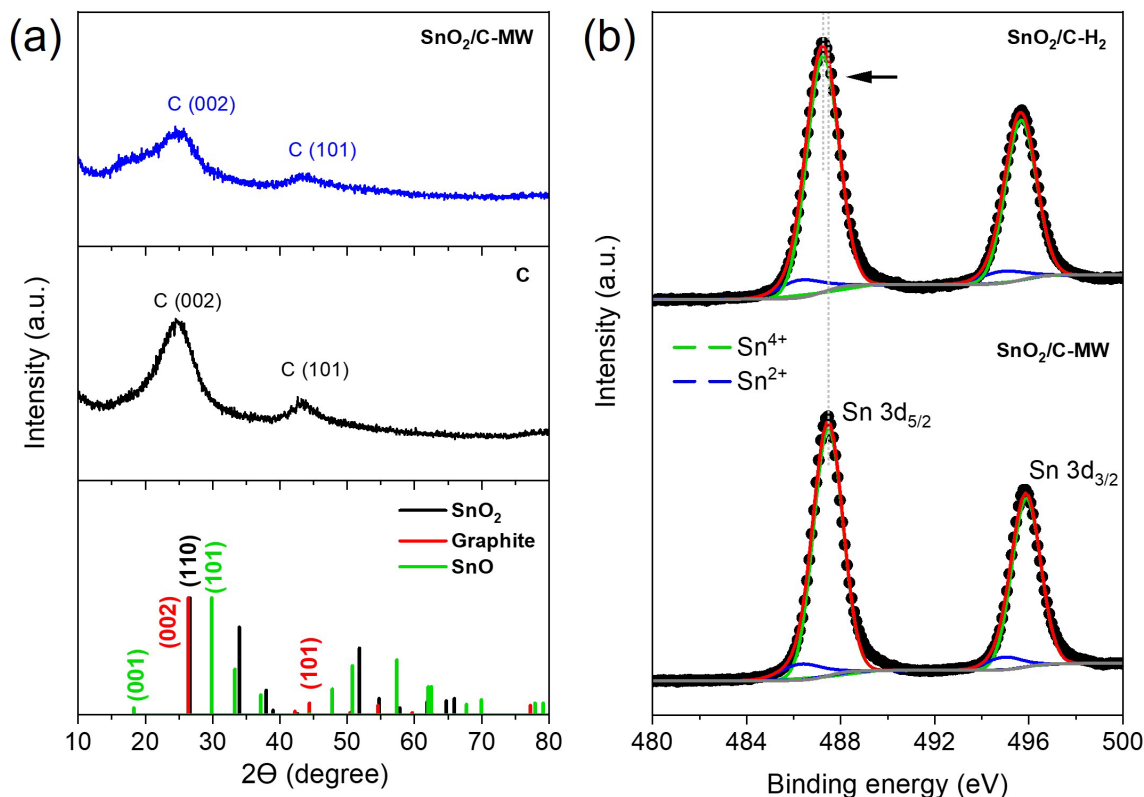


Figure 4.2. (a) XRD patterns in the 2θ range of 10° to 80° of SnO₂ rutile (JCPDS # 06-0663), graphite reference (JCPDS# 75-1621), SnO (JCPDS# 04-0802) compared with KB 600JD (C) and SnO₂/C-MW. (b) Comparison of XPS Sn 3d spectra of SnO₂/C-MW and SnO₂/C-H₂.

This illustrates higher wt% of SnO₂ in PtRu/h-SnO₂/C-H₂ is beneficial in controlling the nanoparticle agglomeration owing to the higher effect of strong-metal-support interaction (SMSI). This agrees with some of the previous literatures.^{8, 157} However, the average PtRu alloy nanoparticle size in PtRu/SnO₂/C-H₂ and PtRu/h-SnO₂/C-H₂ was larger than the PtRu nanoparticles deposited on TiO₂ modified carbon support (KB 600JD) in PtRu/TiO₂/C-H₂ reported in chapter 3. This shows that TiO₂ can be a better choice of metal oxide to make PtRu alloy nanoparticles at optimum size using this synthesis methodology. Effect of different thermal

annealing temperatures on the MOR activity were studied in this work. The PtRu/h-SnO₂/C-MW was annealed in inert nitrogen atmosphere. This may not only enable the formation of PtRu alloy but also will preserve SnO₂ as the dominating oxides in the catalyst support. The as prepared sample is denoted as PtRu/h-SnO₂/C-N₂. The TEM imaging on these samples is yet to be done to shed more insights on the PtRu nanoparticle distribution.

XRD analysis was done to understand the crystal structure of SnO₂ deposited on carbon after microwave deposition as shown in Figure 4.2 (a). As the diffraction peaks of SnO₂ (110) and C(002) overlaps with each other, it is difficult to make a judgement to assign the peak present at 2 θ angles of 24.6°. But diffraction peaks at 2 θ angles of 42.9° corresponding to C(101) of carbon support were present. There was a weak diffraction peak found at ~ 17.0° as a shoulder peak to C(002), which may be attributed to the SnO. More XRD analyses on samples PtRu/SnO₂/C-H₂, PtRu/h-SnO₂/C-H₂ and PtRu/h-SnO₂/C-N₂ are in progress, that may provide clear insights of the nature of SnO₂ present on carbon supports.

4.3.2. Compositional Analysis

Further XPS analysis was conducted for the SnO₂/C-MW and SnO₂/C-H₂ to understand the surface elemental composition as shown in Figure 4.2 (b). The Sn 3d spectra of SnO₂/C-MW and SnO₂/C-H₂ was deconvoluted into two pairs of doublets, 3d_{5/2} and 3d_{3/2} peaks, centered at 486.35 eV & 494.96 eV and 487.46 eV & 495.88 eV corresponding to Sn²⁺ and Sn⁴⁺ of SnO and SnO₂, respectively.¹⁵⁹ There was ~ 8.35% of SnO and ~ 91.65% SnO₂ present in SnO₂/C-MW, indicating the sample predominantly consists of SnO₂. When SnO₂/C-MW was annealed in reducing atmosphere (3% H₂/ 97% Ar), the amount of SnO slightly increased to ~ 10.2% illustrating the reduction of some SnO₂ to SnO. In addition, there was slight shift in binding energy observed for the Sn 3d spectra of SnO₂/C-H₂ depicting a strong-metal oxide carbon support interaction after

annealing. Overall, the XPS analysis confirms that SnO_2 is the predominant metal oxide species present in the SnO_2/C samples. Further XPS analysis on $\text{PtRu}/\text{SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-H}_2$ and $\text{PtRu}/\text{h-SnO}_2/\text{C-N}_2$ are in progress.

TGA experiments were performed on the control $\text{SnO}_2/\text{C-H}_2$ and $\text{SnO}_2/\text{C-N}_2$ samples to understand the changes in elemental composition with the thermal annealing atmosphere. There was $\sim 12.8\%$ and $\sim 15.2\%$ of SnO_2 in $\text{SnO}_2/\text{C-H}_2$ and $\text{SnO}_2/\text{C-N}_2$, respectively, illustrating catalysts annealed in 3% H_2 / 97% Ar atmosphere reduces some SnO_2 to SnO , supporting the XPS analysis. TGA experiments on $\text{PtRu}/\text{SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-N}_2$ and their corresponding control samples were performed to determine the elemental composition as shown in Figure C4. The TGA calculations and analysis was done as established in our previous work, to determine the wt% of Pt, Ru, SnO_2 and C in all the samples. The wt% of Pt, Ru, SnO_2 , and C in the $\text{PtRu}/\text{SnO}_2/\text{C-H}_2$ catalyst was found to be 26.4%, 9.3%, 4.7%, and 59.6%, respectively. Similarly, $\text{PtRu}/\text{h-SnO}_2/\text{C-H}_2$ consisted of 22.1%, 11.3%, 9.3% and 57.3% of Pt, Ru, SnO_2 and carbon, respectively. The $\text{PtRu}/\text{h-SnO}_2/\text{C-N}_2$ was found to have 24.0%, 13.0%, 10.8% and 52.2% of Pt, Ru, SnO_2 and carbon respectively. Overall the platinum metal group (PGM) wt% in $\text{PtRu}/\text{SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-H}_2$, and $\text{PtRu}/\text{h-SnO}_2/\text{C-N}_2$ was found to be 35.7%, 33.3% and 37.0%, respectively.

4.3.3. Electrochemical Analysis

It is crucial to understand the CO oxidation kinetics of different catalysts prepared in this work. Anodic CO stripping voltammogram was performed on $\text{PtRu}/\text{SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-H}_2$, $\text{PtRu}/\text{h-SnO}_2/\text{C-N}_2$ and several commercial PtRu/C catalysts to understand the kinetics and to derive the ECSA. There are three different commercial PtRu/C catalysts such as PtRu/C JM 71%, PtRu/C TKK 77% and PtRu/C TKK 50% studied in this work. Figure 4.3 (a) shows the CO

stripping curves of commercial PtRu/C catalysts. The CO oxidation onset potential of commercial PtRu/C JM, PtRu/C TKK 50% and PtRu/C TKK 77% was found to be 0.435 V, 0.415 V and 0.415 V vs. RHE, respectively. The ECSA was found to be 91.7 m²/g, 99.5 m²/g and 82.3 m²/g for PtRu/C JM, PtRu/C TKK 50% and PtRu/C TKK 77%, respectively. Figure 4.3 (b) shows the CO stripping voltammogram of catalysts prepared using SnO₂ modified carbon support. Among the two catalysts with different SnO₂ composition, PtRu/SnO₂/C-H₂ and PtRu/h-SnO₂/C-H₂, the PtRu/h-SnO₂/C-H₂ showed the earliest CO oxidation onset potential at 0.263 V vs. RHE compared to PtRu/SnO₂/C-H₂ (0.283 V vs. RHE) illustrating the formation of abundant OH species from higher amount of SnO₂.

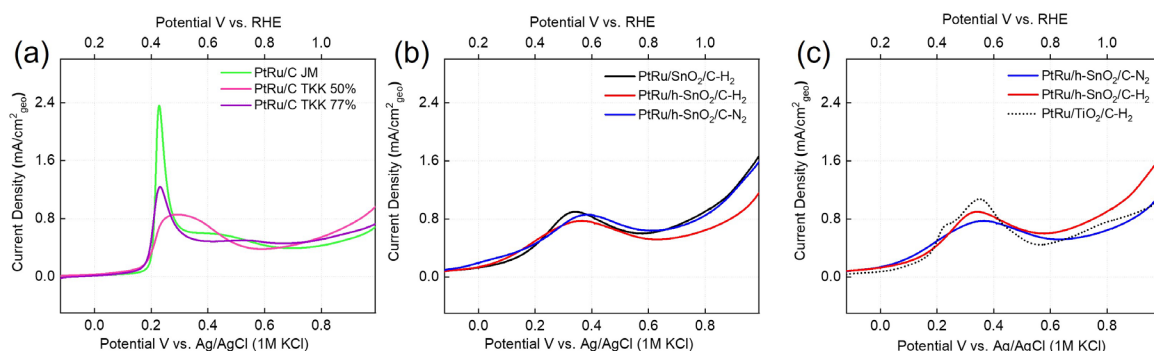


Figure 4.3. Comparison of CO stripping LSV curves of (a) PtRu/C TKK 77%, PtRu/C TKK 50% and PtRu/C JM 71%, (b) PtRu/SnO₂/C-H₂, PtRu/h-SnO₂/C-H₂ and PtRu/h-SnO₂/C-N₂, (c) PtRu/h-SnO₂/C-H₂, PtRu/h-SnO₂/C-N₂ and PtRu/TiO₂/C-H₂ collected in Ar-purged 0.50 M H₂SO₄ at a scan rate of 10 mV/s.

This further shows that the oxophilic nature of SnO₂ plays a important role in oxidation of the poisonous intermediate CO. The ECSA of PtRu/SnO₂/C-H₂ and PtRu/h-SnO₂/C-H₂ was calculated to be 79.8 m²/g_{Pt} and 87.4 m²/g_{Pt}, respectively. The slightly higher ECSA in PtRu/h-SnO₂/C-H₂ can be attributed to the relatively small PtRu nanoparticles. Interestingly, the CO oxidation kinetics of PtRu/h-SnO₂/C-N₂ improved when annealed in nitrogen atmosphere, illustrating an even earlier CO oxidation onset potential at 0.194 V vs. RHE with an ECSA of 76.4 m²/g_{Pt}. This enhanced CO

oxidation kinetics may be attributed to the effect of the much stable and crystalline SnO₂ thin film formed on carbon when annealed in nitrogen atmosphere. However, XRD and XPS analysis on PtRu/h-SnO₂/C-N₂ catalysts will reveal more insights on the enhanced CO oxidation kinetics. It is to be noted that, catalysts prepared using SnO₂ modified carbon supports had superior CO oxidation kinetics when compared to catalysts prepared using TiO₂ modified carbon supports as shown in Figure 4.3 (c). However, the PtRu/TiO₂/C-H₂ catalyst had higher ECSA compared to PtRu/h-SnO₂/C-H₂ or PtRu/h-SnO₂/C-N₂ owing to the relatively small PtRu nanoparticle size formed on TiO₂ modified carbon supports.

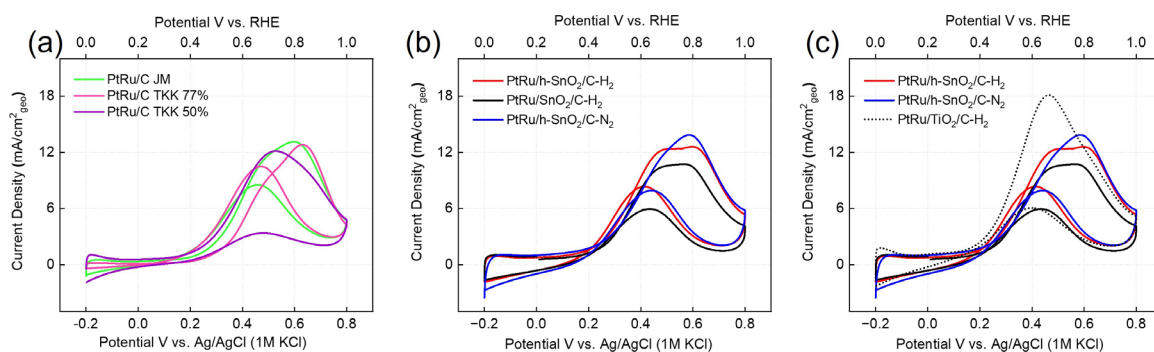


Figure 4.4. Comparison of first MOR CV curve of (a) PtRu/C TKK 77%, PtRu/C TKK 50% and PtRu/C JM 71%, (b) PtRu/SnO₂/C-H₂, PtRu/h-SnO₂/C-H₂ and PtRu/h-SnO₂/C-N₂, (c) PtRu/h-SnO₂/C-H₂, PtRu/h-SnO₂/C-N₂ and PtRu/TiO₂/C-H₂ collected in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s. All the catalysts were tested at 54 $\mu\text{g}/\text{cm}^2$ at I/carbon ratio of 0.4.

The MOR electrocatalytic performance was investigated by CV in Ar-saturated 0.50 M H₂SO₄ containing 0.75 M methanol solution at a PGM catalyst loading of 54 $\mu\text{g}/\text{cm}^2$. Figure 4.4 (a) shows the first MOR CV curves of commercial PtRu/C catalysts. The PtRu/C JM, PtRu/C TKK 50% and PtRu/C TKK 77% catalysts showed the MOR onset potential at 1.5 mA/cm² of 0.50 V vs. RHE, 0.465 V vs. RHE, and 0.556 V vs. RHE with MOR forward peak current density (I_f) of 13.1 mA/cm², 12.2 mA/cm², and 12.8 mA/cm², respectively. As mentioned in previous works and chapters, the forward peak current density and backward peak current density is attributed to the

methanol oxidation. The I_f/I_b ratio can provide the oxophilicity of the catalyst. The I_f/I_b ratio was found to be 1.54, 1.23 and 3.57 for PtRu/C JM, PtRu/C TKK 77% and PtRu/C TKK 50%, respectively. Among the three commercial catalysts, the PtRu/C TKK 50% showed the lowest MOR onset potential and PtRu/C JM showed the highest I_f . Among the in-house prepared PtRu deposited on various SnO₂ modified carbon supports, the PtRu/h-SnO₂/C-N₂ showed the lowest MOR onset potential of about 0.410 V vs. RHE and a MOR forward peak current density (I_f) of ~ 13.9 mA/cm² as shown in Figure 4.4 (b). This high activity can be attributed to the lowest CO oxidation potential of PtRu/h-SnO₂/C-N₂ obtained due to superior oxophilic nature of SnO₂ thin film annealed in nitrogen atmosphere. The PtRu/h-SnO₂/C-H₂ and PtRu/SnO₂/C-H₂ showed a MOR onset potential of 0.437 V and 0.472 vs. RHE with an I_f of 12.6 mA/cm² and 10.7 mA/cm², respectively. The MOR activity trend was same as the trend observed in CO oxidation activity. Overall, the PtRu/h-SnO₂/C-N₂ showed comparable MOR activity to commercial catalysts. This high active PtRu/h-SnO₂/C-N₂ catalyst was compared with the PtRu/TiO₂/C-H₂ as shown in Figure 4.4 (c). The PtRu/h-SnO₂/C-N₂ catalyst was found to have inferior MOR performance when compared to PtRu/TiO₂/C-H₂. This may be due to the lower ECSA of the PtRu catalyst on SnO₂ supported catalyst when compared to PtRu/TiO₂/C-H₂. Figure C5 shows the MOR CV curves of all the catalysts at 100th cycle. It is to be noted that the MOR onset potential shifted to more positive potentials indicating the catalyst have undergone degradation within 100 cycles and MOR I_f increased to higher values owing to the more exposed Pt sites. All of the PtRu catalysts deposited on SnO₂ modified carbon supports at 100th cycle showed lower MOR onset potential when compared to PtRu/TiO₂/C-H₂. This shows superior stability of PtRu electrocatalyst on SnO₂ modified carbon support. The next section will highlight the durability studies of all the catalysts.

4.3.4. AST studies

The most critical effect of SnO_2 modification on carbon supports were observed in the durability studies. The AST protocol 2 established in chapter 3 was employed to understand the stability of the high performing $\text{PtRu/h-SnO}_2/\text{C-N}_2$. The CO stripping curves were collected at different stages of AST tests of $\text{PtRu/h-SnO}_2/\text{C-N}_2$ to understand the practicality of using SnO_2 metal oxide as carbon support in anchoring the PtRu nanoparticles. The CO stripping curve provided plethora of information. This was compared with $\text{PtRu/TiO}_2/\text{C-H}_2$ and commercial PtRu/C JM as shown in Figure 4.5 (a).

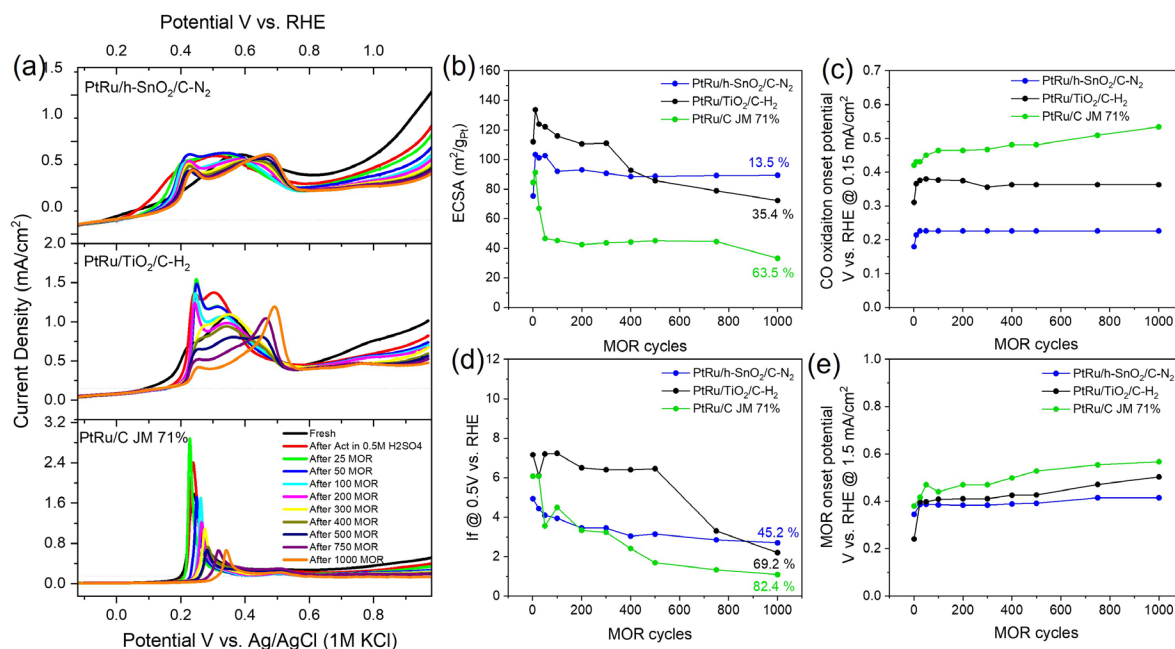


Figure 4.5. (a) Comparison of CO stripping LSV curves collected at different stages of MOR AST CV cycles for commercial PtRu/C JM , $\text{PtRu/TiO}_2/\text{C-H}_2$ and $\text{PtRu/h-SnO}_2/\text{C-N}_2$ catalysts. (b) Plot of change in ECSA, (c) plot of change in CO oxidation onset potential, (d) plot of change in MOR $I(0.5 \text{ V vs. RHE})$ and (e) plot of change in MOR onset potential at 1.5 mA/cm^2 from different stages of the MOR AST CV cycling for commercial PtRu/C JM , $\text{PtRu/TiO}_2/\text{C-H}_2$ and $\text{PtRu/h-SnO}_2/\text{C-N}_2$ catalysts. AST protocol: CV curves were collected in Ar-purged 0.50 M H_2SO_4 solution containing 0.75 M methanol at a scan rate of 500 mV/s in a potential window from 0V to 0.50 V vs. RHE for 1000 cycles. The CO stripping LSV curves were collected in Ar-purged 0.50 M H_2SO_4 at a scan rate of 10 mV/s. All the catalysts were tested at 54 $\mu\text{g}/\text{cm}^2$ at I/carbon ratio of 0.4.

The CO stripping curve collected on fresh catalyst provide the surface exposed sites of fresh catalyst surface. After CV activation in 0.50 M H₂SO₄, the ECSA increased by 37.8%, 19.2% and 8% in PtRu/h-SnO₂/C-N₂, PtRu/TiO₂/C-H₂ and PtRu/C JM, respectively. This may be due to some Ru dissolution and Pt active site exposure. However, by performing just 25 CV cycles in MOR containing electrolytes caused ~26. 6%, 7.3% and 2.0% ECSA loss in PtRu/C JM, PtRu/TiO₂/C-H₂, and PtRu/h-SnO₂/C-N₂, respectively. This shows the efficacy of SnO₂ in strongly anchoring the PtRu nanoparticles. The changes in the ECSA, CO oxidation onset potential, MOR onset potential and $I_{(at\ 0.5V\ vs.\ RHE)}$ over continuous MOR CV cycles for the different catalysts are shown in Figure 4.5 (b)-(e). The $I_{(at\ 0.5V\ vs.\ RHE)}$ at different stages of MOR CV cycles is monitored because 0.5 V is the maximum anode potential that DMFC can achieve. The PtRu/h-SnO₂/C-N₂ catalyst showed superior retention to ECSA with just 13.5% ECSA loss and 45.2% loss in MOR $I_{(at\ 0.5\ V\ vs.\ RHE)}$ after 1000 MOR CV cycles when compared to PtRu/TiO₂/C-H₂ (35.4% ECSA loss and 69.2% loss in MOR $I_{(at\ 0.5\ V\ vs.\ RHE)}$). PtRu/SnO₂/C-N₂ showed 46.3 mV shift in CO oxidation onset potential when compared to 52 mV shift in PtRu/TiO₂/C-H₂. The CO oxidation peak shape changes at different stages of AST CV cycling, illustrates the changes occurring to the PtRu alloy composition which indirectly depends on the stability of the PtRu catalyst. There are two peaks observed in the CO oxidation curves, one at the lower potential and another at higher potential. The peak at the lower potential and higher potential can be attributed to the exposed PtRu lattices and Pt lattices, respectively.¹⁴⁶ For the PtRu/TiO₂/C-H₂, the CO oxidation peak shape changes from two broad peaks to one single peak indicating the Ru dissolution during CV cycling in MOR containing electrolyte. However, in case of PtRu/h-SnO₂/C-N₂, the CO oxidation peak shape remained stable, while performing CV cycling in MOR containing electrolyte, with two broad CO oxidation peaks indicating the strong interaction of PtRu alloy lattice with SnO₂/C support even

after 1000 MOR CV cycles. More importantly, the rate of decrease in current density of the CO oxidation peak at lower potential (corresponding to PtRu lattices) was very low in PtRu/h-SnO₂/C-N₂ compared to PtRu/TiO₂/C-H₂. This demonstrates the superior practicality of SnO₂ in strongly anchoring the Ru nanoparticles than hydrogenated TiO₂. Further XPS analysis may provide more insights about the surface composition of SnO₂ and Ru to correlate with enhanced stability. Overall, we have developed a simple microwave-assisted synthesis methodology to prepare a novel core-shell catalyst support based on SnO₂ modified carbon support which can provide superior stability for PtRu MOR electrocatalysts.

4.4. Conclusion

We have successfully developed a rapid (~ 5 min) microwave-assisted method to deposit an ultra-thin shell of SnO₂ on high surface area carbon supports, for PtRu alloy nanoparticles towards methanol oxidation reaction. The PtRu nanoparticles were deposited on SnO₂/C by microwave-assisted synthesis and were subjected to thermal annealing at 400 °C for 2h to enable PtRu alloy formation and to improve the crystallinity. The effect of different annealing atmosphere (such as nitrogen and 3% hydrogen) and different ratio of SnO₂ and carbon were investigated to optimize the MOR activity of PtRu catalyst alloy nanoparticles. By increasing the amount of SnO₂ precursor, the SnO₂ thin shell thickness was increased. Systematic CO stripping studies at different stages of accelerated stress tests (AST) were done to reveal the excellent MOR stability exhibited by the as-prepared SnO₂ modified carbon support (nitrogen annealed) towards strongly anchoring Ru nanoparticles when compared to the TiO₂ modified carbon supports. Moreover, the PtRu/h-SnO₂/C-N₂ showed enhanced CO oxidation kinetics and comparable MOR activity when compared to the three types of benchmark commercial PtRu/C catalysts from Johnson Matthey (JM) and Tanaka KiKinzoku (TKK), respectively. The enhanced stability of these catalysts may

be attributed to the SMSI provided by SnO_2 to the PtRu nanoparticles, which can be revealed by XPS analysis. The superior CO oxidation kinetics is contributed to the abundant hydroxyl groups provided by the ultrathin SnO_2 shell. This work provides a scalable and simple metal oxide deposition technique to prepare multifunctional catalyst supports to improve the stability of MOR electrocatalysts for DMFCs.

Chapter 5 - Hydrogenated TiO₂ Modified Carbon Support for PtRu

Bimetallic Alloys as HOR Electrocatalyst for High-Performance

AEMFC

5.1. Introduction

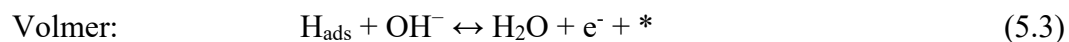
The depletion of fossil fuels has received tremendous attention towards development of sustainable and renewable energy sources to serve human needs. Fuel cells are one of the promising technologies to provide clean energy owing to their high efficiency.²⁰ So far in previous chapters, we focused on developing novel strategies to overcome the hurdles that proton exchange membrane fuel cells (PEMFCs) such as direct methanol fuel cells (DMFCs) face from commercialization.⁸ Another class of PEMFCs are hydrogen-oxygen fuel cells, where hydrogen and air/oxygen are used as anode and cathode fuels, respectively.

Hydrogen is considered as a carbon emission-free alternative for fossil fuels.²⁰ This is because the only byproducts of hydrogen-oxygen PEMFCs is water and electricity. The anode and cathode reactions of hydrogen fuel cell are hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), respectively.²⁰ Unfortunately, PEMFCs requires the most stable and active platinum (Pt) based electrocatalysts to catalyze the HOR and ORR, as it's on the top of the volcano plot.^{20,36} Due to the harsh acidic environment of PEMFCs, it requires stable Pt based metal electrocatalysts and corrosion resistant fuel cell components which makes it an expensive technology. Despite this, a high peak power density of 1.24 W/cm² is achieved with just 0.125 mg_{Pt}/cm² using hydrogen fuel with ambient air as oxidant.²⁹ The long-term goal of U.S. Department of Energy for light duty fuel cells vehicles cost is \$30/kW at 500 000 units per year.³⁰

³¹ But the cost of the current commercially available Toyota Mirai is at \$200/kW, with < 3000

units/year.²⁹ This shows the pressing demand to reduce the cost of fuel cells systems to make it affordable. A promising approach is to switch to alternative cell chemistry, i.e., transition to alkaline medium. Alkaline medium offers less corrosive environment which in turn permits the utilization of inexpensive platinum metal group free (PGM-free) electrocatalysts, low-cost materials for anion membranes and cell components.^{20, 32} On this note, anion or hydroxide exchange membrane fuel cells (AEMFCs) have attracted enormous research interest. Fortunately, the ORR kinetics of inexpensive PGM-free cathodes in alkaline medium are superior, unlike in acid medium, to the Pt based electrocatalysts. But the HOR kinetics is sluggish by an order of two, when comparing to acidic medium, due to the stronger binding of hydrogen to Pt surfaces.³⁶ Hence, there is an urgent necessity to develop highly active HOR anode electrocatalysts for AEMFCs.

Generally, the HOR follows either a Tafel-Volmer (eqn 5.1 & 5.3) or a Heyrovsky-Volmer (5.2 & 5.3) pathway³³ in alkaline medium:



Despite the sluggish kinetics of HOR at Pt, it is still the best electrocatalyst for HOR. The criteria for best HOR electrocatalyst is to have an optimum interaction between catalytic substrate H_{ads} and OH^- in alkaline medium, that is because the OH_{ads} improves the reactivity of H_{ads} from catalytic surface. The H_{ads} and OH_{ads} are evaluated by hydrogen binding energy (HBE) and hydroxide binding energy (OHBE) descriptors, respectively.³² However, the relationship between HBE and OHBE are still unidentified. Precious metal catalysts such as Ir, Pd and Ru are also found to have promising HOR activity along the order of their increasing oxophilic property.⁴² Among these, the Ru possess Pt like hydrogen binding energy (HBE) at much lower cost than Pt. The high

activity of Ru is attributed to its high oxophilic nature, to form Ru-OH_{ads} at relatively low anodic potential (< 0.1 V vs. RHE).⁴³ However, when Ru employed as main catalyst, it suffers from quick surface oxidation at low potential leading to unavailability of fresh metal site for H_{ads} intermediates for further HOR.^{160, 161} Hence, it is usually alloyed with Pt to form bimetallic PtRu alloy or core-shell electrocatalysts, which exhibits superior HOR activity than Pt. This way, the oxophilic Ru metal provides abundant OH_{ads} species which leads to efficient oxidation of H_{ads} at Pt surface by spillover effect.¹⁶² Also, the alloying enables alteration of electronic structure of Pt to reduce the HBE at Pt.²⁰ So far, PtRu based electrocatalysts has evolved as the state-of-the-art anodes for AEMFCs. In general, PtRu alloy nanoparticles are deposited on high surface area carbon supports. Influence of carbon supports, such as nitrogen doped carbon, mesoporous carbon, on the HOR activity of PtRu nanoparticles are currently being studied.^{20, 36, 45, 163}

On the other hand, the deployment of transition metal-oxide as catalysts supports for precious metals have shown considerable improvement in HOR activity. For example, Pt or Pd deposited on various oxophilic transition metal oxide supports such as CeO₂, RuO₂, TiO₂, SnO₂, ZrO₂, etc. has shown an enhanced HOR activity with low CO oxidation onset potential in alkaline environment owing to the strong-metal support interaction (SMSI) and the optimum nanoparticle size control provided by the metal oxide supports.^{41, 46, 47, 164-166} The SMSI between precious metals and transition metal oxide supports leads to weakening of hydrogen binding energy (HBE) on metal surfaces due to the modification of electronic structure of metal.³² In addition, it also helps in the facile removal of hydrogen intermediates due to the improved oxophilicity (OH⁻ spillover capacities) imparted by metal oxides.⁴⁷ Among the various metal oxide supports, TiO₂ gets a special attention owing to the effective nanoparticle size control that it can impart during material synthesis along with its oxophilic property to enhance the HOR activity.^{14, 167} However, due to

the poor electronic conductivity of TiO_2 (wide band gap of ~ 3.6 eV), it has been either doped or formed as hybrids with carbon nanostructures.^{8, 165} Elezovic et.al. developed TiO_x covered Pt/C catalyst by polyol method and found it had high HOR activity with exchange current density 0.4 mA/cm^2 compared to Pt/C counterparts.¹⁶⁸ Cui et.al, explored the effect of different phases of TiO_2 deposited on carbon nitride (CN_x) in controlling nanoparticle size and SMSI between Pt and TiO_2 in enhancing the HOR activity of Pt.¹⁶⁵ Thus far, the HOR activity of Pt supported on TiO_2 have only been studied in acidic medium and not been explored in alkaline medium. Similarly, to the best of our knowledge, the effect of carbon support modification by TiO_2 towards the HOR activity and durability of Pt catalysts has not been investigated.

Recently, Wei and co-workers developed and investigated an oxide-free Ru metal based HOR main catalysts by confining Ru clusters in TiO_2 lattice.^{44, 161} The as-prepared catalysts exhibited a promising HOR activity higher than PtRu/C catalysts with superior CO tolerance. The high HOR activity was attributed to the alteration of electronic structure and oxophilic property of Ru to adsorb surface species such as H_{ads} , due to lattice confinement effect into TiO_2 support lattice.^{44, 161} However, it is to be noted that there are no reports studying the effect of TiO_2 supports on the HOR activity of bimetallic precious metal alloy nanoparticles such as PtRu. Very recently, we reported a novel and rapid microwave-assisted synthesis of defective hydrogenated TiO_2 modified oxygenated nitrogen-doped carbon nanotube (ONCNT) as multifunctional carbon support for PtRu alloy nanoparticles as highly active and stable electrocatalysts for methanol oxidation reaction (MOR) in DMFCs. The PtRu/ TiO_2 /ONCNT catalyst exhibited superior CO oxidation and MOR kinetics in both acidic and alkaline medium, owing to the SMSI and oxophilic properties imparted by the defective hydrogenated TiO_2 on PtRu alloy nanoparticles.

Encouraged by our recent study and as an effort to address the lacking studies in HOR electrocatalysis, here in, we report and employ a superior HOR anode electrocatalyst based on defective hydrogenated TiO₂-modified carbon support for PtRu bimetallic alloy nanoparticle for high-performance AEMFC using poly(ethylene-co-tetrafluoroethylene)-benzyltrimethylammonium chloride (ETFE) based AEM membranes. A facile microwave-assisted synthesis method was used to prepare the novel core-shell type catalyst support, TiO₂/C. The TiO₂ modification on carbon was found to be defective, hydrogenated, and amorphous in nature. The SMSI provided by the defective hydrogenated TiO₂ shell to PtRu nanoparticles was revealed by the XPS analysis. A high AEMFC performance with a P_{max} of 1.27 W/cm² was achieved with PtRu/TiO₂/C-400 anode and commercial Pt/C cathode. The SMSI provided by the TiO₂ on the PtRu not only helped to control the nanoparticle size to provide abundant exposed active sites but also improved the oxophilicity of the electrocatalyst which resulted in high OHBE. The SMSI in PtRu/TiO₂/C-400 resulted in excellent AEMFC stability with a voltage loss of 1.5 mV/h at 600 mA/cm² for 20 h.

5.2. Experimental Section

5.2.1. Chemical and Materials

The potassium hexachloroplatinate (K_2PtCl_6), ruthenium chloride ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), and Nafion[®] solution (5 wt% in lower aliphatic alcohols) were purchased from Sigma-Aldrich (St. Louis, MO). The titanium tetraisopropoxide (TTIP), ethylene glycol (EG), potassium hydroxide (KOH), nitric acid (HNO_3), pure ethanol 200 proof, and methanol (ACS grade) were purchased from Fisher Scientific (Hampton, NH). Ultrapure water (18.2 M Ω .cm at 25 °C) purified from a Millipore water system (EASYPURE II, Thermo Scientific, Waltham, MA) was used to prepare all aqueous solutions for the experiments. The commercial PtRu/C catalyst (TEC 66E50 – 32.8 wt% Pt and 16.9 wt% Ru on carbon) was purchased from Tanaka Kikinzoku International (America) Inc. (Schaumburg, IL), referred as TKK.

5.2.2. Material Synthesis

5.2.2.1. Preparation of TiO_2/C

KB 600JD and ONCNT were used as carbon support in this study. Both the carbon supports are first oxygenated by refluxing 1.0 g of each carbon separately in an aqueous mixture of 2.0 M H_2SO_4 and 4.0 M HNO_3 at 120 °C for 12 h under constant stirring. The obtained oxygenated carbon was washed with ultrapure water till the pH reached 7.0, filtered, and dried at 80 °C in a vacuum oven. Then, 10.0 mg of carbon was dispersed in 6.0 ml of ethanol by ultrasonication for 30 min. Further, 10.0 mg of TTIP was added to this dispersion and sonicated in a water bath. After 30 min sonication, this mixture was transferred to a 10 ml Pyrex glass microwave vessel and put into Discover[®] SP microwave synthesizer (CEM Corporation., Matthews, NC). A microwave irradiation was applied in the standard mode with the power up to 300 W to maintain a reaction temperature of 150 °C for 5 min. The reaction pressure rose to ~ 19 bar during the process. After

reaction, the naturally cooled product mixture was washed 2-3 times using ethanol to remove the unreacted precursors and dried at 80 °C in a vacuum oven to obtain the TiO₂ coated C, referred as TiO₂/C or TiO₂/ONCNT.

5.2.2.2. Preparation of PtRu/TiO₂/C-400

To deposit PtRu catalysts, 12.5 mg of K₂PtCl₆, 5.1 mg of RuCl₃.xH₂O, and 16.0 mg of different TiO₂/C were dispersed in 20 ml of mixture of ethylene glycol and water (at 4:1 volume ratio) by ultrasonication for 1 hour. The solution was then transferred to 35 ml Pyrex glass microwave vessel. The weight ratio of Pt and Ru is maintained at 2:1 in the precursors. Ethylene glycol serves as a reducing agent and solvent in this reaction. The mixture was irradiated with a 300 W microwave under the standard mode to maintain a reaction temperature of 190 °C for 20 min in Discover[®] SP microwave synthesizer to deposit Pt and Ru NPs onto TiO₂/C. The reaction pressure rose to ~8 bar during this process. The cooled product mixture was washed several times using acetone to remove residual ethylene glycol and then dried at 80 °C in a vacuum oven to obtain PtRu/TiO₂/C. The dried catalyst material was annealed in a tube furnace at 400 °C for 2 h in 3% H₂/97% Ar atmosphere at a ramp rate of 10 °C/min, to form crystalline PtRu alloyed NPs and defective hydrogenated TiO₂ shell on the carbon support. The as-prepared catalyst is named as, PtRu/TiO₂/C-400 and PtRu/TiO₂/ONCNT-400 depending on the carbon support used. Synthesis of control samples was carried out using the same reaction conditions as mentioned above with appropriate precursors but skipping some specific intermediate steps.

5.2.3. Materials Characterization

The structure of the catalysts was characterized using two transmission electron microscopes (TEM), including: a Tecnai Osiris Scanning/Transmission Electron Microscope (S/TEM, FEI, Hillsboro, OR) at a 200 kV acceleration voltage, located at University of Nebraska,

Lincoln; a Hitachi H-8100 TEM (Hitachi, Krefeld, Germany) at a 200 kV acceleration voltage, located at University of Kansas, Lawrence and a Philips CM 100 TEM at a 100 kV acceleration voltage located at Department of Biology, KState. The crystal structure of the catalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 1 mm, located at Department of Chemistry, KState. XRD reference spectra are used from Joint Committee on Powder Diffraction Standards (JCPDS). The composition of the catalysts was determined using a Thermogravimetric Analyzer (TGA) Q50 system (TA instruments - Waters LLC, New Castle, DC) from the room temperature to 900 °C in a compressed air atmosphere. The surface chemical composition of the catalysts was characterized using a PHI 5000 Versa XPS system (Chanhasen, MN) with a monochromatized Al K α source (1486.7 eV). All the XPS spectra were obtained using a 400 μ m spot size, located at University of Nebraska, Lincoln. Shirley background was used in the curve fitting. The binding energy (B.E.) of all XPS data was calibrated vs. the standard C 1s peak at 284.60 eV. The BET specific surface area and pore size distribution of the prepared samples were tested by N₂ adsorption at 77 K in a Quantichrome Autosorp IQ (Anton Paar - Ashland, VA).

5.2.4. Electrochemical Characterization

The HOR LSV RDE studies were carried out by our collaborators Dr. Dario R Dekel and John C. Douglin from the Wolfson Department of Chemical Engineering, Technion, Israel Institute of Technology, Haifa 3200003, Israel. CO stripping electrochemical experiments were performed in a standard three-electrode setup using a CHI 760D electrochemical workstation (CH Instruments, Austin, TX) at room temperature at KSU. A mercury-mercuric oxide (Hg/HgO in 1.0 M NaOH solution) reference electrode and a coiled Pt counter electrode (0.55 mm in diameter and

23 cm in length) were used. The working electrode was prepared by drop-casting the catalyst ink onto a glassy carbon electrode (GCE) encased in a PEEK rod. Before drop-casting the catalyst ink, the GCE was polished using 0.05 μm alumina slurry. The catalyst ink was prepared by dispersing the required amount of catalyst powder in 1.0 ml of mixture of ethanol and ultrapure water (at 3:1 volume ratio) with addition of the 30 μl of Nafion[®] solution (5 wt% in lower aliphatic alcohols). The loading of the platinum group metal (PGM, specifically Pt and Ru in this study) was maintained at 54 $\mu\text{g}/\text{cm}^2$ for all catalysts in the CO stripping studies. For direct comparison of the potentials with literature, the measured electrode potential vs. the Hg/HgO (1.0 M NaOH) reference electrode is converted to the value vs. the reversible hydrogen electrode (RHE) using the following equation:

$$E_{(\text{vs. RHE})} = E_{(\text{vs. Hg/HgO})} + E_{(\text{Hg/HgO vs. SHE})} + 0.059\text{pH} = E_{(\text{vs. Hg/HgO})} + 0.907 \text{ V} \quad (5.4)$$

where $E_{(\text{vs. Hg/HgO})}$ is the measured potential vs. the Hg/HgO (1.0 M NaOH) reference electrode, $E_{(\text{Hg/HgO vs. SHE})} = 0.140 \text{ V}$ is the Hg/HgO (1.0 M NaOH) reference electrode potential vs. SHE, and $\text{pH} = 13.0$ for 0.1 M KOH.

The CO stripping voltammetry experiments were performed in 0.1 M KOH to evaluate the oxophilicity of the catalysts and to determine the active electrochemical surface area (ECSA) of the catalyst. In CO stripping experiments, the electrolyte was first purged with Ar gas to remove any dissolved oxygen species in the electrolyte. Then, a pure CO gas was used to purge the electrolyte for 10 min while the potential of the working electrode was held at 0.10 V vs. RHE. After 10 min, the purging gas was switched back to pure Ar to purge for 30 min to remove the dissolved CO gas from the electrolyte, while the potential of the working electrode was still held at 0.10 V vs RHE which retained the adsorbed CO monolayer on the Pt surface. Subsequently, the CO monolayer on the Pt surface was stripped off with a linear anodic sweep at 10 mV/s from 0.10

V to 1.222 V vs. RHE. A few CV cycles were taken following CO stripping to evaluate the baseline of the electrode.

The ECSA of Pt in the catalysts was determined using the following equation:

$$\text{ECSA} = \frac{Q_a}{Q_{\text{CO}}^0 \times m_{\text{Pt}}} \quad (5.5)$$

where Q_a ($\mu\text{C}/\text{cm}^2$) is the charge associated with the integrated area of CO oxidation peak; $Q_{\text{CO}}^0 = 420 \mu\text{C}/\text{cm}^2$ is the charge required to oxidize a monolayer of CO adsorbed on 1 cm^2 of flat Pt surface and m_{Pt} ($\text{g}_{\text{PtRu}}/\text{cm}^2$) is the mass loading of PtRu on the working electrode surface.

5.2.5. Full AEMFC Characterization

The full AEMFC tests were done by our collaborators Dr. Dario R Dekel and John C. Douglin from the Wolfson Department of Chemical Engineering, Technion, Israel Institute of Technology, Haifa 3200003, Israel. The anode and cathode catalyst loadings were $0.5 \text{ mg}_{\text{PtRu}}/\text{cm}^2$ and $0.5 \text{ mg}_{\text{Pt}}/\text{cm}^2$, respectively. Test conditions: cell temperature at 80.0°C , at $1 \text{ L}/\text{min}$ H_2 and O_2 flow rate with 150 kPa back pressure. An ETFE based AEM membrane was used in all the fuel cell tests.

5.3. Results and Discussion

5.3.1. Morphological and Structural Characterization

Ketjen black carbon with a BET specific surface area of $\sim 1447 \text{ m}^2/\text{g}$ was used as carbon support in this work. Ketjen black is chosen owing to its high BET SSA and high density of micropores which is essential for narrow PtRu nanoparticle size distribution and for better mass transport properties. Ultrathin shell of TiO_2 was deposited on the carbon support using a simple and rapid 5 min microwave-assisted synthesis reported in our Chapter 2.⁸ The high tangent loss value of the carbon supports ($\tan \delta \sim 1.0$) compared to ethanol solvent (< 0.9), enabled preferential

deposition of TiO_2 as ultrathin shells on carbon supports.¹⁴⁴ Figure 5.1 (a) shows the TEM image of microwave deposited TiO_2 on carbon, denoted as TiO_2/C . Owing to the poor contrast difference, it was difficult to observe the carbon and TiO_2 interface. However, TGA experiments on TiO_2/C (see blue curve in Figure D2 (a)) revealed the presence $\sim 19.2\%$ of material left after thermal treatment at 900°C , which can be attributed to the TiO_2 . The shift in the carbon decomposition temperature to lower temperature ($\sim 450^\circ\text{C}$) in the TGA of TiO_2/C , also indicated the presence of TiO_2 , as metal oxides are proven to catalyze carbothermal reaction.

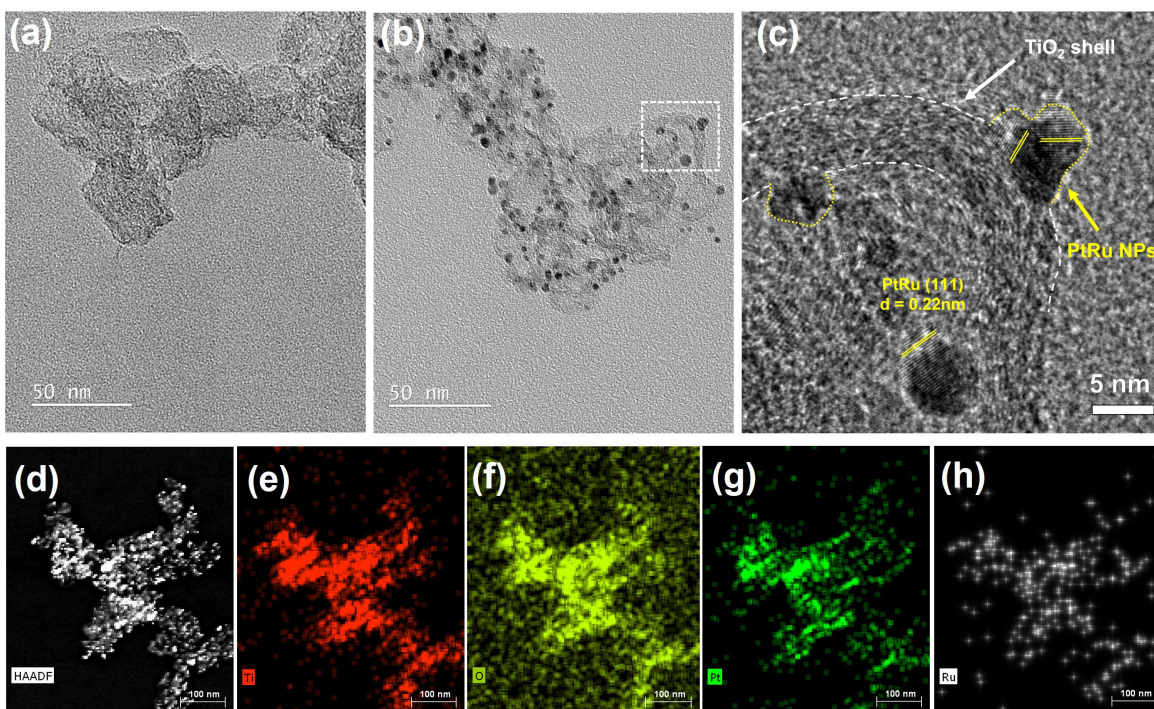


Figure 5.1. TEM image of (a) TiO_2/C , (b) $\text{PtRu}/\text{TiO}_2/\text{C-400}$, (c) HRTEM image of enlarged portion of Fig 1b) of $\text{PtRu}/\text{TiO}_2/\text{C-400}$, (d) HAADF-STEM image and (e–h) STEM-EDX elemental mapping of Ti, O, Pt and Ru from $\text{PtRu}/\text{TiO}_2/\text{C-400}$.

A second microwave-assisted synthesis method developed in our previous work was used to deposit PtRu nanoparticles on the TiO_2/C to form $\text{PtRu}/\text{TiO}_2/\text{C}$. This sample was annealed at 400°C for 2h in 3% H_2 / 97% Ar to enable PtRu alloy formation and to form hydrogenated TiO_2 as will be revealed later. The thus prepared catalyst is denoted as $\text{PtRu}/\text{TiO}_2/\text{C-400}$ and is shown

in Figure 5.1 (b). Uniform dispersion of PtRu alloy nanoparticles was found on to TiO₂/C. The average PtRu nanoparticle size was found to be 3.1 ± 0.6 nm (Figure D1 (b)). Interestingly, after PtRu deposition and annealing, a clear TiO₂ and carbon interface (indicated by white arrows) was observed for PtRu/TiO₂/C-400 demonstrating a TiO₂ shell thickness of ~ 3 to 4 nm, shown in the HRTEM image of PtRu/TiO₂/C-400 in Figure 5.1 (c). The lattice fringes of PtRu (111) crystals are clearly observed and are found to be embedded on the TiO₂ shell at the edge of the carbon support. Figure 5.1 (d) – (h) shows the STEM-HAADF image and EDX elemental mapping of Ti, O, Pt and Ru on the carbon support revealing the uniform distribution of TiO₂ shell on the carbon support. The critical effect of TiO₂ shell in controlling the PtRu nanoparticle size was illustrated by preparing a control sample PtRu/C-400 (without TiO₂). Figure D1 (c) and (d) shows the TEM image and its corresponding PtRu nanoparticle size distribution of PtRu/C-400. The average PtRu nanoparticle size was found to be 5.5 ± 1.4 nm, which is ~ 2 nm larger when compared to the PtRu/TiO₂/C-400. This reveals that nanoparticle agglomeration during annealing at 400 °C was mitigated when TiO₂ modification on carbon support was done owing to the strong interaction of metal nanoparticles with metal oxide supports.⁸ The catalyst nanoparticle size control is very important in electrocatalysis as smaller nanoparticles offers high exposed active surface sites.¹⁶⁵ As a comparison, the TEM image and PtRu nanoparticle distribution (4.4 ± 0.9 nm) of commercial PtRu/C is shown in Figure D1 (e) – (f). TGA experiments on PtRu/TiO₂/C-400 and its corresponding control samples were done to determine the elemental composition of the catalysts as shown in Figure D2. TGA analysis established in Chapter 2 was followed to determine the PtRu (PGM) wt% as 32.6% in PtRu/TiO₂/C-400.

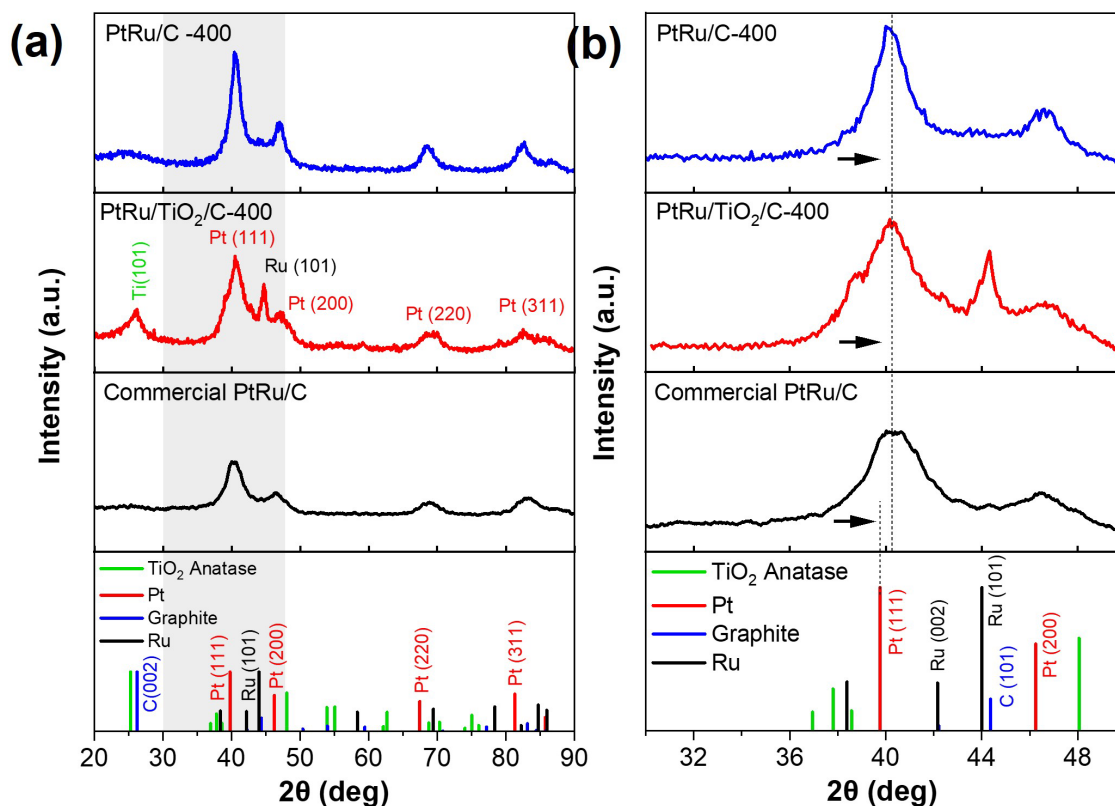


Figure 5.2. XRD patterns in the 2θ range of (a) 20° to 90° and (b) 30° to 50° of Ru reference (JCPDS # 06-0663), graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), TiO₂ anatase reference (JCPDS# 21-1272) compared with commercial PtRu/C, PtRu/TiO₂/C-400 and control PtRu/C-400 (w/o TiO₂).

XRD was done to understand the crystal structure of the catalysts. Figure 5.2 shows the XRD patterns of PtRu/TiO₂/C-400 and PtRu/C-400 (w/o TiO₂) compared to commercial PtRu/C and standard reference spectra of Pt (JCPDS# 04-0802), Ru (JCPDS # 06-0663), TiO₂ anatase (JCPDS# 21-1272) and graphite (JCPDS# 75-1621). The diffraction peaks at 2θ angles of 40.2° , 46.72° , 69.03° and 82.76° , corresponding to fcc Pt (111), Pt (200), Pt (220) and Pt (311), respectively, were observed for PtRu/TiO₂/C-400, PtRu/C-400 (w/o TiO₂) and commercial PtRu/C catalysts. This illustrates the crystalline nature of PtRu nanoparticles deposited on PtRu/TiO₂/C-400 and PtRu/C-400. The PtRu alloy formation was uncovered from the peak shift in Pt (111) to

higher 2θ angles, compared to Pt reference spectrum (JCPDS: 04-0802). These diffraction peak shifts reveal the introduction of Ru atoms into Pt lattice resulting in shrinking of lattice constant of Pt which are consistent with the commercial PtRu/C catalysts. The atomic fraction of Pt and Ru was calculated to be $\sim 1.6:1$, for all the catalysts, by Vegard's law.¹¹⁰ The diffraction peak corresponding to hcp Ru (101) at 2θ angle of 44.2° was observed for PtRu/TiO₂/C-400 indicating the presence of some individual Ru nanoparticles along with PtRu alloy nanoparticles. Such individual Ru nanoparticles may be beneficial for HOR as it may also serve as HOR active site.¹⁴⁵ Such Ru (101) peak was not observed for commercial PtRu/C and PtRu/C-400 depicting the complete PtRu alloy formation. Scherrer's formula was used to calculate the PtRu crystallite size as 2.90 nm and 4.69 nm for PtRu/TiO₂/C-400 and PtRu/C-400, respectively.⁸ The PtRu crystallite size was close to the nanoparticle size determined from TEM analysis. Diffraction peaks for anatase TiO₂ (101) was observed at 2θ angle of 25.6° indicating the crystalline nature of TiO₂ shell deposited on carbon support for PtRu/TiO₂/C-400 sample. This supports the TiO₂ anatase nanocrystals embedded into TiO₂ shell in the HRTEM images (Figure 5.1 (c)).

5.3.2. Materials Compositional Analysis

The surface elemental composition of all the catalysts were studied by XPS analysis. Figure D3 shows the XPS survey spectra of PtRu/TiO₂/C-400 indicating the presence of C, Ti, O, Pt and Ru. The interaction of PtRu catalyst with TiO₂ support was studied by comparing the XPS spectra of Ti 2p, Pt 4f and Ru 3p for various catalysts as shown in Figure 5.3. Firstly, the surface chemical composition of the amorphous TiO₂ deposited on C was understood by deconvoluting the Ti 2p of TiO₂/C-400 as shown in Figure 5.3 (a). The Ti 2p spectrum of TiO₂ /C-400 was fitted into a pair of Ti 2p_{3/2} and Ti 2p_{1/2} doublet at 458.17 eV and 463.88 eV corresponding to Ti⁴⁺ of TiO₂.¹²² However, another pair of doublet corresponding to Ti³⁺, in addition to Ti⁴⁺ was required to fit the

Ti 2p spectra of TiO₂/C-400 indicating the formation of hydrogenated TiO₂ with oxygen vacancies during thermal annealing in 3% H₂/ 97% Ar.^{8, 122} Such observation were studied in-depth in our previous works.⁸ It is worth to note that the defective hydrogenated TiO₂ enhances the electronic conductivity when compared to pristine TiO₂ anatase.^{82, 88, 89} Similarly, the Ti 2p spectra of PtRu/TiO₂/C-400 were deconvoluted in to two pairs of 2p_{3/2} and 2p_{1/2} doublets corresponding to Ti⁴⁺ and Ti³⁺ of TiO₂ and hydrogenated TiO₂, respectively, as shown in Figure 5.3 (a). Interestingly, the BE position Ti⁴⁺ peak upshifted to 458.85 eV for PtRu/TiO₂/C-400 when compared to the BE of TiO₂/C-400 (w/o PtRu) suggesting a lower electron density at Ti⁴⁺ sites of PtRu/TiO₂/C-400, likely due to partial electron transfer to PtRu from Ti⁴⁺. The binding energy (BE) positions of these samples are summarized in Table D1.

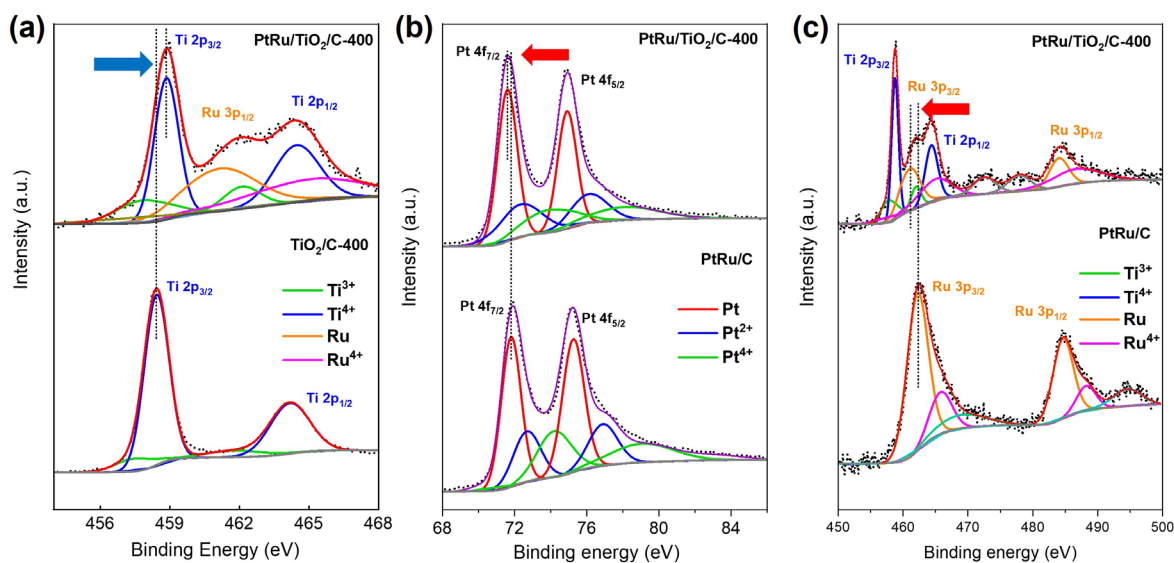


Figure 5.3. XPS analysis of (a) Ti 2p spectra of TiO₂/C-400 and PtRu/TiO₂/C-400; (b) Pt 4f spectra and (c) Ru 3p spectra of commercial PtRu/C and PtRu/TiO₂/C-400; . The legends in each panel apply to all three curves in that panel.

Figure 5.3 (b) shows the Pt 4f spectra of PtRu/TiO₂/C-400 and commercial PtRu/C JM. The Pt 4f spectra was deconvoluted into three pairs of Pt 4f_{7/2} and Pt 4f_{5/2} doublets attributed to

Pt⁰, Pt²⁺ and Pt⁴⁺ states in metallic, PtO & Pt(OH)₂, and PtO₂ species, respectively.¹²⁴ In contrast to BE shift observed in Ti 2p peak, the BE of Pt 4f_{7/2} of metallic Pt of PtRu/TiO₂/C-400 downshifted to 71.59 eV compared to 71.82 eV in commercial PtRu/C catalyst. This depicts a higher electron density at Pt atomic sites of PtRu/TiO₂/C-400 due to partial electron transfer happening from Ti⁴⁺ to Pt resulting in strong-metal support interaction (SMSI). Figure 5.3 (c) showed the Ru 3p spectra of PtRu/TiO₂/C-400 and commercial PtRu/C. The Ru 3p spectra was deconvoluted into two pairs of doublets corresponding to Ru⁰ and Ru⁴⁺ in metallic and RuO₂ species, respectively.¹²⁵ Similar to Pt 4f, the BE of Ru 3p_{3/2} of metallic Ru downshifted to 461.06 eV compared to commercial PtRu/C (462.43 eV), indicating partial electron transfer to metallic Ru sites from Ti⁴⁺ sites, resulting in SMSI between TiO₂ support and PtRu nanoparticles. The SMSI imparted by metal oxides in general are found to alter the electronic structure of both Pt and Ru precious metals in optimizing the HBE and OHBE towards improvement of their HOR activity.^{32, 44, 165} The binding energy (BE) positions of all the catalysts are summarized in Table B1. It is worth to note that, in case of PtRu/TiO₂/C-400, the relative at% of metallic Pt (53.4%) and Ru (68.2%) were higher than the metallic Pt (50.6%) and Ru (64.0%) sites in commercial PtRu/C. This depicts presence of higher amount of metallic active sites available for adsorption of surface species such as H_{ads} and OH_{ads} for efficient HOR at the PtRu/TiO₂/C-400.

5.3.3. Assessment of AEMFC performance

AEMFC performance was evaluated for the various anode electrocatalysts, prepared in this study, against commercial Pt/C cathodes as shown in Figure 5.4 (a). All the MEAs were tested at similar test conditions. The anode and cathode catalyst loadings were maintained at 0.5 mg_{PtRu}/cm² and 0.5 mg_{Pt}/cm², respectively. The cell temperature was kept at 80.0 °C, with 1 L/min of H₂ and O₂ flow rate with 150 kPa back pressure. An ETFE based AEM membrane was used in all the fuel

cell tests. A maximum peak power density ($P_{\max}$) of 1.27 W/cm^2 was achieved for PtRu/TiO₂/C-400. A $P_{\max}$ of 1.14 W/cm^2 and 1.02 W/cm^2 was achieved for the commercial PtRu/C anode and PtRu/C-400 anode.

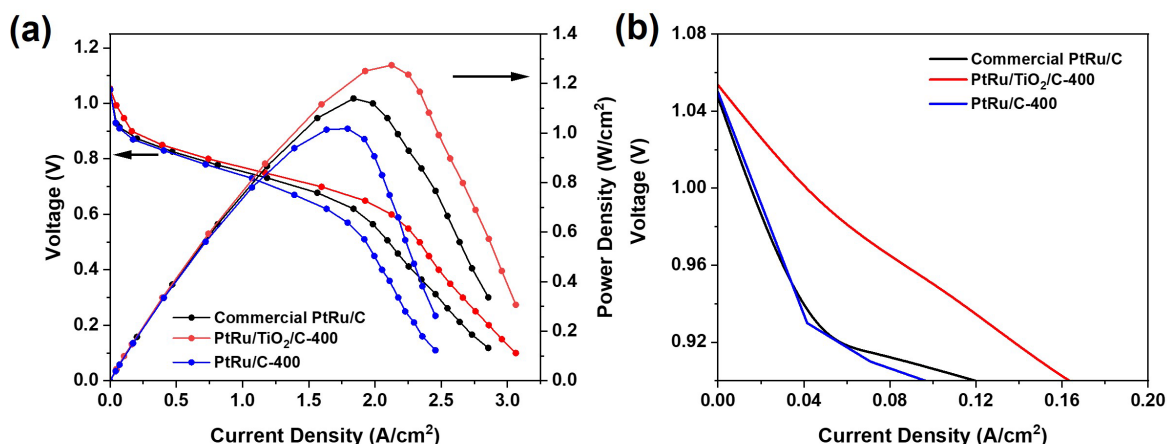


Figure 5.4. (a) Comparison of AEMFC performance of various anode such as commercial PtRu/C, PtRu/TiO₂/C-400 and PtRu/C-400 against commercial Pt/C cathode catalyst. (b) Comparison of polarization curve of (a) at low current density region illustrating the intrinsic catalyst activity. The anode and cathode catalyst loadings were $0.5 \text{ mg}_{\text{PtRu}}/\text{cm}^2$ and $0.5 \text{ mg}_{\text{Pt}}/\text{cm}^2$, respectively. Test conditions: cell temperature at 80.0°C , at 1 L/min H₂ and O₂ flow rate with 150 kPa back pressure. An ETFE based AEM membrane was used in all the fuel cell tests. Credit: AEMFC tests were done by John in Dr. Dario Dekel's lab at Israel Institute of Technology.

Critical differences were observed in the polarization curves at low current density region and high current density region which correspond to voltage losses due to intrinsic catalytic activity and mass transport of fuel, respectively. The enlarged portion of the low current density region is shown in Figure 5.4 (b) which depicts the voltage loss due to intrinsic electrocatalytic activity of the three HOR anode electrocatalysts. The PtRu/TiO₂/C-400 shows enhanced intrinsic electrocatalytic activity with lower voltage loss when compared to commercial PtRu/C and PtRu/C-400. The enhanced HOR intrinsic catalytic activity can be explained by the strong oxophilicity, abundantly exposed metallic active sites, and SMSI imparted by the TiO₂ modified

carbon support on PtRu nanoparticles. Moreover, the PtRu/TiO₂/C-400 showed improved mass transport properties at the high current density region of the polarization curve when compared to other two catalysts. This is due to the favorable pore size distribution provided by the TiO₂ modified carbon supports for efficient mass transport for gaseous H₂ fuel at the anode. The stability test was conducted for all the samples as shown in Figure 5.5.

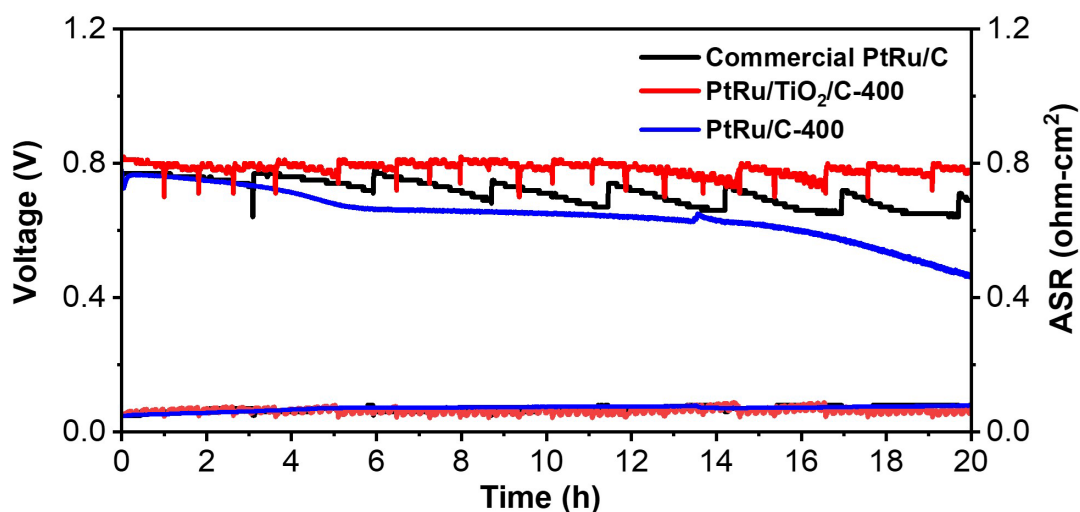


Figure 5.5. Comparison of AEMFC stability data at a constant current density of 600 mA/cm² of commercial PtRu/C anode and PtRu/TiO₂/C anode. Both the MEAs were tested against commercial Pt/C cathode. Anode catalyst loading: 0.5 mg_{PtRu}/cm²; cathode catalyst loading: 0.5 mg_{Pt}/cm²; cell temperature at 80.0 °C, at 0.2 L/min H₂ and O₂ flow rate with 150 kPa back pressure. Credit: AEMFC tests were done by John in Dr. Dario Dekel's lab at Israel Institute of Technology.

The AEMFC was tested at a constant current density of 600 mA/cm² at a cell temperature of 80 °C with 0.2 L/min of H₂ and O₂ flow at anode and cathode with 150 kPa backpressure. The MEA with PtRu/TiO₂/C-400 anode exhibited excellent stability with about 1.5 mV/h voltage loss for 20 h, when compared to the commercial PtRu/C (5.5 mV/h loss) and PtRu/C-400 (15.1 mV/h loss) sample. This clearly illustrates the beneficial role of hydrogenated TiO₂ in providing SMSI to the PtRu active nanoparticles in improving the stability. We were able to increase the P_{max} further to 1.42 W/cm² with utilization of PtRu/TiO₂/ONCNT-400 as anode which possessed

carbon nanotube-based catalyst support as shown in Figure 5.6. The PtRu/TiO₂/ONCNT-400 is the catalyst that was reported in Chapter 2,⁸ which was prepared using the same synthesis methodology used to prepare catalysts in this work. The major improvement was observed at the high current density region of the polarization curve owing to the superior mass transport of gaseous H₂, enabled by the CNT catalyst support, to the active sites of PtRu/TiO₂/ONCNT-400.

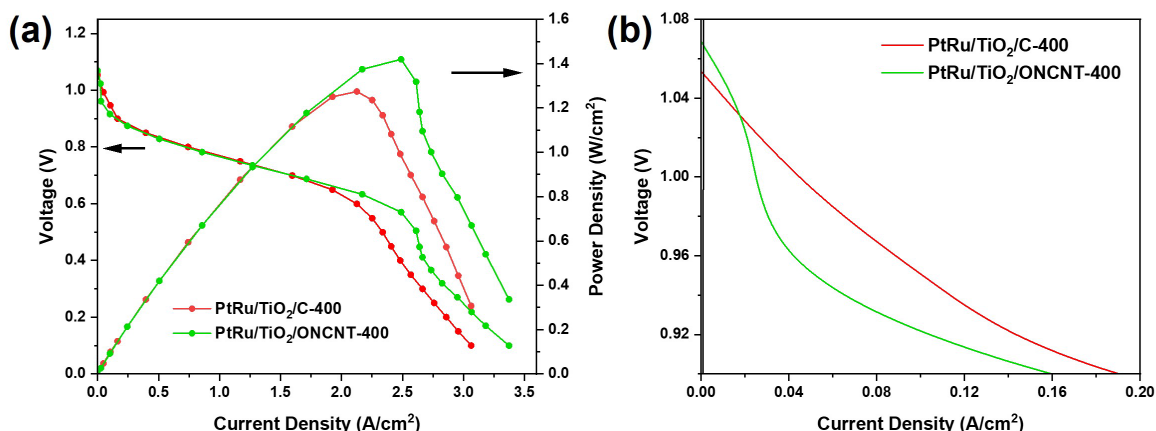


Figure 5.6. Comparison of AEMFC performance of various anode such as PtRu/TiO₂/C-400 and PtRu/TiO₂/ONCNT-400 against commercial Pt/C cathode catalyst. (b) Comparison of polarization curve of (a) at low current density region illustrating the intrinsic catalyst activity. The anode and cathode catalyst loadings were 0.5 mg_{PtRu}/cm² and 0.5 mg_{Pt}/cm², respectively. Test conditions: cell temperature at 80.0 °C, at 1 L/min H₂ and O₂ flow rate with 150 kPa back pressure. An ETFE based AEM membrane was used in all the fuel cell tests. Credit: AEMFC tests were done by John in Dr. Dario Dekel's lab at Israel Institute of Technology.

5.3.4. Assessment of CO oxidation and HOR activity

In order to gain more mechanistic understanding for the enhanced AEMFC performance of PtRu/TiO₂/C-400, half-cell CO stripping analysis was conducted for all the catalysts in this study as shown in Figure 5.7 (a). The PtRu/TiO₂/C-400 showed earlier CO oxidation onset and peak potential at 0.429 V vs. RHE and 0.528 V vs. RHE, respectively, when compared the commercial PtRu/C and PtRu/C-400 anode catalysts. The superior CO oxidation kinetics of

PtRu/TiO₂/C-400 is due to the high oxophilicity imparted by the Ru and defective hydrogenated TiO₂ in providing abundant OH species. The formation of abundant OH_{ads} species at low electrode potentials at the vicinity of active Pt and Ru catalyst will improve the OHBE of the electrocatalyst which thereby can enhance AEMFC performance of the PtRu/TiO₂/C-400 catalyst. The PtRu/C-400 anode catalyst had a CO oxidation peak potential of 0.536 V vs. RHE, and it was followed by the commercial PtRu/C catalyst at 0.542 V vs. RHE.

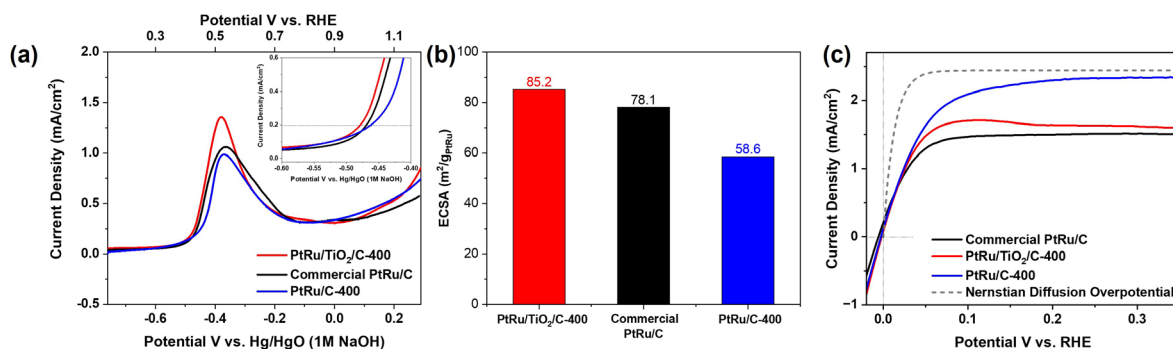


Figure 5.7. Comparison of HOR RDE LSV curves of (a) commercial PtRu/C, PtRu/TiO₂/C-400 and PtRu/C-400 collected in H₂-saturated 0.1 M KOH with 1600 rpm at a scan rate of 5 mV s⁻¹ and (b) HOR polarization curves from (a) normalized to the maximum limiting current density, i_{lim} , (c) Comparison of CO stripping curves of commercial PtRu/C, PtRu/TiO₂/C-400 and PtRu/C-400 collected in Ar-saturated 0.1 M KOH at a scan rate of 10 mV s⁻¹. Credit: Figure 5.5 (c) was tested by Dr. Ramesh in Dr. Dario Dekel's lab at Israel Institute of Technology.

The electrochemical active surface area (ECSA) of the catalyst was determined by integrating the charge of the CO oxidation curve. The ECSA of PtRu/TiO₂/C-400, commercial PtRu/C and PtRu/C-400 was found to be 85.1 m²/g_{PtRu}, 78.1 m²/g_{PtRu}, and 58.6 m²/g_{PtRu} as shown in Figure 5.7 (b). The highest ECSA of PtRu/TiO₂/C-400 nicely corroborates with the narrow PtRu nanoparticle size distribution on the TiO₂ modified carbon support revealed by TEM and XRD analyses. Such high ECSA also contributes to abundant exposed active sites in enhancing AEMFC performance of PtRu/TiO₂/C-400. The decreasing trend in the ECSA values matches well with the

decreasing PtRu nanoparticle size distribution of the various electrocatalysts. Further three-electrode rotating disk electrode (RDE) measurements were carried out for various anode electrocatalysts at different rotation speed in H₂ saturated 0.1 M KOH. All the electrocatalysts loading were maintained at 54 µg/cm². Figure D4 (a) to (c) shows the RDE LSV HOR curves of commercial PtRu/C, PtRu/TiO₂/C-400, and PtRu/C-400 electrocatalysts at different rotation speeds. Figure 5.7 (c) shows the comparison of HOR LSV curves of different catalysts at 1600 rpm. Interestingly, the PtRu/C-400 electrocatalyst reached a high H₂ limiting current density of 2.34 mA/cm², close to the theoretical Nernstian diffusion limited current density. Whereas the PtRu/TiO₂/C-400 had lower H₂ limiting current density of 1.63 mA/cm² than the PtRu/C-400. But it was higher than the commercial PtRu/C (1.51 mA/cm²). This trend in H₂ limiting current density was completely mismatching with the trend observed in the AEMFC performance and CO stripping analyses. This illustrates the technical complexities of using RDE measurement to screen the catalytic activity of HOR electrocatalysts due to the combination of mass transport limitation of H₂ and fast reaction kinetics of HER at 0 V.¹⁶⁹ This is a quite common phenomenon observed in HOR electrocatalysis community where the activity of HOR catalysts is vastly underestimated in RDE measurements.⁵⁷ Kinetic parameters of the catalysts can be studied by other bridging techniques such as H₂-pump method, ultramicroelectrode (UME), scanning electrochemical microscopy (SECM) and floating electrode method.^{35, 57, 169} Nevertheless, only MEA level catalysts testing in AEMFC can reveal the true overall performance of the catalyst as revealed in this work.

5.4. Conclusion

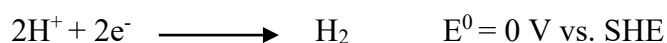
We have demonstrated a rapid microwave-assisted synthesis method to prepare a novel core-shell type catalysts support based on defective hydrogenated TiO₂ modified carbon supports for PtRu nanoparticles as HOR electrocatalysts in AEMFCs. A high AEMFC performance with P_{max} of 1.27 W/cm² was achieved with PtRu/TiO₂/C-400 anodes. The SMSI provided by the TiO₂ on the PtRu not only helped to control the nanoparticle size to provide abundant exposed active sites but also improved the oxophilicity of the electrocatalyst which resulted in high OHBE. The SMSI imparted by the TiO₂ on PtRu nanoparticles resulted in excellent AEMFC stability with 1.5 mV/h voltage loss at 600 mA/cm² for 20 h. This work will help to develop novel synthesis methods to prepare metal oxide modified carbon supports for HOR electrocatalysts.

Chapter 6 - Controllable Synthesis of Defect-Engineered Molybdenum Sulfides to Improve Hydrogen Evolution Reaction Kinetics

6.1. Introduction

The depletion of fossil fuel has created an ever-increasing demand for alternate energy source to drive the humanity. In previous chapters, energy conversion of green fuels to renewable energy was discussed. This chapter focuses on production of green hydrogen fuel as alternate green energy carrier. Hydrogen is a promising energy carrier which finds applications in industries for ammonia production, oil refining and methanol production.¹⁷⁰ In addition, hydrogen is a potential fuel in transportation sectors owing to its high gravimetric energy density (~142 MJ/kg) when present as compressed gas form.⁴⁸ More than 95% of today's hydrogen is produced by steam methane reforming and coal gasification leading to enormous carbon emissions. In addition, the exponential growth of global hydrogen demand pushes the need to reduce carbon emission substantially.^{48, 170} Hence, the development of a renewable and green technology to produce hydrogen is very essential. Water electrolyzer is the best zero-carbon emission alternative technology for green hydrogen gas production by splitting of water by means of electricity (from renewable sources such as solar). The green hydrogen gas produced this way has the highest purity of about 99.999%.⁴⁸

Hydrogen is produced at the cathode compartment of a proton exchange membrane water electrolyzer and is called as hydrogen evolution reaction (HER).⁴⁹ In an acid electrolyte, the protons are reduced to hydrogen following the equation⁴⁹ given below,



The state-of-the-art catalyst to catalyze HER is platinum. Pt being at the top of volcano plot has negligible overpotential for HER due to the very low (~ 0 eV) H_2 adsorption Gibbs free energy (ΔG_H).⁴⁹ Given that it is an expensive metal that accounts for more than 25% of the cost of the water electrolyzer stack, it is one of the main factors impeding the viability of this technology's commercialization. Recently, The U.S. Department of Energy's first energy earth shot has announced to reduce the cost of green H_2 to 80% to \$1/kg of H_2 in a decade to realize the hydrogen economy.⁵³ As a result, the need for less expensive, earth-abundant alternatives to Pt for HER has increased, which has driven the creation of numerous non-precious catalysts.

Among various non-precious electrocatalyst,¹⁷¹ molybdenum sulfides (MoS_x) have acquired special interest in acidic electrolyte owing to their good stability in low pH compared to other transition metals.⁵⁴ MoS_x exists in crystalline, molecular clusters and amorphous forms.¹⁷² Crystalline MoS_2 (c- MoS_2) are two-dimensional sandwich like structures which gained considerable attention as HER electrocatalyst owing to their low ΔG_H for hydrogen adsorption on their edge sites (0.08 eV).¹⁷¹ However, experimental HER activity of c- MoS_2 was lower to Pt due to the very few exposed active edge sites and inactive basal plane.¹⁷³ Several research groups reported novel strategies to control the size, morphology, number of layers, creating sulfur vacancies and dopants to enhance exposed edge sites and create new active sites to improve the HER activity.¹⁷³⁻¹⁷⁷ Nevertheless, increasing the active site density of 2D structure was challenging and remains far from the Pt HER activity. Several research groups also explored molecular sulfido clusters (such as dinuclear $[Mo_2^V S_{12}]^{2-}$ and trinuclear $[Mo_3^{IV} S_{13}]^{2-}$)¹⁷⁸ molecular analogues of c- MoS_2 and achieved low Tafel slopes of ~ 40 mV/decade close to Pt/C (~ 30 mV/decade).¹⁷⁹

On the other hand, amorphous MoS_x ($x = 2$ to 3), commonly called a- MoS_3 , have attracted special attention due to their disordered and defect rich structure.¹⁷³ They have shown enhanced HER activity compared to the bulk c- MoS_2 counterparts.⁵⁴ In contrast to the 2D layered c- MoS_2 , a- MoS_3 was found to have 1D chain-like nanostructures, with abundantly exposed bridging S_2^{2-} , terminal S_2^{2-} , unsaturated S^{2-} , and apical S^{2-} ligands.^{180, 181} The a- MoS_3 has been given two competing structures proposed by Hibble et al.¹⁸² and Weber et al.¹⁸¹ Hibble's a- MoS_3 structure formula is given as $\text{Mo}^{\text{V}}(\text{S}^{2-})_2(\text{S}_2^{2-})_{0.5}$. Three sulfides (S^{2-}) and the mixed ligands (one sulfide (S^{2-}) and one disulfide (S_2^{2-})) alternately bridge the two neighboring molybdenum(V) centers in the chain.¹⁸² In contrast, in Weber's a- MoS_3 structure, with the formula of $\text{Mo}^{\text{IV}}(\text{S}^{2-})(\text{S}_2^{2-})$, the neighboring molybdenum(IV) centers are all bridged by one sulfide (S^{2-}) and two disulfides (S_2^{2-}) at the two terminals.¹⁸¹ Both structures are accepted as good catalysts for HER.

Hu and co-workers first investigated a- MoS_3 thin films on glassy carbon electrodes by anodic electrodeposition using $(\text{NH}_4)_2(\text{MoS}_4)$ in 0.1 M NaClO_4 as electrolyte and reported an HER overpotential of 200 mV at 5 mA/cm^2 with TOF value of 0.23 H_2/s per site.⁵⁴ The abundant S_2^{2-} sites were suggested to be the active sites for the enhanced HER activity. In a later study, they suggested that protons bind to the terminal S_2^{2-} ligands of a- MoS_3 to generate H_2 by in-situ X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) experiments.¹⁸³ However, using operando Raman spectroscopy and DFT studies, Yeo et. al revealed the bridging S_2^{2-} to be the active sites for HER rather than the terminal S_2^{2-} owing to the $\nu(\text{S-H})$ vibrations in Raman and low ΔG_{H} of protons at bridging S_2^{2-} compared to terminal S_2^{2-} .^{184, 185} In contrast to this, Tran et al. reported the formation of $\text{Mo}^{\text{V}}\text{-H}$ moiety, and thus suggested Mo^{V} as the active species to produce hydrogen.¹⁸⁶ This Mo^{V} based mechanism was supported by a few other studies.^{187, 188} Li et. al attributed the high catalytic activity of the a- MoS_3 , synthesized by laser ablation method,

to the increased density of Mo^{V} defect sites and bridging S_2^{2-} ligands.¹⁸⁸ Anyways, the HER mechanism and origin of active site in a- MoS_3 is not well understood and requires further studies. On this note, the a- MoS_3 employed for HER electrocatalysis in reports so far are synthesized by electrodeposition, liquid phase/wet-chemical synthesis, chemical plating, chemical/vapor deposition, femtosecond laser ablation, and hydrothermal synthesis.^{54, 105, 173, 183, 188, 189} All the methods reported, are either unscalable, time consuming, energy intensive or having limited control to modulate the defect density. Hence, there remains a considerable demand for developing a rapid and scalable synthesis method with better control to prepare active a- MoS_3 with abundant active sites for HER.

Here in, we report a simple and controllable, rapid microwave-assisted synthesis to prepare amorphous MoS_3 (a- MoS_3) on reduced graphene oxide (rGO) template to employ it as a HER electrocatalyst. Subsequent thermal annealing of the microwave synthesized a- MoS_3 /rGO at various temperatures produced a family of defect-engineered MoS_x /rGO hybrids with tunable S to Mo ratio from 3.6 to 2.2. By annealing the microwave synthesized a- MoS_3 /rGO sample at 250 °C (a- MoS_3 /rGO 250), the composition of a- MoS_3 was tuned. While annealing at higher temperatures such as 325 °C and 600 °C, a phase change was observed to form defect rich crystalline MoS_2 (c- MoS_2 /rGO). XPS analysis provided in-depth understanding of the compositional changes of a- MoS_3 and c- MoS_2 with increasing annealing temperature. We deduced the a- MoS_3 compositional formula of each MoS_x /rGO hybrid prepared in this work. The optimized a- MoS_3 /rGO 250 exhibited excellent HER catalytic activity with an overpotential of 208 mV at 10 mA/cm^2 , a low Tafel slope of 52 mV/decade, a high double layer capacitance of 3.7 mF/cm^2 and a high turnover frequency (TOF) value of 0.43 H_2/s per site at an overpotential of 208 mV. The enhanced catalytic activity can be attributed to the high density of Mo^{V} active sites and abundant sulfur ligands of the

a-MoS₃/rGO 250. This study introduces a rapid and a controllable synthesis method to prepare a family of amorphous MoS₃ and crystalline MoS₂ hybrids with rGO for HER electrocatalysis.

6.2. Experimental Section

6.2.1. Chemicals and Materials

Ammonium tetra thiomolybdate ((NH₄)₂MoS₄), tetrahydrofuran (THF), and Nafion[®] solution (5 wt% in lower aliphatic alcohols) were purchased from Sigma-Aldrich (St. Louis, MO). The single-layer graphene oxide (GO) flakes were purchased from ACS Material LLC (Pasadena, CA). Sulfuric acid (H₂SO₄) and pure ethanol 200 proof were purchased from Fisher Scientific (Hampton, NH). Ultrapure water (18.2 MΩ.cm at 25 °C) purified from a Millipore water system (EASYPURE II, Thermo Scientific, Waltham, MA) was used to prepare all aqueous solutions for the experiments. The commercial Pt/C catalyst (20 wt% Pt on carbon, HiSPEC[®] 3000) by Johnson Matthey (JM) was purchased from Alfa Aesar (Tewksbury, MA) to use as the benchmark reference.

6.2.2. Materials Synthesis

15.0 mM ATM and 5.0 mg of GO were mixed and sonicated in a solvent mixture consisting of 6.0 mL of THF and 1.0 mL of water for 20 minutes. This mixture was irradiated with microwaves (Discover SP, CEM Corp., Mathews, NC) in a dynamic mode at a temperature of 170 °C for 10 min. The reaction pressure rose up to ~ 21 bar. The microwave synthesized sample was then centrifuged to collect the product. The collected product was dried on a hotplate at ~80 °C overnight and is denoted as a-MoS₃/rGO int. The dried powder was then annealed in 3% H₂/ 97% Ar atmosphere at 250 °C, 325 °C and 600 °C at a ramp rate of 10 °C/min. These samples were denoted as a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600, respectively.

6.2.3. Materials Characterization

The catalyst morphology was characterized using a Philips CM 100 transmission electron microscope (TEM) at a 100 kV acceleration voltage located at Department of Biology, KState. The crystal structure of the catalysts was examined using Bruker AXS D8 Advance Discover Diffractometer (Bruker Corporation, Karlsruhe, Germany) with a Cu K α radiation of wavelength 0.15418 nm and a detector slit width of 1 mm, located at Department of Chemistry, KState. XRD reference spectra are used from Joint Committee on Powder Diffraction Standards (JCPDS). The Raman spectroscopic measurements were performed with a DXR Raman microscope (Thermo fisher Scientific, Madison, WI)) with a 532 nm laser at the power of 10 mW, under a 10X objective lens with a slit width of 50 μ m. The surface chemical composition of the catalysts was characterized using a PHI 5000 Versa XPS system (Chanhassen, MN) with a monochromatized Al K α source (1486.7 eV) located at University of Nebraska, Lincoln. All the XPS spectra were obtained using a 400 μ m spot size. The binding energy (B.E.) of all XPS data was calibrated vs. the standard C 1s peak at 284.60 eV before the curve fitting. Shirley background was used in the curve fitting. We fit the Mo 3d and S 2p XPS spectra using a rigorous procedure by fixing spin-orbital splitting energy and area ratio at appropriate standard values. Elemental analysis results (%C,%H,%N,%S) presented in this work were acquired using a PE 2100 Series II combustion analyzer (Perkin Elmer Inc., Waltham, MA). The combustion tube packing was supplied with the instrument and consisted of the following components: copper oxide wires and electrolytic copper was used for CHNS reduction, and the oxygen reduction tube was packed with nickel plated carbon and quartz turning. The compounds were sampled using pressed tin capsules for CHNS Analysis and silver capsules for O analysis. 2,5-Bis(5-tert-butyl-benzoxazol-2-yl) thiophene was used as calibration standard for all the samples unless notified otherwise in the discussion. The combustion

and reduction temperature were 975°C for CHNS analysis. All the standards and reagents were purchased from Perkin Elmer or Elemental America's Inc. The precision and accuracy of the results were estimated to be as low as +/- 0.3%. Vanadium pentoxide was used as combustion aid for sulfur analysis.

6.2.4. Electrochemical Characterization

All the half-cell electrochemical experiments were performed in a standard three-electrode setup using a CHI 760D electrochemical workstation (CH Instruments, Austin, TX) at room temperature in Ar-purged 0.50 M H₂SO₄ electrolyte throughout the study. A mercury/mercurous sulfate (MSE, Hg/Hg₂SO₄ in saturated K₂SO₄) reference electrode and a graphite counter electrode were used. The working electrode was prepared by drop-casting the catalyst ink onto a 3 mm diameter glassy carbon electrode (GCE). Before drop-casting the catalyst ink, the GCE was polished using 0.05 µm alumina slurry. The catalyst ink was prepared by dispersing the required amount of catalyst powder in 1.0 ml of mixture of ethanol and ultrapure water (at 3:1 volume ratio) with addition of the 30 µl of Nafion solution. The MoS_x/rGO loading was maintained at 125 µg/cm² for all catalysts in the half-cell studies. For direct comparison of the potentials with literature, the measured electrode potential vs. MSE reference electrode is converted to the value vs. the reversible hydrogen electrode (RHE) using the following equation:

$$E_{(vs. RHE)} = E_{(vs. MSE)} + E_{(MSE vs. SHE)} + 0.059 \times \text{pH} \quad (6.1)$$

$$E_{(vs. RHE)} = E_{(vs. MSE)} + 0.640 \text{ V} \quad (6.2)$$

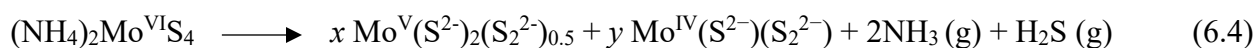
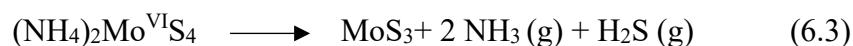
where $E_{(vs. MSE)}$ is the measured potential vs. the Hg/Hg₂SO₄ (sat'd K₂SO₄) reference electrode, $E_{(MSE vs. SHE)} = 0.640 \text{ V}$ vs. SHE, and pH = 0 for 0.50 M H₂SO₄.

After catalyst drop casting and subsequent drying in room temperature, first HER polarization curve is collected in the potential range of 0.4 V to -0.4 V vs. RHE at the scan rate of

10 mV/s. As the next step, the catalysts were subjected to activation by cyclic voltammetry (CV) in the potential range of 0.4 V to -0.1 V vs. RHE at a sweep rate of 50 mV/s for 50 cycles. Then another LSV curve is collected in the potential range of 0.4 V to -0.4 V vs. RHE at 10 mV/s after the CV activation and this LSV curve is reported. CV measurements in non-faradaic region (0.7 V to 0.5 V vs. RHE) at different scan rates were done to estimate the double-layer capacitances (C_{dl}) and ECSA values. Tafel analysis was performed to determine the kinetic parameters of the HER. The chronopotentiometry measurements were performed by fixing the current density at -10 mA/cm^2 for a duration of 23 h. 100% iR correction was done as per previous reported literatures.⁵² Briefly, the iR dropped potential was calculated by multiplying the observed current by R_s (uncompensated solution resistance), followed by subtracting the iR dropped potential from the experimentally measured potential to obtain the iR compensated potential. The R_s was determined by fitting the electrochemical impedance spectroscopy (EIS) spectra obtained for all catalysts to an appropriate equivalent circuit using ZsimpWin software. The EIS measurements were carried out from 1.8 MHz to 10 Hz with a sinusoidal AC potential amplitude of 5 mV at OCV.

6.3. Results and Discussion

Figure 6.1. shows the two-step microwave-assisted electrocatalyst synthesis. Briefly, 15 mM of ammonium tetra thiomolybdate (ATM) and 5 mg of graphene oxide (GO) were sonicated in THF and water solvent for 20 min. Then this mixture was irradiated with microwave at 170 °C and 21 bar pressure for 10 min. This resulted in the formation of amorphous MoS_3 deposited on reduced GO (rGO), following the reaction equation (6.3)¹⁸¹ shown below. This intermediate sample is denoted as a- MoS_3/rGO int.



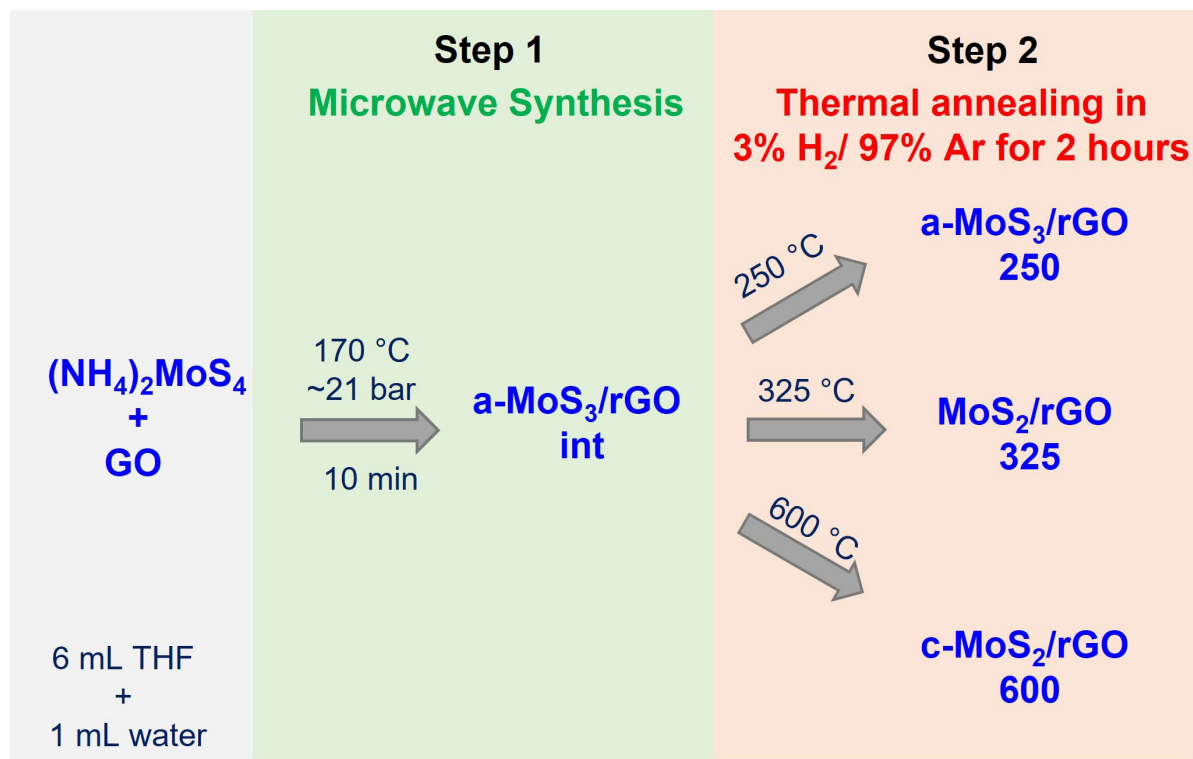
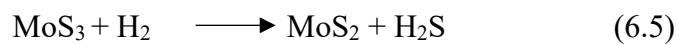


Figure 6.1. Illustration of the two-step synthesis of MoS_x/rGO hybrid materials by followed by thermal annealing in 3% H₂/ 97% Ar in a tube furnace.

The microwave transparency of THF ($\tan \delta = 0.042$) enabled the specific microwave heating of GO, which has a high $\tan \delta$ loss value of 0.8 to 1.0, for the selective deposition of MoS₃ on the GO. The a-MoS₃/rGO int is a 1D chain like structure with a composition of Mo^V(S²⁻)₂(S²⁻)_{0.5} or Mo^{IV}(S²⁻)(S²⁻) as proposed by Hibble et. al and Weber et.al, respectively.^{181, 182} This intermediate sample was further annealed at three different temperature such as 250 °C, 325 °C, and 600 °C in reducing atmosphere (3% H₂/ 97% Ar) to obtain different compositions of MoS_x/rGO ($x = 3.6$ to 2.2) due to reduction of S²⁻ to S²⁻ and Mo^V to Mo^{IV}, following the equation shown below,



The annealed catalysts are denoted as a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600 with annealing temperature as suffix following the hybrid name. Detailed synthesis process can be found in the materials synthesis section.

6.3.1. Structural and Morphological Characterization:

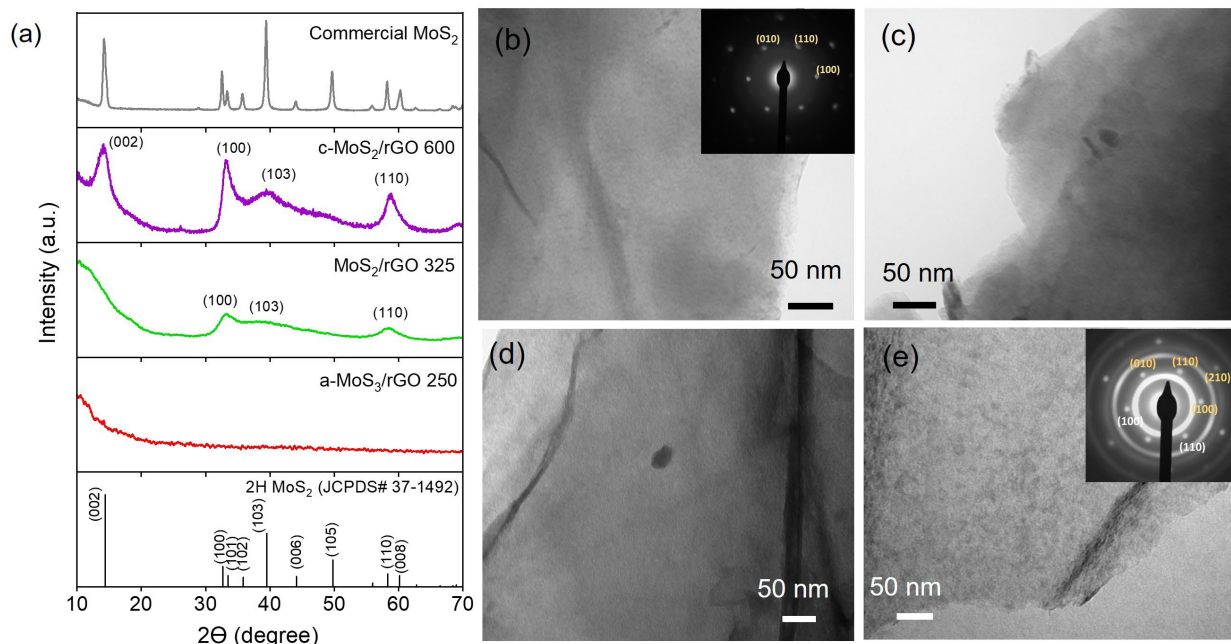


Figure 6.2. (a) XRD patterns of a-MoS₃/rGO 250, MoS₃/rGO 325 and c-MoS₂/rGO 600 compared with commercial MoS₂ and JCPDS data of 2H MoS₂. (b) TEM image of a-MoS₃/rGO int, (c) a-MoS₃/rGO 250, (d) MoS₂/rGO 325, and (e) c-MoS₂/rGO 600. Credits: Dr. Kamalambika Muthukumar for materials synthesis and materials characterization.

The phase and crystal structure of the as synthesized and annealed hybrid structures (MoS_x/rGO hybrids) were studied using XRD as shown in Figure E1 (b) and Figure 6.2.(a), respectively. The a-MoS₃/rGO int and a-MoS₃/rGO 250 does not show any diffraction peaks revealing the amorphous and disordered nature of MoS₃ deposited on rGO after microwave step and annealing at 250 °C, respectively. This agrees with the other MoS₃ structures prepared by wet-chemical synthesis reported in literatures.^{172, 173} It is to be noted that the a-MoS₃ are said to have

1D chain-like nanostructures as shown in Figure E2 (a) and are HER active. But when the intermediate sample was annealed at 325 °C (MoS₂/rGO 325), broad and weak diffraction peaks at 33.09°, 38.97° and 58.44° corresponding to (100), (103) and (110) peaks of 2H-MoS₂ were observed, suggesting partial conversion of 1D a-MoS₃ to 2D 2H-MoS₂ (structure shown in Figure E.2.(b) and (c)). However, the (002) plane was not observed to determine the number of MoS₂ layers. Also, due to broad overlapping (100) and (103) peaks, the domain size along (100) direction was also hard to determine. However, the domain size along (110) direction was found to be ~ 2.78 nm. Hence, the MoS₂ layers deposited on rGO for MoS₂/rGO 325 are considered as “nanopatches”. The nanoscale morphology of the MoS₂ is expected to provide more exposed edge sites which are electrochemically active for HER. The c-MoS₂/rGO 600 sample showed much stronger characteristic diffraction peaks at 14.15°, 33.21°, 39.42° and 58.66°, corresponding to diffraction from (002), (100), (103) and (110) planes of 2H-MoS₂. Interestingly, the 2 θ position of (002) plane of c-MoS₂/rGO 600 shifts to lower 2 θ value (14.15° < 14.37° of bulk 2H MoS₂) and (100) plane shifts to higher 2 θ value (33.21° > 32.67° of bulk 2H MoS₂), revealing the interlayer expansion between MoS₂ layers and in-plane contraction in c-MoS₂/rGO 600.¹⁴⁴ The inter layer (002) distance was found to be 6.28 Å which was greater than 6.16 Å of bulk 2H MoS₂ and corresponding to ~ 6 to 7 layers of MoS₂ layers deposited on rGO. Such expansion in interlayer may be due to some defective sulfur or Mo sites at the basal/edge of MoS₂ layers. The MoS₂ layer domain size along (100) and (110) direction was found to be ~ 4.36 nm and ~ 4.35 nm, respectively. This further corroborates the consideration of MoS₂ layers as nanopatches.

Figure E1 (a) shows the TEM image of single layer GO flakes of few microns in size, used in this work. Figure 6.2 (b)-(e) shows the TEM images of the MoS_x/rGO hybrid structures. The MoS_x deposited on rGO flakes were difficult to observe in TEM images owing to the nanoscale

morphology and amorphous nature. Selected area electron diffraction (SAED) patterns on the a-MoS₃/rGO int (shown in inset of Figure 6.2 (b)), only showed the sharp hexagonal diffraction spots of rGO without any diffraction rings or spots matching the MoS₂ structure, which further ascertains the presence of amorphous MoS₃ in a-MoS₃/rGO int. The hexagonal real-space lattice parameter was calculated to be 2.46 Å from the diffraction spots. This value matches well with the lattice parameter of graphene. In c-MoS₂/rGO 600 sample shown in Figure 6.2 (e), dark MoS₂ nanopatches were observed on the rGO surface. Due to the low contrast, it was difficult to analyze the particle size distribution using the TEM image. Interestingly, the SAED pattern (shown in inset of Figure 6.2 (e)) of c-MoS₂/rGO 600 showed both isolated hexagonal diffraction spots of rGO and continuous rings corresponding to randomly oriented 2D MoS₂ nanopatches. The first and second ring are denoted as (100) and (110) rings of 2H MoS₂ structure. The 2D lattice parameter of MoS₂ nanopatches was determined to be 3.16 Å matching well with the 2H MoS₂. The details of SAED calculations can be found in our previous report.¹⁴⁴

6.3.2. Materials Compositional Analysis

XPS analysis was carried to understand the chemical composition of the MoS_x/rGO hybrids. Figure 6.3 (a) shows the Mo 3d spectra of a-MoS₃/rGO int, deconvoluted into three pairs of Mo 3d_{5/2} and Mo 3d_{3/2} doublets positioned at 229.15 eV and 232.25 eV, 230.41 eV and 233.51 eV, and 232.48 eV and 235.59 eV corresponding to Mo^{IV}, Mo^V, and Mo^{VI} from MoS₃ and MoO₃ or ATM precursors, respectively.^{188, 190} It is worth noting that the shape of Mo 3d raw spectra was quite different with shifts in binding energies when compared to the other MoS_x/rGO hybrids may be due to the amorphous 1D chain-like structure. The S 2p spectra of MoS₃/rGO int was deconvoluted into two pairs of doublets (2p_{3/2} and 2p_{1/2}), one at lower binding energy range at

162.65 eV and 163.95 eV and the other at higher binding energy region at 165.42 eV and 166.69 eV as shown in Figure 6.3 (b).

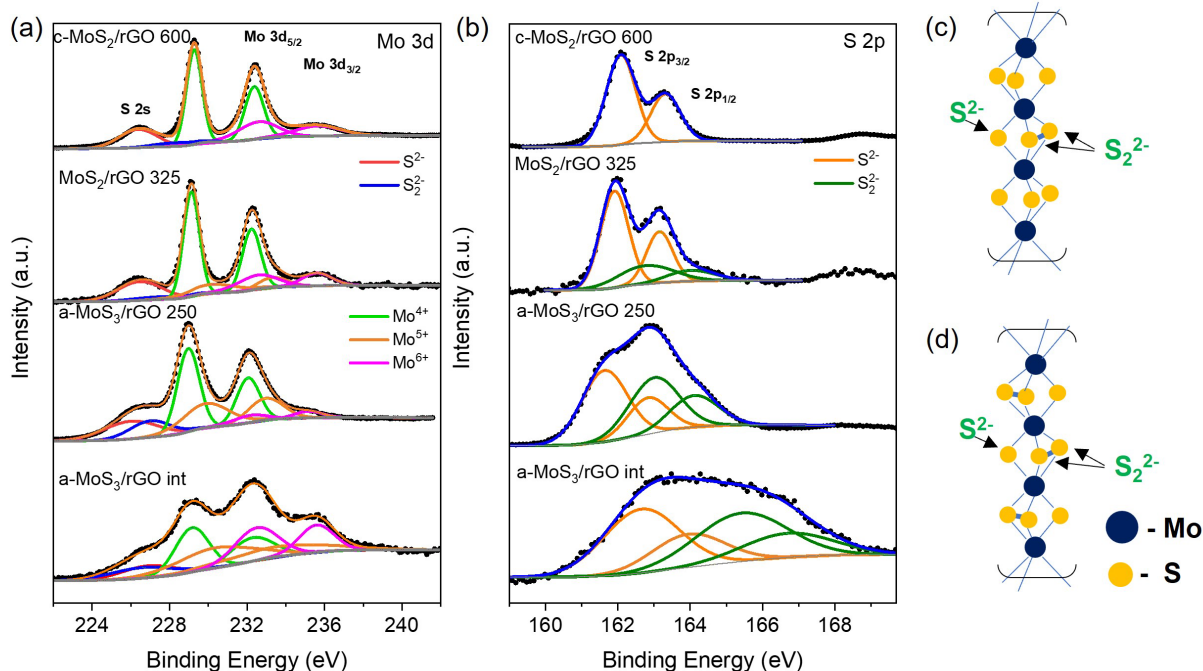


Figure 6.3. XPS high resolution spectra of (a) Mo 3d and (b) S 2p of a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600. (c) Schematic drawing of 1D MoS₃ chain structure with S₂²⁻ bond in alternate S₃ links, resulting in the formula Mo^V(S₂²⁻)₂(S₂²⁻)_{0.5}. (d) Schematic drawing of 1D MoS₃ chain structure with S₂²⁻ in every link with the formula Mo^{IV}(S₂²⁻)(S₂²⁻).

The lower binding energy doublet is attributed to the S₂²⁻ of MoS₃ (orange curves).^{188, 190} It may also consist of terminal S₂²⁻ at this binding energy position. The higher binding energy doublet (green curves) is assigned to the bridging S₂²⁻ of MoS₃.^{188, 190} This may consist of apical S₂²⁻ at this binding energy position and is considered negligible. There was about 52.4% of S₂²⁻ and ~ 47.6% of S₂²⁻, giving a S₂²⁻/S₂²⁻ ratio of 0.91:1 in a-MoS₃/rGO int. It is to be noted that Mo 3d spectra has a shoulder peak at around 222 eV owing to S 2s. Like the S 2p spectra, S 2s spectra was fitted into two peaks corresponding to S₂²⁻ and S₂²⁻ ligands of MoS₃. The relative at% of each of Mo and S species derived from the XPS is shown in Figure 6.4. It is to be noted that, the presence of both

Mo^{IV} (33.3%) and Mo^V (35.1%) states reveals that the a-MoS₃/int consists of a mixture of 1D chain like amorphous MoS₃ structures proposed by Hibble et.al and Weber et.al as shown in Figure 6.3 (c) and (d). The binding energy positions and relative at% of all Mo and S species of different MoS_x/rGO hybrids are given in Table E1. From the relative at% of Mo^{IV}, Mo^V, S₂²⁻ and S²⁻ (from Figure 6.4 and Table E1), the stoichiometric formula of a-MoS₃/rGO int is deduced to consist of ~35% of Mo^V (S²⁻)₂(S₂²⁻)_{0.5} and ~33% of Mo^{IV} (S²⁻) (S₂²⁻) as shown in Table 6.1. It is to be noted that there was no MoS₂ that can be contributed to a-MoS₃/rGO int. The remaining ~ 32% of Mo atoms was in Mo^{VI} state which can be attributed to unreacted ATM precursors or MoO₃ in a-MoS₃/int. The total at% ratio of Mo and S was found to be 1: 3.6. This was supported by the at% ratio of Mo and S (1:3.3) determined by elemental analysis (Figure E3 (b)).

Similarly, Mo 3d spectrum of a-MoS₃/rGO 250 consisted of three pairs of Mo 3d_{5/2} and Mo 3d_{3/2} doublets of Mo^{IV}, Mo^V, and Mo^{VI} corresponding to MoS₃ and ATM precursor or MoO₃ respectively. In this case, the relative at% of Mo^{VI} decreased substantially from 31.6% to 8.2% while the Mo^{IV} and Mo^V increased from 33.3% to 55.3% and 35.1% to 36.5%, respectively, suggesting the thermal reduction of Mo^{VI} to Mo^V and Mo^{IV} states. The S 2s shoulder peak and the S 2p spectra was deconvoluted into two peaks corresponding to S²⁻ and S₂²⁻ ligands of MoS₃. And the relative at% of S₂²⁻ slightly reduced and S²⁻ increased, resulting in a lower S₂²⁻/S²⁻ of 0.81:1 on a-MoS₃/rGO 250. This shows that thermal annealing modulates the composition of the a-MoS₃ structure. The composition and stoichiometric formula of a-MoS₃/rGO 250 was found to be ~37% of Mo^V (S²⁻)₂(S₂²⁻)_{0.5} and ~55% of Mo^{IV} (S²⁻) (S₂²⁻). There was only ~ 8% of Mo^{VI} states remaining, which can be attributed to the MoO₃. The total at% ratio of Mo and S was calculated to be 1: 2.97, which is consistent with the elemental analysis result of 1:3.1.

Table 6.1. The stoichiometric formula of different MoS_x/rGO hybrids.

	a-MoS ₃ /rGO int		a-MoS ₃ /rGO 250		MoS ₂ /rGO 325		c-MoS ₂ /rGO 600	
	Stoichiometric formula	Frac %	Stoichiometric formula	Frac %	Stoichiometric formula	Frac %	Stoichiometric formula	Frac %
Mo^{IV}	Mo ^{IV} (S ²⁻)(S ₂ ²⁻)	33 %	Mo ^{IV} (S ²⁻)(S ₂ ²⁻)	55 %	Mo ^{IV} (S ²⁻)(S ₂ ²⁻)	54 %	Mo ^{IV} (S ²⁻)(S ₂ ²⁻)	0 %
	Mo ^{IV} (S ²⁻) ₂	0 %	Mo ^{IV} (S ²⁻) ₂	0 %	Mo ^{IV} (S ²⁻) ₂	7 %	Mo ^{IV} (S ²⁻) ₂	80 %
Mo^V	Mo ^V (S ²⁻) ₂ (S ₂ ²⁻) _{0.5}	35 %	Mo ^V (S ²⁻) ₂ (S ₂ ²⁻) _{0.5}	37 %	Mo ^V (S ²⁻) ₂ (S ₂ ²⁻) _{0.5}	16 %	Mo ^V (S ²⁻) ₂ (S ₂ ²⁻) _{0.5}	0 %
Mo^{VI}	ATM or Mo ^{VI} O ₃	32 %	Mo ^{VI} O ₃	8 %	Mo ^{VI} O ₃	23 %	Mo ^{VI} O ₃	20 %

When the sample was annealed at 325 °C, the relative at% of Mo^V was further reduced to Mo^{IV} as expected at the relatively higher temperature in the reducing gas atmosphere (i.e., 3%H₂/97%Ar). The corresponding decrease in relative at% of S₂²⁻ (27.4%) and increase in S²⁻ at% (72.6%) in S 2p spectra was observed, resulting in further lowered S₂²⁻/S²⁻ value of 0.38:1. The composition and stoichiometry of MoS₂/rGO 325 was found to be 16% of Mo^V(S²⁻)₂(S₂²⁻)_{0.5}, 54% of Mo^{IV}(S²⁻)(S₂²⁻) and 7% of Mo^{IV}(S²⁻)₂. In this case, there was about 7% of MoS₂ formation, supporting the weak diffraction peaks of 2H MoS₂ observed in XRD for MoS₂/rGO 325. This confirms that, at this annealing temperature, it not only alters the composition of MoS₃ but also induces critical structure change by converting some of the 1D chain-like MoS₃ to 2D 2H MoS₂. The total at% of Mo:S was found to be 1:2.31, which was supported by the ratio of at% of Mo:S (1:2.5) determined from the elemental analysis. It is to be noted that, there was an increase in the Mo^{VI} states (8.2% to 22.9%), which may be due to the formation of more MoO₃ from the oxygen residue in the rGO structure at 325 °C.

For the c-MoS₂/rGO 600 sample, the Mo 3d spectra contained only two pairs of doublets at corresponding to Mo^{IV} and Mo^{VI} and no doublet found for Mo^V states. The S 2p spectra only consisted of S²⁻ sulfur atoms. This shows that there was no MoS₃ present and that all MoS_x was completely converted to 2H MoS₂ by the thermal reduction of S₂²⁻ and Mo^V units at 600 °C. The composition of the Mo compounds was ~80% of Mo^{IV}(S²⁻)₂ and ~20% MoO₃. The at% ratio of

Mo:S was found to be 1:2.2 and agreeing with the at% ratio of Mo:S (1:2) determined using elemental analysis.

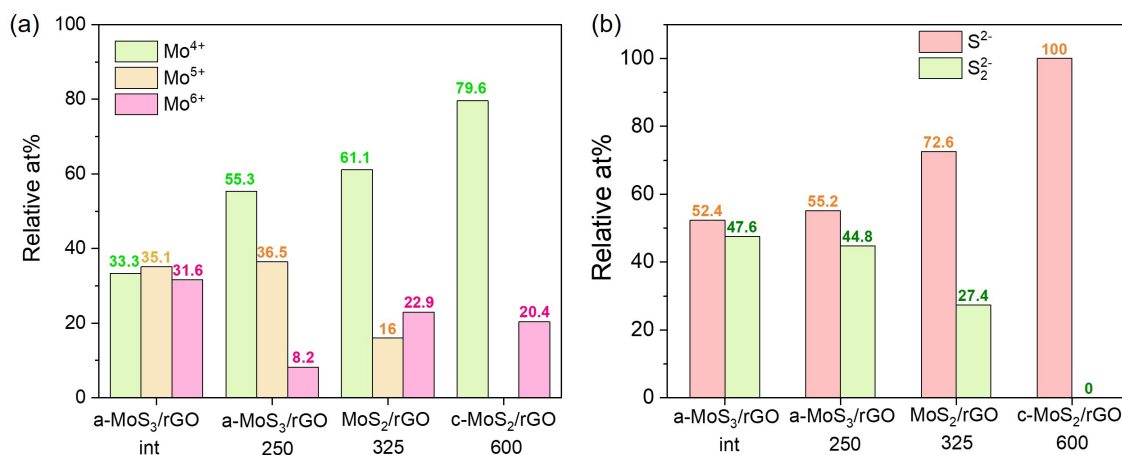


Figure 6.4. Comparison of relative at% of (a) different Mo species and (b) S²⁻ and S₂²⁻ among MoS_x/rGO hybrids.

As a result, it is clear from the XPS analysis that the ratio of S to Mo can be varied in a large range from 3.6 to 2.2 by raising the thermal annealing temperature as shown in Figure E3 (a). Also, the composition of the MoS_x compounds can be tuned among two a-MoS₃, 1D chain-like structures, i.e., Mo^V(S²⁻)₂(S₂²⁻)_{0.5} and Mo^{IV}(S²⁻)(S₂²⁻), and the 2D MoS₂ nanopatches, which provides rich materials to investigate the performance HER catalysts. There was about ~68% and ~92% MoS₃ in a-MoS₃/rGO int and a-MoS₃/rGO 250, respectively. Whereas MoS₂/rGO 325 and c-MoS₂/rGO 600 consisted of ~7% and ~80% MoS₂, respectively. More details can be found in Table E1 and 6.1.

6.3.3. Electrocatalytic Activity of MoS_x/rGO hybrid

Electrochemical characterization of the MoS_x/rGO hybrids were conducted to evaluate their electrocatalytic activity for HER. The catalyst loading was maintained as 125 μg/cm² for all

catalysts in this work. The HER performance of precious metal catalyst Pt/C JM (20 $\mu\text{g}/\text{cm}^2$) was collected for comparison.

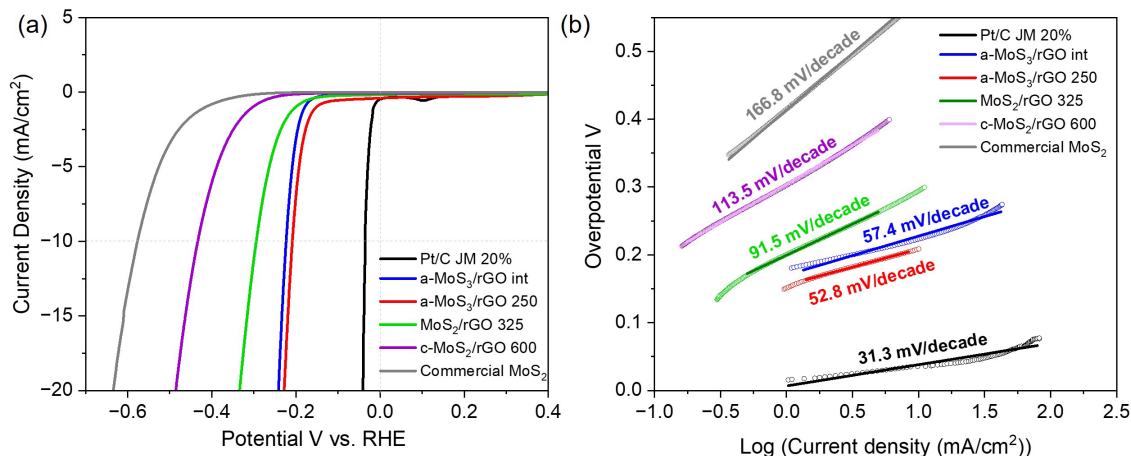


Figure 6.5. Electrochemical LSV HER studies. (a) LSV polarization curves and (b) corresponding Tafel plots of commercial Pt/C JM 20%, a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325, c-MoS₂/rGO 600 and commercial MoS₂.

The Pt/C JM showed an overpotential of 40 mV at 10 mA/cm^2 for HER. From the LSV curves shown in Figure 6.5 (a), it was found that among all the MoS_x/rGO hybrid catalysts, a-MoS₃/rGO 250 exhibited the lowest overpotential of 208.2 mV for HER at 10 mA/cm^2 current density indicating its high catalytic activity. This enhanced activity of a-MoS₃ agrees with the literature values and can be attributed to the abundant exposed active sites.^{54, 172} The c-MoS₂/rGO 600 exhibited the lowest electrocatalytic activity for HER with an overpotential of 433.6 mV at 10 mA/cm^2 . However, when compared to commercial bulk crystalline 2H MoS₂ (575.8 mV at 10 mA/cm^2), c-MoS₂/rGO 600 showed enhanced electrocatalytic activity due to their nanopatch morphology with relatively higher exposed active sites compared to bulk MoS₂. The a-MoS₃/rGO int and MoS₂/rGO 325 showed an overpotential of 221 mV, and 293.4 mV, respectively, at 10 mA/cm^2 . Interestingly, the order of increasing Mo^V deduced from XPS is in the same order as the

increasing HER activity as follows: c-MoS₂/rGO 600 < MoS₂/rGO 325 < a-MoS₃/rGO < a-MoS₃/rGO 250. It is to be noted that all the LSV curves shown this section are iR-corrected. Figure E4 (a) shows the LSV curves before and after iR correction for all catalysts. Figure E4 (b) shows the EIS spectra of all the catalysts, which was circuit fitted to find the uncompensated solution resistance to perform iR correction to the LSV curves. Figure E5 shows the LSV curves of all electrocatalysts till 90 mA/cm² of HER current density.

Further, Tafel analysis was done for LSV curves of MoS_x/rGO hybrid catalysts, as shown in Figure 6.5 (b), to determine the rate-determining step for HER. The Tafel slope can provide information on the charge transfer rate at the electrode-electrolyte interface. Briefly, lower the Tafel slope, there will be faster charge transfer process occurring across the interface.¹⁷³ The three steps involved in HER in acidic media are the Volmer ($H^+ + e^- = H_{ads}$, < 120 mV/decade), Heyrovsky ($H_{ads} + H^+ + e^- = H_2$, < 40 mV/decade) and Tafel reaction ($H_{ads} + H_{ads} = H_2$, < 30 mV/decade) which shows the adsorption, desorption, and recombination of protons to form hydrogen, respectively.¹⁹¹ The best performing a-MoS₃/rGO 250 showed the lowest Tafel slope of 52.8 mV/decade, revealing that HER follows via Volmer-Heyrovsky pathway agreeing with previous reports.^{184, 185} The a-MoS₃/rGO int was found to have a Tafel slope of 57.4 mv/decade, followed by MoS₂/rGO 325 (91.5 mV/decade) and c-MoS₂/rGO 600 (166.8 mV/decade).

For further evaluation, turnover frequency (TOF) was calculated to determine the intrinsic catalytic activity of the MoS_x/rGO hybrids. TOF is defined as the number of hydrogen molecules produced on each electrocatalytic active site per unit time. We followed an estimation process proposed by Jaramillo and co-workers, more details can be found in the Appendix E.¹⁷³ It was calculated using the equation^{192, 193} given below,

$$TOF (s^{-1}) = \frac{j \times N_A}{n \times F \times \Gamma}$$

where j is the current density (mA/cm^2), N_A is the Avogadro constant, F is the Faraday constant, n is the number of electrons transferred to generate one molecule of H_2 , Γ is the surface concentration of electrocatalytic active sites. The surface concentration of MoS_2 active sites is calculated by the equation below,

$$\Gamma = N_{\text{MoS}_2} \times \text{ECSA}$$

where N_{MoS_2} is the number of MoS_2 units/ cm^2 which is equal to 1.164×10^{15} MoS_2/cm^2 and ECSA is the electrocatalytic active surface area.^{192, 193} The ECSA of MoS_x based materials is measured by dividing the non-faradaic capacitance (C_{dl}) associated with the double layer charging by specific capacitance of flat monolayer MoS_2 standard. Figure 6.6 (a) and Figure E6 shows the CV in the non-faradaic potential region conducted at different scan rates. The difference in anodic and cathodic current density at the center of the CV curves (Δj) at different scan rates are plotted (Figure 6.6 (b)). The magnitude of C_{dl} was calculated from the slope of resulting linear curves (see Figure E7 for more details). The C_{dl} values of a- MoS_3/rGO int, a- MoS_3/rGO 250, MoS_2/rGO 325 and c- MoS_2/rGO 600 were found to be $2.83 \text{ mF}/\text{cm}^2$, $3.7 \text{ mF}/\text{cm}^2$, $3.17 \text{ mF}/\text{cm}^2$ and $0.37 \text{ mF}/\text{cm}^2$, respectively. The high C_{dl} of a- MoS_3/rGO 250 indicates that it has the highest quantity of exposed electrochemical active sites. Correspondingly, the TOF of a- MoS_3/rGO 250 was calculated to be $0.43 \text{ H}_2/\text{s}$ per site at 208 mV overpotential corresponding to $10 \text{ mA}/\text{cm}^2$. The TOF values of the a- MoS_3/rGO int, MoS_2/rGO 325 and c- MoS_2/rGO 600 were found to be $0.27 \text{ H}_2/\text{s}$, $0.063 \text{ H}_2/\text{s}$ and $0.061 \text{ H}_2/\text{s}$ per site, respectively, at an overpotential of 208 mV. The TOF values are listed in Figure 6.6 (c). Overall, the a- MoS_3/rGO 250 showed the highest intrinsic catalytic activity for HER among the various MoS_x/rGO hybrids studied in this work.

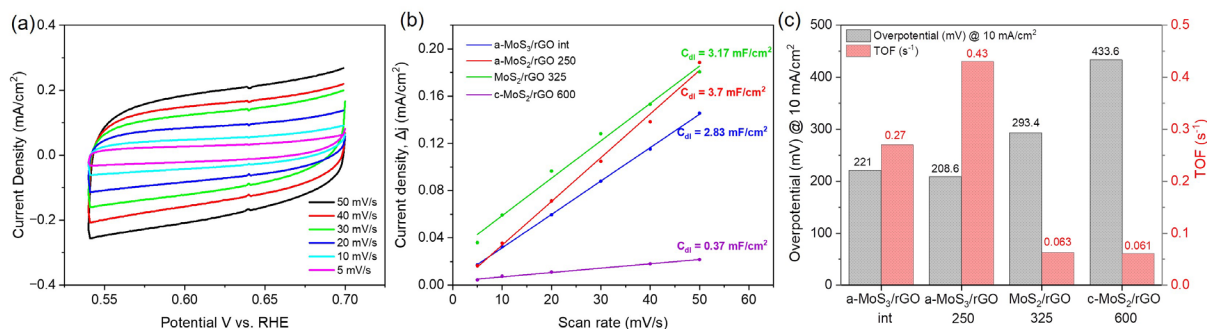


Figure 6.6. (a) Electrode stability test of a-MoS₃/rGO 250 at 10 mA/cm² for over 23 h with inset showing the polarization curves of a-MoS₃/rGO 250 before and after stability tests. (b) Electrode stability test of a-MoS₃/rGO int at 10 mA/cm² for over 23 h with inset showing the polarization curves of a-MoS₃/rGO int before and after stability tests.

Finally, the durability tests were conducted using chronopotentiometry for a period of 23 hours at 10 mA/cm² as shown in Figure 6.7. The a-MoS₃/rGO 250 showed excellent stability with the HER overpotential increase at the rate of 0.58 mV/h during the durability test. Whereas the HER overpotential increased much faster at a rate of 2.47 mV/h for the a-MoS₃/rGO int. In addition, an LSV was performed after the completion of durability test to evaluate the change in their electrocatalytic activities. The a-MoS₃/rGO 250 hybrid showed negligible change in overpotential in the LSV curve when compared to the one acquired before the durability test indicating the robustness of the electrocatalyst. This indicates that the active sites on a-MoS₃/rGO 250 remain stable after continuously operating for long durations. However, for the a-MoS₃/rGO int, the HER overpotential increased further by an additional ~ 37 mV after the long-term durability test indicating the instability of the active sites during continuous operation. The excellent stability and activity of a-MoS₃/rGO 250 over MoS₃/rGO int can be attributed to the stable and active MoS₃ structures aided by the additional annealing step at 250 °C in 3% H₂/ 97% Ar.

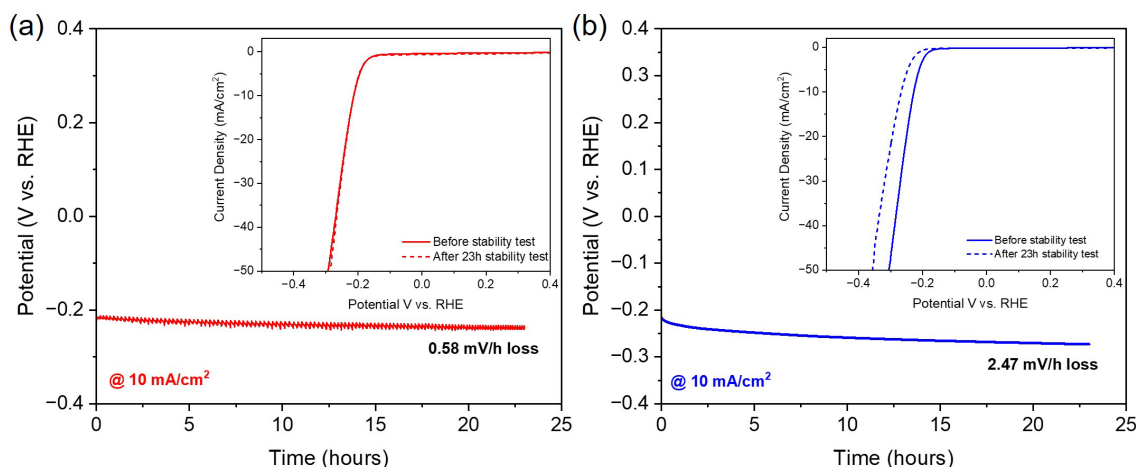


Figure 6.7. Electrochemical HER studies. (a) Cyclic voltammogram of a-MoS₃/rGO 250 collected at different scan rates in non-faradic region to measure the capacitive current from double layer charging. (b) Linear fitting of the capacitive currents of catalysts vs scan rates to determine the electrochemical double-layer capacitance values for a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600 electrocatalysts. (c) Comparison of overpotential at 10 mA/cm² and TOF values for a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600 electrocatalysts.

6.3.4. Insights on the Catalytic Active Sites

It is important to uncover the catalytic active sites that are responsible for the high intrinsic catalytic activity and facile HER kinetics of a-MoS₃/rGO 250 to design and develop better electrocatalysts for HER in future. From previous sections, correlating chemical composition and electrocatalytic activity from XPS and electrochemical data, respectively, it was found that the density of Mo^V(S²⁻)₂(S₂²⁻)_{0.5} was highest in a-MoS₃/rGO 250 which exhibits the highest HER activity among all the hybrid catalysts. When the density of Mo^V(S²⁻)₂(S₂²⁻)_{0.5} decreased in the order of a-MoS₃/rGO int, MoS₂/rGO 325, and c-MoS₂/rGO 600, the electrocatalytic activity for HER decreased in the same sequence. The enhancement in HER activity with increasing density of Mo^V of Mo^V(S²⁻)₂(S₂²⁻)_{0.5} structure implies that Mo^V could be a possible catalytic active site for

HER. Similar observations of enhanced HER activity with increase in the defect density of Mo^V were made by Li et. al and Tran et. al.^{186, 188}

On the other hand, while examining the HER polarization curve shown in Figure 6.5 (a) closely, a broad reduction region from 0.4 V to -0.1V vs. RHE was observed before onset of HER for all MoS_x/rGO hybrid catalysts (see Figure E8). Similar reduction process was observed by Hu et.al and was attributed to the electroreduction of S₂²⁻ to S²⁻.⁵⁴ It is to be noted that the LSV curves shown in Figure 6.5 (a) were collected after CV activation. Hence, to understand the effect of activation cycles, LSV curves were collected without any prior activation (Figure E9 (a)). Interestingly, two reduction peaks were observed at 0.050 V and -0.086 V vs. RHE for a-MoS₃/rGO int and a-MoS₃/rGO 250 hybrids on freshly collected LSV curves as shown in Figure E9 (a). While MoS₂/rGO 325 and c-MoS₂/rGO 600 showed relatively low intense peaks. With CV activation, the magnitude of these reduction peaks decreased significantly to form the broad reduction region as shown in Figure E10. The fresh LSVs of both a-MoS₃/rGO int and a-MoS₃/rGO 250 overlapped with each other. But, after CV activation, the electrocatalytic activity of a-MoS₃/rGO 250 showed an enhancement with a positive shift in the LSV curve by 13 mV at 10 mA/cm² (Figure E10 (b)), while the activity of a-MoS₃/rGO int did not show any such enhancement. The boost in activity of a-MoS₃/rGO 250 with CV activation cycles indicates creation of new HER active sites. As reduction of S₂²⁻ to S²⁻ occurs during the activation, it is likely that these sulfur ligands may contribute to the improvement in HER activity as the newly generated HER active sites. Similar observations were reported by Hu et.al and Yeo et.al.^{54, 185} Further investigation by XPS, monitoring the changes in the S₂²⁻ and S²⁻ in S 2p spectra at different stages of activation, might be able to identify the type of sulfur ligand involved as catalytic active sites.

From these perspectives, it can be concluded that both Mo^{V} and sulfur ligands play a catalytic role in the HER activity of a- MoS_3 .

6.4. Conclusion

A controllable microwave-assisted synthesis was used to prepare amorphous MoS_3 (a- MoS_3) on rGO template to employ it as a HER electrocatalyst. By thermal annealing of the microwave synthesized a- MoS_3/rGO at various temperatures, a family of MoS_x/rGO hybrids with a- MoS_3 and c- MoS_2 were produced. When annealed at 250 °C (a- MoS_3/rGO 250), the composition of the a- MoS_3 was modulated. Defect-rich crystalline MoS_2 hybrids (c- MoS_2/rGO) were produced when annealed at higher temperatures, such as 325 °C and 600 °C. XPS analysis provided in-depth understanding of the MoS_3 compositional changes with annealing temperature and was helpful to deduce the MoS_3 stoichiometric formula of each MoS_x/rGO hybrid. The optimized a- MoS_3/rGO 250 exhibited excellent HER catalytic activity with an overpotential of 208 mV at 10 mA/cm^2 , a low tafel slope of 52 mV/decade, a high double layer capacitance of 3.7 mF/cm^2 and a high TOF value of 0.43 H_2/s per site at 208 mV. The enhanced catalytic activity can be attributed to the catalytic role of both Mo^{V} and sulfur ligands of the a- MoS_3/rGO 250. This study introduces a rapid and a controllable synthesis method to prepare a family of a- MoS_3/rGO and c- MoS_2/rGO hybrids for HER electrocatalysis.

Chapter 7 - Conclusion and Future Work

Nanomaterials play a critical role in improving the performance of electrochemical renewable energy conversion devices. In this dissertation, microwave assisted synthesis method has been used to develop novel catalysts supports and electrocatalysts for fuel cells and water electrolyzers. The specific heating of the microwaves has been utilized to preferentially deposit various transition metal oxides, transition metal nanoparticles and transition metal sulfides (1D and 2D) on various carbon supports. The as developed electrocatalysts have demonstrated significant enhancements in the electrochemical reaction kinetics of methanol oxidation, hydrogen oxidation, and hydrogen evolution. We hope this dissertation will shed light on new and rapid approaches based on microwave methods in the development of novel electrode nanomaterials.

In chapter 2, a multifunctional hybrid catalyst support for PtRu-based MOR catalysts were developed and introduced. A thin hydrogenated TiO₂ shell was deposited on the oxygenated N-doped carbon nanotube by rapid microwave-assisted synthesis. PtRu nanoparticles were further deposited on the exterior surface of the hydrogenated TiO₂ shell by another microwave-assisted synthesis step. The hydrogenated TiO₂ shell was found to exhibit a strong interaction with the PtRu nanoparticles and was effective in controlled the PtRu nanoparticle size during the thermal annealing at 400 °C. XPS spectra revealed the SMSI between the defective hydrogenated TiO₂ support to PtRu catalyst which aided in reducing the CO stripping onset potential. The synergistic effects of electron transfer and the increased oxophilicity provided by the defective hydrogenated TiO₂ support help to accelerate the CO oxidation and lead to higher mass activity, higher ECSA-specific activity and stability in methanol oxidation than the two state-of-the-art commercial PtRu/C catalysts from JM and TKK.

In chapter 3, the effect of modification of various carbon catalyst supports such as ONCNT, Vulcan and KB 600JD, in the activity and durability of PtRu electrocatalysts were studied. The materials synthesis established in Chapter 2 was used. The MOR electrocatalytic activity and ECSA of PtRu electrocatalysts improved with greater BET SSA of carbon supports, demonstrating the importance of carbon support structures. Systematic accelerated stress tests (ASTs) were carried to understand the degradation mechanism of electrocatalysts on hydrogenated TiO₂ modified different carbon supports by conducting CO stripping experiments at various stages of ASTs. PtRu/TiO₂/KB 600JD-400 with high BET SSA carbon support exhibited the highest MOR activity whereas PtRu/TiO₂/ONCNT-400 with abundant N-dopants, oxygen functional groups and graphitic nature exhibited excellent stability in MOR conditions. Full DMFC evaluation incorporating these anode catalysts against the commercial Pt/C cathode and PGM-free Fe-N-C based cathodes were performed to understand the kinetic and mass transport effects of various anode carbon support structures in the peak power density ($P_{\max}$). The PtRu/TiO₂/KB 600JD-400 catalysts presented high selectivity to high concentration methanol solutions. Preliminary results on TiO₂ modified ONCNT-supported anode tested with PGM-free cathode catalysts revealed the insignificant dependence of $P_{\max}$ with increasing methanol feed concentration from 1.0 M to 4.0 M further illustrating either the high selectivity of anode catalysts towards high methanol concentrations or reduction of methanol crossover due to TiO₂ modification on carbon supports. Further DMFC testing on control electrocatalysts without TiO₂ modification and electrocatalysts on different carbon supports would be essential to answer the scientific reasoning behind the retention in peak power density in DMFC operated at high concentrations of methanol. Further investigations to measure the methanol diffusion flux current density at the cathode of DMFC

would be very helpful to corroborate the reduction of methanol crossover at high methanol concentrations by using different metal oxides and carbon supports at the anode.

In chapter 4, an ultra-thin shell of SnO_2 on high surface area carbon supports was developed as novel hybrid catalyst support for PtRu alloy nanoparticles towards methanol oxidation reaction. Same microwave-assisted synthesis established in chapter 2 was followed to deposit SnO_2 and PtRu nanoparticles. By increasing the amount of SnO_2 precursor, the SnO_2 thin shell thickness was increased had better control over PtRu nanoparticle size. Annealing the catalyst in nitrogen atmosphere resulted in MOR electrocatalyst with higher stability. Systematic CO stripping studies at different stages of accelerated stress tests (AST) were done to reveal the excellent MOR stability exhibited by the as-prepared SnO_2 modified carbon support (nitrogen annealed) towards strongly anchoring Ru nanoparticles when compared to the TiO_2 modified carbon supports. Moreover, the PtRu/h- SnO_2 /C- N_2 showed enhanced CO oxidation kinetics and comparable MOR activity when compared to the three types of benchmark commercial PtRu/C catalysts from Johnson Matthey (JM) and Tanaka KiKinzoku (TKK), respectively. Further TEM studies on the electrocatalysts after AST studies would reveal the actual PtRu nanoparticle size which would strengthen effect of using SnO_2 based metal oxides as catalysts supports for MOR.

In chapter 5, the PtRu/ TiO_2 /C-400 anode developed in chapter 3 was used as an HOR electrocatalyst for AEMFC. A high AEMFC performance with P_{max} of 1.27 W/cm^2 was achieved with PtRu/ TiO_2 /C-400 anodes. The SMSI provided by the TiO_2 on the PtRu not only helped to control the nanoparticle size to provide abundant exposed active sites but also improved the oxophilicity of the electrocatalyst which resulted in high OHBE. The SMSI imparted by the TiO_2 on PtRu nanoparticles resulted in excellent AEMFC stability with 1.5 mV/h voltage loss at 600 mA/cm^2 for 20 h. However, half-cell RDE electrochemical characterization of these HOR

electrocatalysts did not provide much useful information. Further studies by optimizing the catalyst loading in half-cell RDE measurements may provide actual HOR kinetic activity of these electrocatalysts.

In chapter 6, a PGM-free electrocatalyst based on amorphous molybdenum trisulfide ($a\text{-MoS}_3$) on rGO template was studied as a HER electrocatalyst. Microwave-assisted synthesis followed by thermal annealing in 3% H_2 / 97% Ar at various temperatures resulted in MoS_x/rGO hybrids with tunable S to Mo ratio from 3.6 to 2.2. Tuning of temperature from 250 °C to 600 °C, modulated the composition of MoS_3 of $a\text{-MoS}_x/\text{rGO}$ hybrids and also enabled phase change to form crystalline MoS_2 at high temperatures. The optimized $a\text{-MoS}_3/\text{rGO}$ 250 exhibited excellent HER catalytic activity with an overpotential of 208 mV at 10 mA/cm^2 , a low tafel slope of 52 mV/decade, a high double layer capacitance of 3.7 mF/cm^2 and a high TOF value of 0.43 H_2/s per site at 208 mV overpotential. The HER trend in various MoS_x/rGO was correlated to the density of Mo^V sites and sulfur ligands calculated from XPS of the amorphous MoS_3 structure. Both Mo^V and sulfur sites may act as active sites for HER. Further studies by investigating the surface composition of MoS_x/rGO by XPS, especially monitoring the changes in XPS spectra of S 2p and Mo 3d at different stages/steps of HER would reveal the actual HER active site in amorphous MoS_3 electrocatalyst. Nevertheless, the theoretical DFT calculations will be very helpful to determine the proton binding energy at different sites of MoS_3 to support the XPS revelations. Such findings would strengthen the understanding of HER active sites in the PGM-free amorphous MoS_3 nanostructures which would lead to significant reduction of electrocatalyst cost in PEMWE stacks for hydrogen production.

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Appendix A - Supplementary Information for Chapter 2

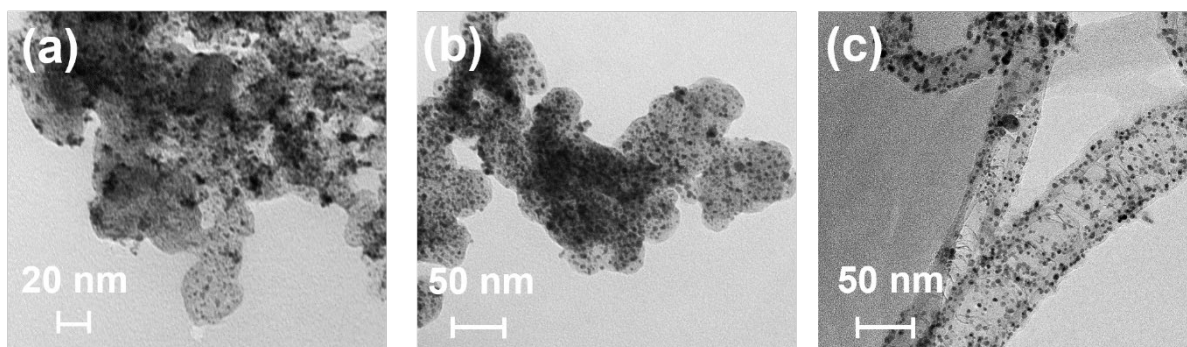


Figure A1: TEM images of (a) commercial PtRu/C JM, (b) commercial PtRu/C TKK, and (c) PtRu/TiO₂/ONCNT-400.

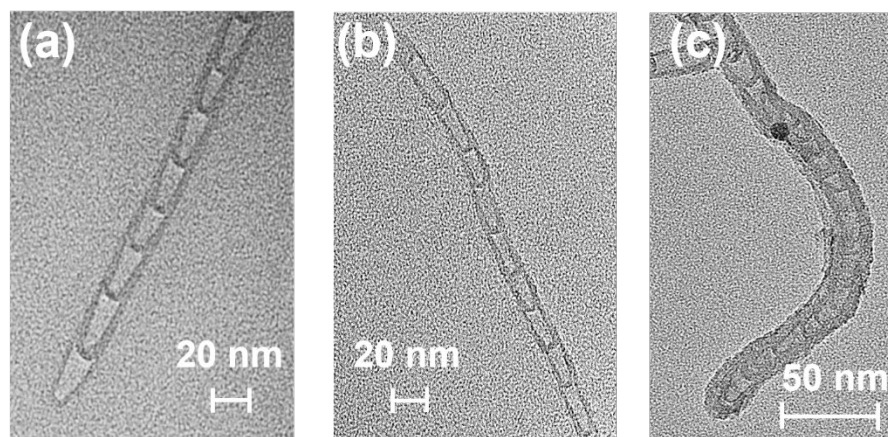


Figure A2: TEM images of (a) NCNT, (b) ONCNT, and (c) TiO₂/ONCNT-400.

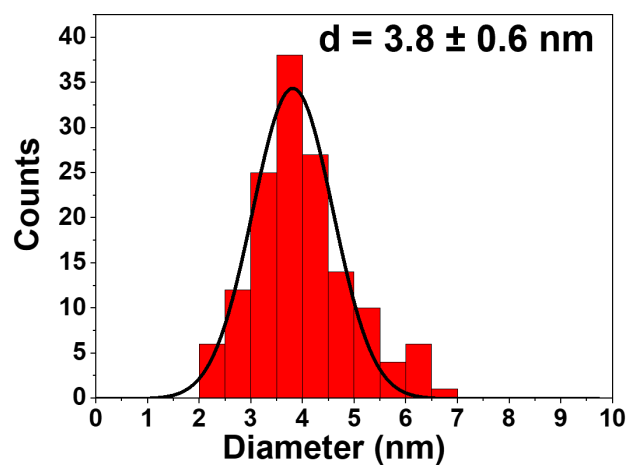


Figure A3: The size distribution of PtRu nanoparticles in PtRu/TiO₂/ONCNT-400.

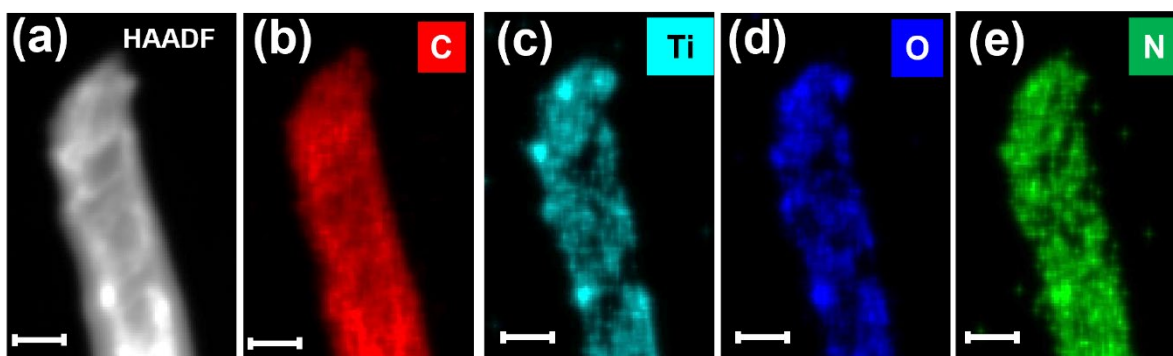


Figure A4: (a) HAADF-STEM image and (b-e) EDS elemental mapping of C, Ti, O and N in TiO₂/ONCNT. The scale bars in panels (a) – (e) are 20 nm.

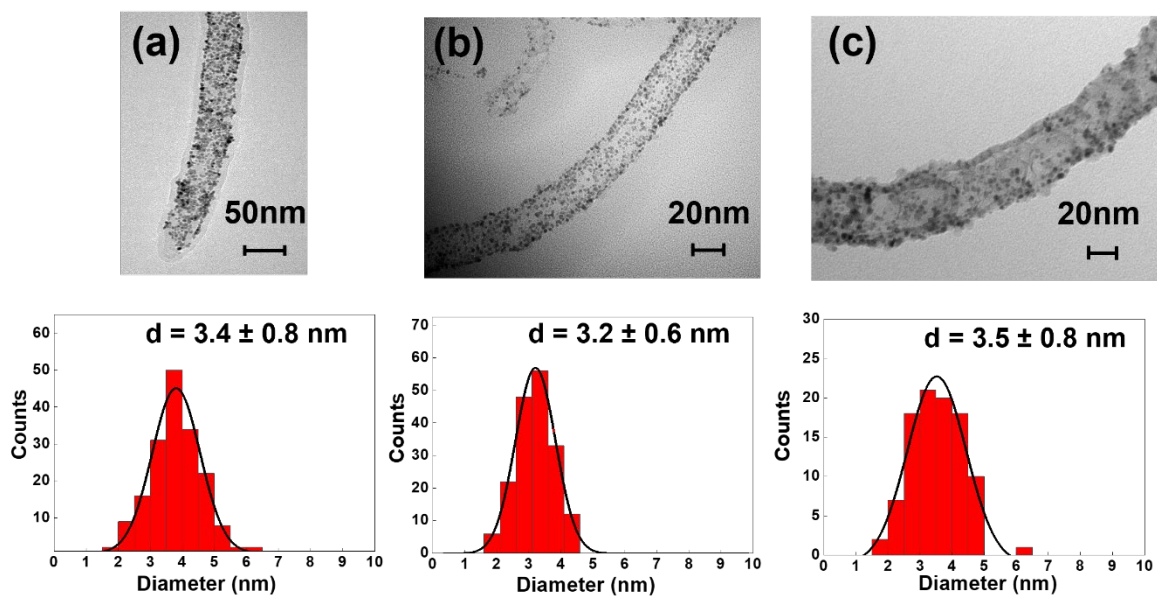


Figure A5: TEM image and its corresponding particle size distribution curve of (a) Pt/ONCNT, (b) Pt/TiO₂/ONCNT, and (c) Pt/TiO₂/ONCNT-400.

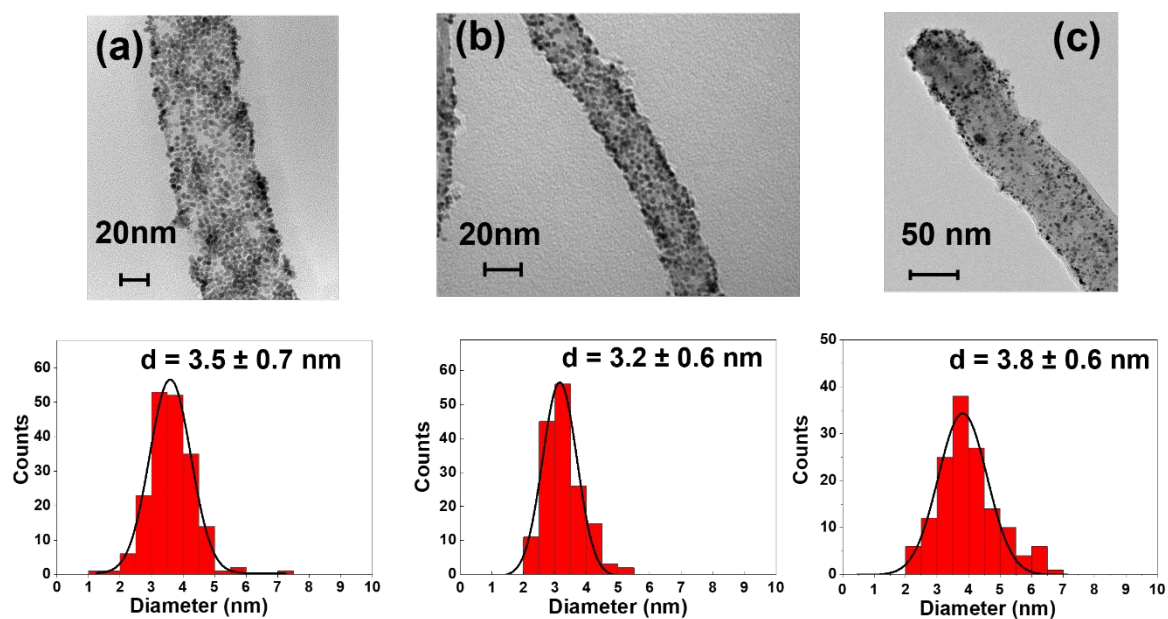


Figure A6: TEM image and its corresponding particle size distribution curve of (a) PtRu/ONCNT, (b) PtRu/TiO₂/ONCNT, and (c) PtRu/TiO₂/ONCNT-400.

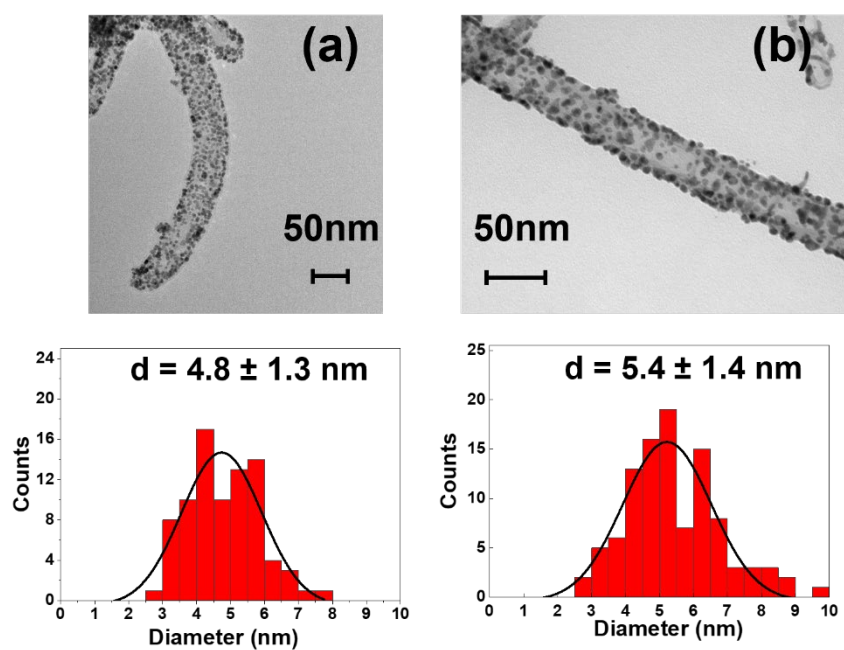


Figure A7: TEM image and its corresponding particle size distribution curve of (a) Pt/ONCNT-400 and (b) PtRu/ONCNT-400.

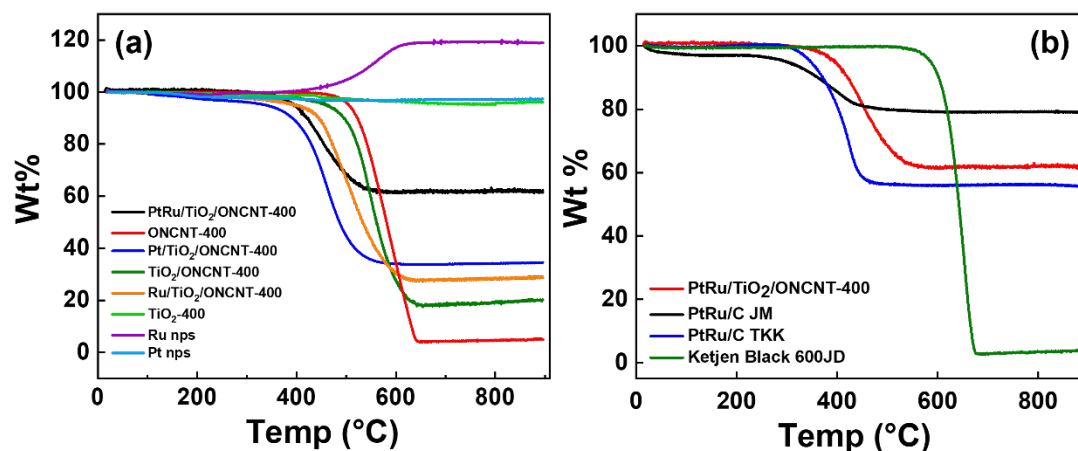


Figure A8: TGA curves of (a) Pt NPs, Ru NPs, TiO₂-400, ONCNT-400, Ru/ TiO₂/ONCNT-400, TiO₂/ONCNT-400, Pt/TiO₂/ONCNT-400 and PtRu/TiO₂/ONCNT-400. (b) TGA curves of commercial Ketjen Black 600JD, commercial PtRu/C TKK, commercial PtRu/C JM with PtRu/TiO₂/ONCNT-400.

TGA for all the catalysts were done in compressed air atmosphere. The wt% of PGM in PtRu/TiO₂/ONCNT-400 is determined using the stoichiometric calculations done using the control samples. The weight loss observed at 450 - 600 °C region for control ONCNT-400 (red curve in Fig. A8 (a)) corresponds to the decomposition of carbon to CO₂ in compressed air atmosphere. In the TGA of the control sample of Ru nanoparticles (purple curve in Fig. A8 (a)), the weight increases to ~119% above 625 °C, which corresponds to:



This weight gain is considered in all TGA calculations to find the Ru wt% in catalysts.

Calculation of TiO₂% in TiO₂/ONCNTs-400 (dark green curve in Fig. A8 (a)) using TGA data

A = fraction of TiO₂ in TiO₂/ONCNT-400

B = fraction of ONCNT in TiO₂/ONCNT-400

A + B = 1, which is,

$$\text{TiO}_2\% + \text{ONCNT}\% = 1 \text{ ----- (A.1)}$$

% of material remaining after TGA from TiO₂/ONCNT-400 = 20.5%

% of material remaining after TGA from ONCNT-400 = 4.25%

% of material remaining after TGA from TiO₂-400 = ~100%

% material remaining after TGA from TiO₂/ONCNT-400 = E *% of TiO₂ left after TGA in TiO₂-400 + F *% of ONCNT left after TGA in ONCNT-400

$$20.5\% = \text{TiO}_2\% * 100\% + \text{ONCNT}\% * 4.25\% \text{ ----- (A.2)}$$

Substitute (1) in (2) to solve the equation,

$$20.5\% = \text{TiO}_2\% + (1 - \text{TiO}_2\%) * 4.25\%$$

$$\text{\% of TiO}_2 \text{ in TiO}_2/\text{ONCNT-400} = 17.0\% \text{ ----- (A.3)}$$

Calculation of Pt:C ratio in Pt/TiO₂/ONCNT-400 (blue curve in Fig. A8 (a) using TGA data:

C = fraction of Pt in Pt/TiO₂/ONCNT-400

D = fraction of TiO₂ in Pt/TiO₂/ONCNT-400

E = fraction of ONCNT in Pt/TiO₂/ONCNT-400

$$C + D + E = 1 \text{ ----- (A.4)}$$

% of material remaining after TGA from Pt/ TiO₂/ONCNT-400 = C *% of Pt left after TGA in Pt nanoparticles + D *% of TiO₂ left after TGA in TiO₂ control + E *% of ONCNT left after TGA in ONCNT control

$$34.4\% = C*100\% + D*100\% + E *4.25\% \text{ ----- (A.5)}$$

$$\text{From eqn (3), TiO}_2\text{:ONCNT} = D:E = 0.204 \text{ ----- (A.6)}$$

$$D = 0.204 E$$

$$C = 1 - 1.204 E \text{ (using eqn 4)}$$

Substitute D and C in (5) and solve to get,

$$C = \text{Pt}\% = 17.5\%$$

$$D = \text{TiO}_2\% = 14.0\%$$

$$E = \text{ONCNT}\% = 68.5\%$$

$$C:E = \text{Pt}\% : \text{ONCNT}\% = 0.255\% \text{ ----- (A.7)}$$

Calculation of Ru:C ratio in Ru/TiO₂/ONCNT-400 (orange curve in Fig. S8 (a) using TGA data:

F = fraction of Ru in Ru/TiO₂/ONCNT-400

G = fraction of TiO₂ in Ru/TiO₂/ONCNT-400

H = fraction of ONCNT in Ru/TiO₂/ONCNT-400

$$F + G + H = 1 \text{ ----- (A.8)}$$

% of material remaining after TGA from Ru/ TiO₂/ONCNT-400 = F *% of Ru left after TGA in Ru nanoparticles + G *% of TiO₂ left after TGA in TiO₂ control + H *% of ONCNT left after TGA in ONCNT control

$$28.2\% = F*119\% + G*100\% + H*4.25\% \text{ ----- (A.9)}$$

$$\text{From eqn (3), TiO}_2\% : \text{ONCNT}\% = G:H = 0.204$$

$$G = 0.204 H$$

$$F = 1 - 1.204 H \text{ (using eqn 4)}$$

Substitute G and F in (5) and solve to get,

$$F = \text{Ru}\% = 7.8\%$$

$$G = \text{TiO}_2\% = 15.6\%$$

$$H = \text{ONCNT}\% = 76.6\%$$

$$F:H = \text{Ru}\% : \text{ONCNT}\% = 0.102\% \text{ ----- (A.10)}$$

Calculation of Pt%, Ru%, TiO₂% and ONCNT% in PtRu/TiO₂/ONCNT-400 (black curve in Fig. S8 (a) using TGA data:

X = fraction of Pt in PtRu/TiO₂/ONCNT-400

Y = fraction of Ru in PtRu/TiO₂/ONCNT-400

Z = fraction of TiO₂ in PtRu/TiO₂/ONCNT-400

J = fraction of ONCNT in PtRu/TiO₂/ONCNT-400

$$X + Y + Z + J = 1 \text{ ----- (A.11)}$$

% of material remaining after TGA from PtRu/ TiO₂/ONCNT-400 = X *% of Pt left after TGA in Pt nanoparticles + Y *% of Ru left after TGA in Ru nanoparticles + Z *% of TiO₂ left after TGA in TiO₂ control + J *% of ONCNT left after TGA in ONCNT control

$$60\% = X*100\% + Y*119\% + Z*100\% + J*4.25\% \text{ ----- (A.12)}$$

From (7) and (10),

$$\frac{X}{Y} = \frac{\text{Pt:ONCNT (from eqn (7))}}{\text{Ru:ONCNT (from eqn (10))}} = 2.5 \text{ ----- (A.13)}$$

$$\frac{Z}{Y} = \frac{\text{TiO}_2\text{:ONCNT (from eqn (6))}}{\text{Ru:ONCNT (from eqn (10))}} = 2.0 \text{ ----- (A.14)}$$

$$X = 2.5 Y$$

$$Z = 2.0 Y$$

$$J = 1 - 5.5 Y \text{ (using eqn 11)}$$

Substitute X, J and Z in (12) and solve to get,

$$X = \text{Pt}\% = 25.5\%$$

$$Y = \text{Ru}\% = 10.2\%$$

$$Z = \text{TiO}_2\% = 20.4\%$$

$$A = \text{ONCNT}\% = 43.9\%$$

$$\text{PGM}\% = 35.7\%$$

calculation of Pt% and Ru% in commercial PtRu/C JM (black curve in Fig. S8 (b) using above TGA analysis:

X = fraction of Pt in PtRu/C JM

Y = fraction of Ru in PtRu/C JM

A = fraction of carbon in PtRu/C JM

$$X+Y+A = 1 \text{ ----- (15)}$$

% of material remaining after TGA from PtRu/C JM = X *% of Pt left after TGA in Pt nanoparticles + Y *% of Ru left after TGA in Ru nanoparticles + A *% of carbon left after TGA in Ketjen Black 600JD

$$78.9\% = X*100\% + Y*119\% + A *3.82\% \text{ ----- (A.16)}$$

From the vendor specified weight ratio between Pt and Ru which is 2:1

$$X = 2.0 Y$$

$$A = 1 - 3.0 Y \text{ (using eqn 15)}$$

Substitute X and A in (16) and solve to get,

$$X = \text{Pt}\% = 48.8\%$$

$$Y = \text{Ru}\% = 24.4\%$$

$$A = \text{carbon}\% = 26.8\%$$

$$\text{PGM}\% = 73.2\%$$

Calculation of Pt% and Ru% in commercial PtRu/C TKK (blue curve in Fig. S8 (b)) using above TGA analysis:

X = fraction of Pt in PtRu/C TKK

Y = fraction of Ru in PtRu/C TKK

A = fraction of carbon in PtRu/C TKK

$$X+Y+A = 1 \text{ ----- (A.17)}$$

% of material remaining after TGA from PtRu/C TKK = X *% of Pt left after TGA in Pt nanoparticles + Y *% of Ru left after TGA in Ru nanoparticles + A *% of carbon left after TGA in Ketjen Black 600JD

$$55.6\% = X*100\% + Y*119\% + A *3.82\% \text{ ----- (A.18)}$$

From the vendor specified atomic ratio of 1:1, the weight ratio between Pt and Ru is 1.93:1.

$$X = 1.93 Y$$

$$A = 1 - 2.93 Y \text{ (using eqn 14)}$$

Substitute X and A in (15) and solve to get,

$$X = \text{Pt}\% = 33.3\%$$

$$Y = \text{Ru}\% = 17.3\%$$

$$A = \text{carbon}\% = 49.6\%$$

$$\text{PGM}\% = 50.6\%$$

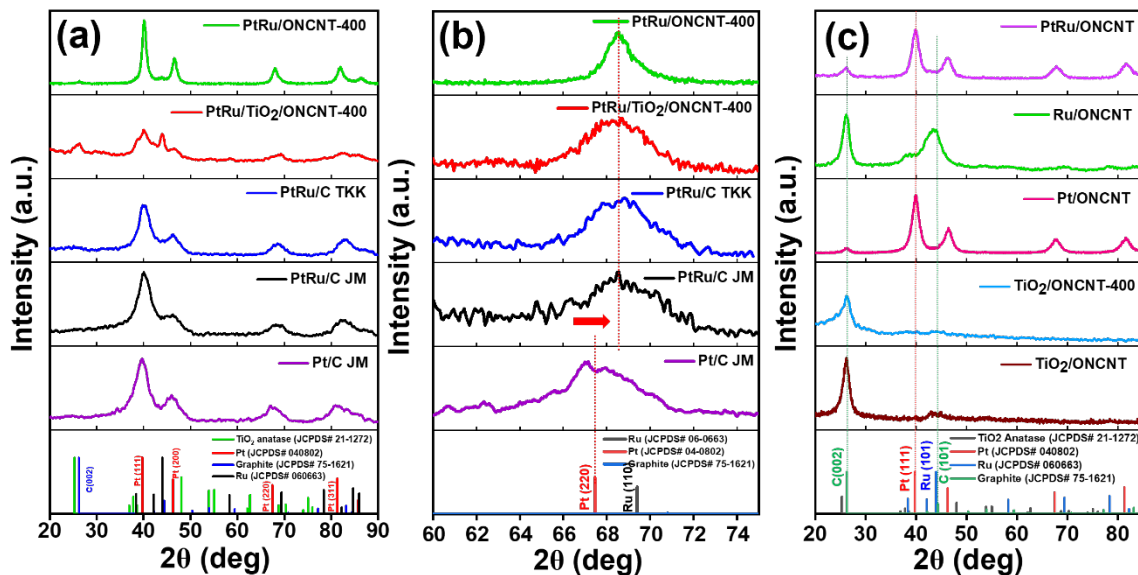


Figure A9: XRD patterns (a) in the full 2θ range of 20° to 90° , (b) in the narrow 2θ range of 60° to 75° of TiO_2 anatase (JCPDS# 21-1272), graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), Ru reference (JCPDS# 06-0663) compared with Pt/C, PtRu/C JM, PtRu/C TKK, PtRu/ TiO_2 /ONCNT-400 and PtRu/ONCNT-400. (c) XRD patterns in the narrow 2θ range of 20° to 90° of Graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), Ru reference (JCPDS# 06-0663), TiO_2 anatase (JCPDS# 21-1272) compared with TiO_2 /ONCNT, TiO_2 /ONCNT-400, Pt/ONCNT, Ru/ONCNT and

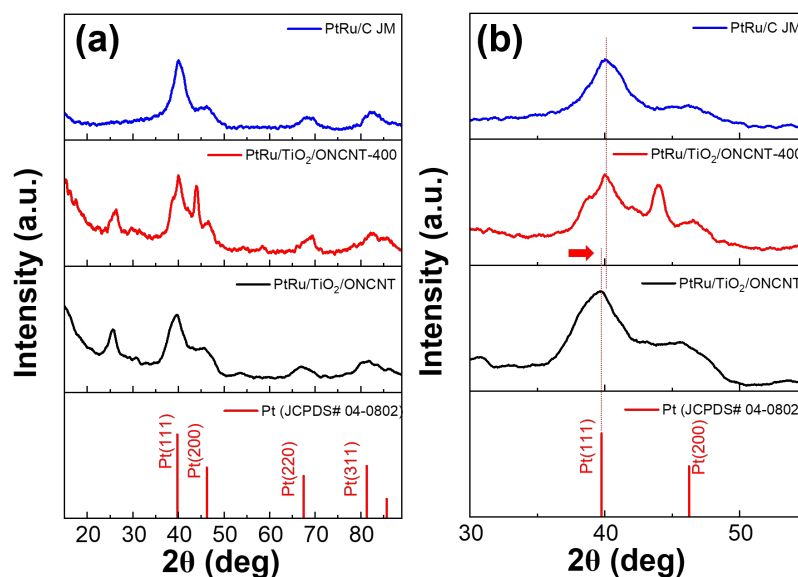


Figure A10: XRD patterns (a) (2θ range: 20° to 90°), (b) (2θ range: 30° to 50°) of Pt reference (JCPDS# 04-0802), compared with PtRu/TiO₂/ONCNT, PtRu/TiO₂/ONCNT-400 and PtRu/C JM

XRD calculations:

Degree of alloying is determined using Vegard's law^{110, 111}, according to empirical relationship:

$$a_{fcc} = 3.8013 + 0.1249 X_{Pt} \text{ ----- (A.19)}$$

X_{Pt} - atomic fraction of Pt in PtRu alloy

a_{fcc} - lattice parameter of Pt fcc

For cubic lattice,

$$a_{fcc} = \frac{\sqrt{(h^2 + k^2 + l^2)} \times \lambda_{K\alpha}}{2 \times \sin\theta} \text{ ----- (A.20)}$$

h, k, l = the diffraction plane

$\lambda_{K\alpha}$ = X-ray source wavelength (Cu K α (λ) = 1.5418 Å)

θ = Bragg angle

Atomic fraction of Ru in PtRu alloy (X_{Ru}) can be determined using,

$$X_{Ru} = 1 - X_{Pt} \text{ ----- (A.21)}$$

For PtRu/TiO₂/ONCNT-400, at $2\theta = 40.28$ for Pt (111), the calculated atomic fraction of Pt:Ru is 1.6:1, using eqn (17), (18) and (19).

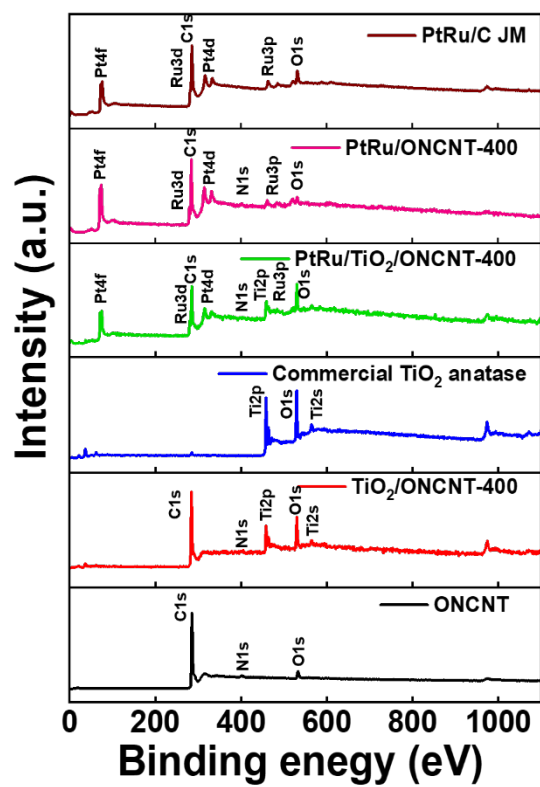


Figure A11: XPS survey spectra comparing (a) ONCNT, TiO₂/ONCNT-400, commercial TiO₂ anatase nano powder, PtRu/TiO₂/ONCNT-400, PtRu/ONCNT-400 and PtRu/C JM.

Table A1 Atomic percentage (at%) of the elemental species derived from the XPS survey spectra.

Sample	C	O	N	Pt	Ru	Ti
NCNT	76%	15%	9%	-	-	-
ONCNT	74%	16%	10%	-	-	-
TiO ₂ /ONCNT-400	81.6 %	12.4 %	2.0 %	-	-	4.1 %
Commercial TiO ₂ anatase	-	65.6 %		-	-	34.4 %
PtRu/TiO ₂ /ONCNT-400	83.3 %	7.1 %	0.1 %	2.3 %	3.6 %	3.5 %
PtRu/ONCNT-400	88.5 %	1.6 %	1.3 %	3.8 %	4.8 %	-
PtRu/C JM	83.3 %	10.5 %	-	3.2 %	3.1 %	-

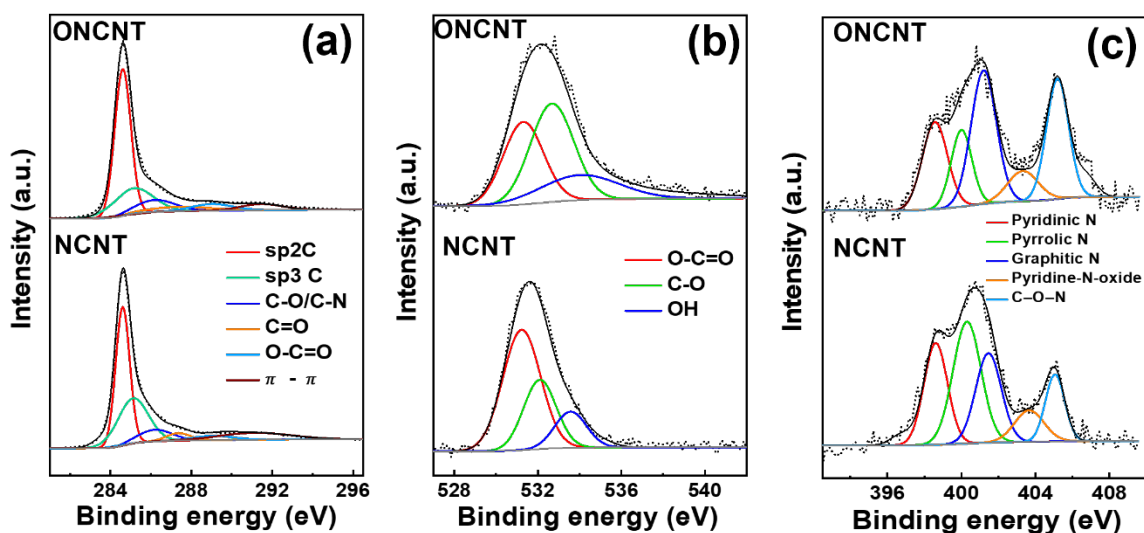


Figure A12: The comparison of (a) C 1s, (b) O 1s and (c) N 1s XPS spectra of NCNT and ONCNT.

Table A2 Binding energies and relative deconvoluted peak area % of individual chemical component from Fig. A12.

Element	Different species	ONCNT (in at%)	NCNT (in at%)	Element	Different species	ONCNT (in at%)	NCNT (in at%)	Element	Different species	ONCNT (in at%)	NCNT (in at%)
C 1s	sp ²	38.9 %	31.6 %	O 1s	O-C=O	5.6 %	8.6 %	N 1s	Pyridinic N	2.0 %	2.1 %
	sp ³	16.4 %	22.3 %		C-O	7.2 %	4.2 %		Pyrrolic N	1.5 %	3.0 %
	C-O/C-N	7.8 %	6.4 %		-OH	3.2 %	2.2 %		Graphitic N	3.1 %	2.0 %
	C=O	4.4 %	2.9 %						Pyridinic-N-oxide	0.9 %	0.8 %
	O-C=O	4.4 %	2.9 %						C-O-N	2.5 %	1.1 %
	π - π	4.0 %	7.9 %								

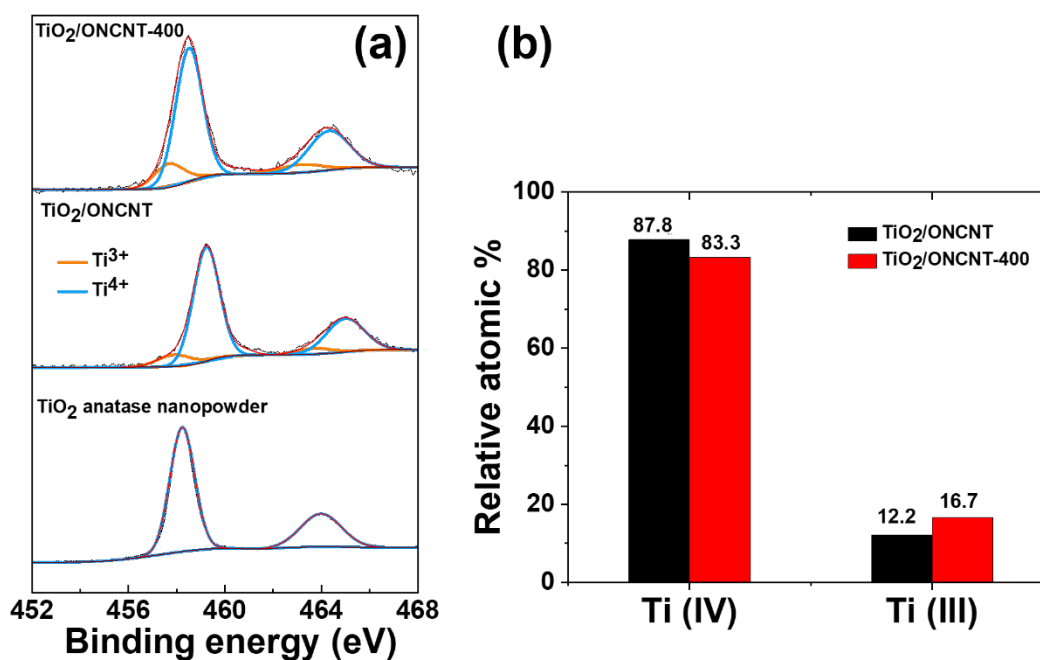


Figure A13: The comparison of (a) Ti 2p XPS spectra of commercial TiO₂ anatase nano powder, TiO₂/ONCNT and TiO₂/ONCNT-400. (b) Relative at% of individual Ti states from Ti 2p XPS spectra of TiO₂/ONCNT-400 and TiO₂/ONCNT.

Table A3 Binding energies and relative deconvoluted peak area % of individual chemical component from Pt 4f, Ru 3p and Ti 2p XPS spectra from Fig. 2.4.

		PtRu/TiO ₂ /ONCNT-400		PtRu/ONCNT-400		PtRu/C JM	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Pt	metallic	71.41	61.1 %	71.47	67.8 %	71.82	50.6 %
		74.77		74.80		75.26	
	(II)	72.26	23.7 %	72.32	21.2 %	72.70	23.2 %
		76.14		75.94		76.86	
	(IV)	73.50	15.3 %	73.68	11.0 %	74.22	26.2 %
		78.27		77.44		76.94	
		PtRu/TiO ₂ /ONCNT-400		PtRu/ONCNT-400		PtRu/C JM	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ru	metallic	461.32	69.2 %	461.87	64.2 %	462.43	64.0 %
		483.80		484.07		484.83	
	(IV)	464.49	30.8 %	466.07	35.8 %	465.97	18.3 %
		485.81		488.36		488.41	
	(IV) hydrate	-	-	-	-	469.27	17.7 %
		-		-		494.70	
		PtRu/TiO ₂ /ONCNT-400		TiO ₂ /ONCNT-400		Commercial anatase	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ti	(III)	458.02	27.0 %	457.63	16.7 %	-	-
		462.37		462.30		-	
	(IV)	458.92	73.0 %	458.50	83.3 %	458.32	100 %
		464.64		464.32		464.08	

Table A4 CO oxidation onset and peak potential of commercial PtRu/C JM, commercial PtRu/C TKK, PtRu/ONCNT-400 and PtRu/TiO₂/ONCNT-400.

Sample	CO oxidation onset potential V @ 0.150 mA/cm ² _{geo}		CO oxidation peak potential V	
	vs Ag/AgCl (1M KCl)	vs RHE	vs Ag/AgCl (1M KCl)	vs RHE
PtRu/C JM	0.190	0.412	0.228V	0.450
PtRu/C TKK	0.170	0.392	0.302V	0.524
PtRu/ONCNT-400	0.205	0.427	0.234 V	0.456
PtRu/TiO ₂ /ONCNT-400	0.170	0.392	0.214 V	0.436

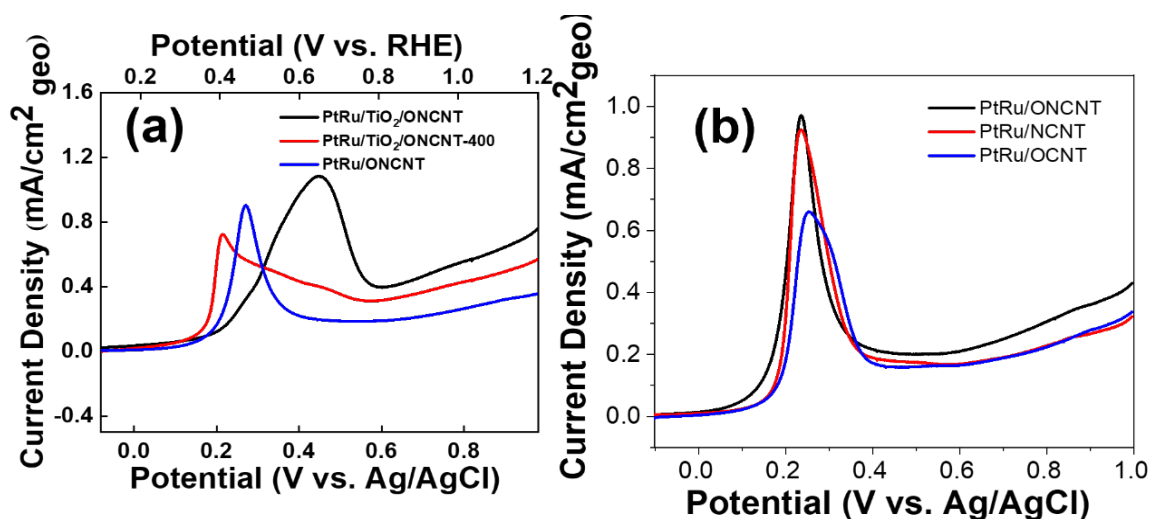


Figure A14: (a) PtRu/TiO₂/ONCNT, PtRu/TiO₂/ONCNT-400 and PtRu/ONCNT recorded in Ar-purged 0.50 M H₂SO₄ solution at a scan rate of 10 mV/s. (b) Comparison of first anodic scan of CO stripping curves of PtRu/ONCNT, PtRu/NCNT and PtRu/OCNT recorded in Ar-purged 0.10 M HClO₄ at a scan rate of 10 mV/s; The filling solution in Ag/AgCl reference electrode is 1.0 M KCl.

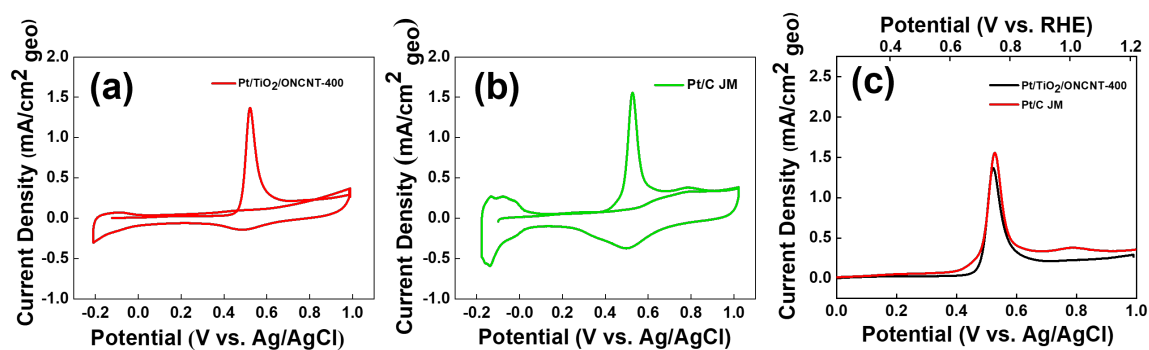


Figure A15: CO stripping voltammogram of (a) Pt/TiO₂/ONCNT-400 and (b) Pt/C JM recorded in Ar purged 0.50 M H₂SO₄ solution at a scan rate of 10 mV/s. (c) Comparison of first anodic scan of CO stripping curves of Pt/TiO₂/ONCNT-400 and Pt/C JM.

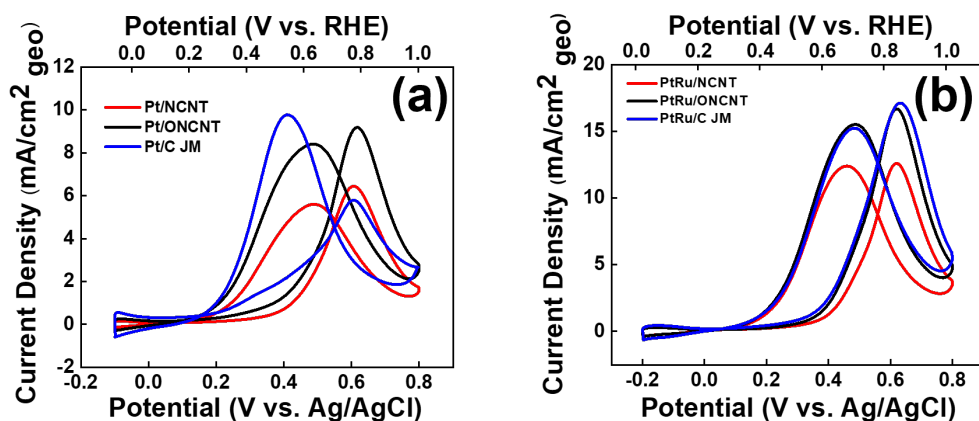


Figure A16: (a) Cyclic voltammetry curves (100th cycle) of Pt/C JM, Pt/ONCNT and Pt/NCNT recorded in Ar purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s; (b) Cyclic voltammetry curves (100th cycle) of PtRu/C JM, PtRu/ONCNT and PtRu/NCNT recorded in Ar-purged 0.5 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s;

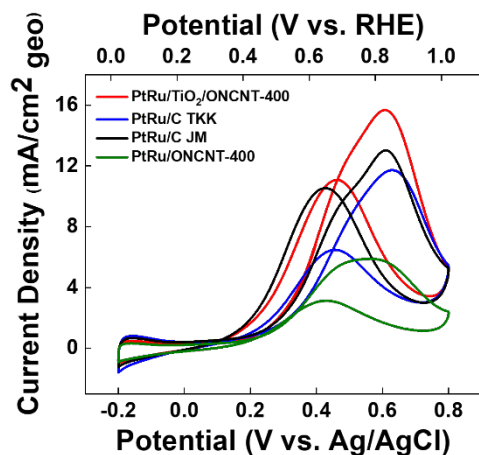


Figure A17: Cyclic voltammetry curves (in the 3rd cycle) of PtRu/ONCNT-400, commercial PtRu/C JM, commercial PtRu/C TKK and PtRu/TiO₂/ONCNT-400 catalysts recorded in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s.

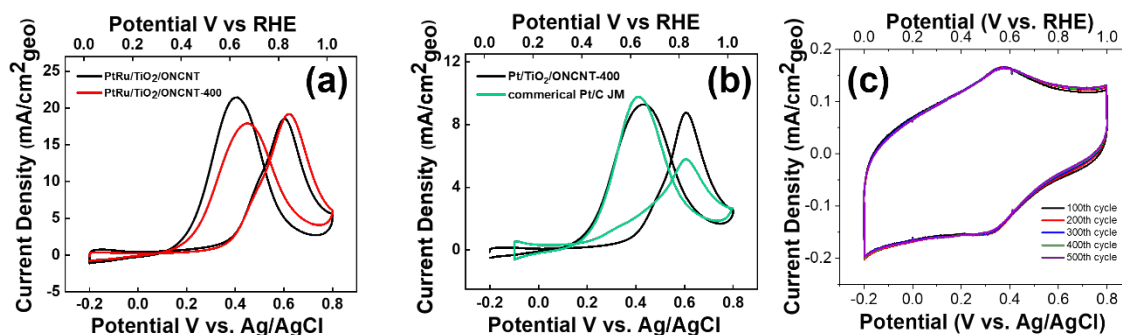


Figure A18: Comparison of cyclic voltammetry curves of (a) PtRu/TiO₂/ONCNT-400 and PtRu/TiO₂/ONCNT; (b) Pt/TiO₂/ONCNT-400 and commercial Pt/C JM catalysts recorded in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s; (c) TiO₂/ONCNT recorded in Ar-purged 0.5 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s;

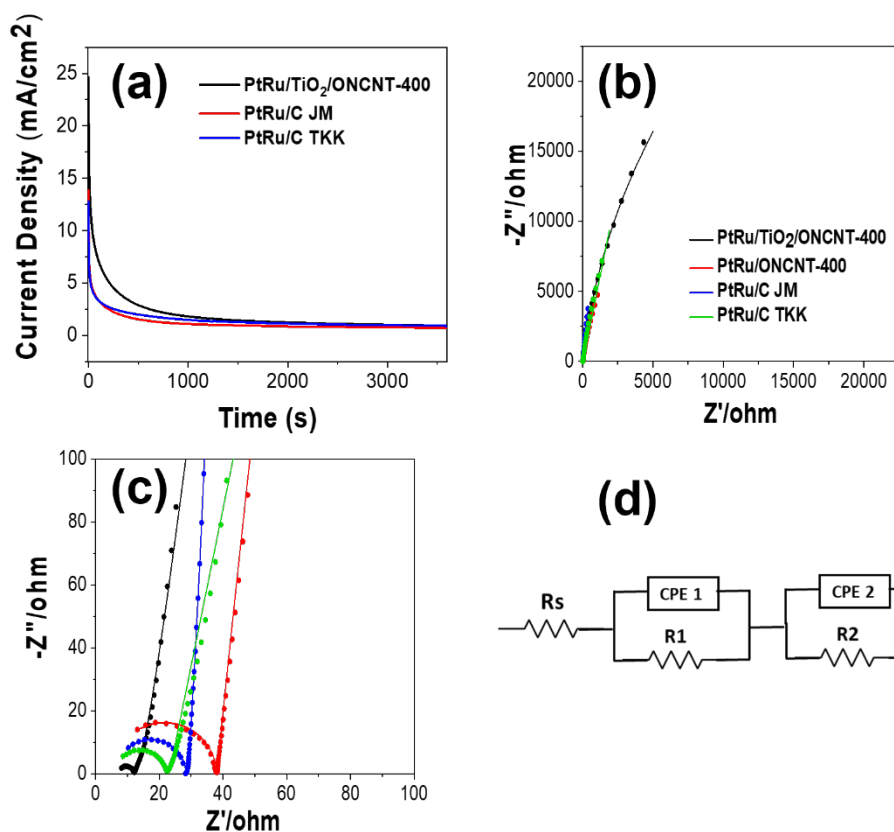


Figure A19: (a) Amperometric i-t curve of PtRu/TiO₂/ONCNT-400, PtRu/C JM and PtRu/C TKK at 0.62 V vs Ag/AgCl (1.0 M) in 0.50 M H₂SO₄ solution containing 0.75 M methanol. Nyquist plots the electrochemical impedance spectra (EIS) of PtRu/TiO₂/ONCNT-400, PtRu/ONCNT-400, PtRu/C JM and PtRu/C TKK catalysts recorded in Ar-purged 0.50 M H₂SO₄ solution at OCV at 54 $\mu\text{g}/\text{cm}^2$ PGM loading (b) in the full frequency range (1.75 MHz to 0.01 Hz) and (c) in the high frequency. (d) The corresponding equivalent circuit to fit the EIS. The legends in Figure A19 (b) applies to Figure A19 (c).

Description of Nyquist plots in Figure A19 (b) and (c):

Two semicircle regions are observed in the Nyquist plots: one at the high-frequency region and the other one at the low-frequency region attributing to the resistance to the charge transfer process and the ion mass transfer process occurring at the electrode-electrolyte interface,¹⁹⁴ respectively. Figure A9 (d) shows the corresponding equivalent circuit model for fitting the Nyquist plots in Figures A9 (b) and A9 (c).

Table A5 Equivalent circuit fitting parameters for all catalysts shown in the Nyquist plot in Figure A19 (b).

Parameters	Rs		R1		CPE 1				R2		CPE 2			
	Ohm	Error %	Ohm	Error %	Yo (S sec ⁿ)	Error %	n	Error %	Ohm	Error %	Yo (S sec ⁿ)	Error %	n	Error %
PtRu/TiO ₂ /ON CNT-400	7.12	3.45	4.45	9.63	8.08×10^{-8}	6.606	0.9835	5.251	9088	13.23	0.0002545	4.47	0.9335	13.23
PtRu/ONCNT400	5.41	7.13	32.5	3.01	9.93×10^{-9}	15.46	0.9987	2.026	1556	7.398	0.001074	5.01	0.8697	5.148
PtRu/C JM	6.61	1.28	21.8	5.58	1.87×10^{-8}	5.54	0.9921	4.32	3865	8.17	0.001839	6.17	0.8699	4.058
PtRu/C TKK	4.903	6.01	18.3	6.44	1.84×10^{-7}	7.69	0.8634	5.36	2843	6.91	0.0006411	6.89	0.8741	1.689

Table A6 Electrochemical activity of the catalysts reported in the literature currently and compared with our PtRu/TiO₂/ONCNT-400 catalyst.

Catalyst	I_f/I_b @ 100 th cycle	CO oxidation onset potential V	Mass activity (A/g _{Pt})	Specific activity (mA/cm ² ECSA)	MOR Scan rate	Electrolyte	Ref
PtRu/TiO ₂ /ONCNT-400	1.1	0.415 V vs RHE	523.6	0.78	50 mV/s	0.75 M MeOH + 0.5 M H ₂ SO ₄	This work
PtRu/C JM	1:1	0.435 V vs RHE	471.7	0.36	50 mV/s	0.75 M MeOH + 0.5 M H ₂ SO ₄	
PtRu/C JM	1.8	0.435 V vs RHE	430.0	0.32	50 mV/s	0.75 M MeOH + 0.1 M HClO ₄	23
PtRu/C JM	6	0.430 V vs RHE	410.0	0.83	50 mV/s	0.5 M MeOH + 0.1 M HClO ₄	195
TiO ₂ /CNT/PtRu	1.2	-	436.5	-	100 mV/s	1 M MeOH + 0.5 M H ₂ SO ₄	196
PtRu/RGO/TNTs	> 1	-	316.0	-	50 mV/s	1 M MeOH + 0.5 M H ₂ SO ₄	197
PtRu/C-TiO ₂	1.4	-	366.7	-	50 mV/s	1 M MeOH + 0.5 M H ₂ SO ₄	85
PtRu/TECNF[1.0] (TECNF – TiO ₂ embedded CNFs)	> 1	-	516.0	-	20 mV/s	2 M MeOH + 0.5 M H ₂ SO ₄	198
TiO ₂ -PtRu/C- 600C	4.1	0.01 V vs Ag/AgCl	393.0	-	20 mV/s	1 M MeOH + 0.5 M H ₂ SO ₄	199

Catalyst	I_f/I_b @ 100 th cycle	CO oxidation onset potential V	Mass activity (A/g _{Pt})	Specific activity (mA/cm ² ECSA)	MOR Scan rate	Electrolyte	Ref
PtRu/ NC@MTNWs-FI (MTNWs-FI - Mo modified TiO ₂ nanowires on func interface)	1.1	~ 0.380 V vs RHE	1230.0	0.00142	50 mV/s	0.5 M MeOH + 0.5 M H ₂ SO ₄	200
Ru@Pt/C-TiO ₂	0.9	~ 0.360 V RHE	-	1.08	50 mV/s	0.5 M MeOH + 0.5 M H ₂ SO ₄	201
PtRu/TiO ₂ -NW		2	40.0	-	50 mV/s	2 M MeOH + 0.5 M H ₂ SO ₄	202
Pt/RuO ₂ /TiO ₂ -NTs		~0.090 V vs SCE	416	-	5 mV/s	1 M MeOH + 0.5 M H ₂ SO ₄	203

as

Appendix B - Supplementary Information for Chapter 3

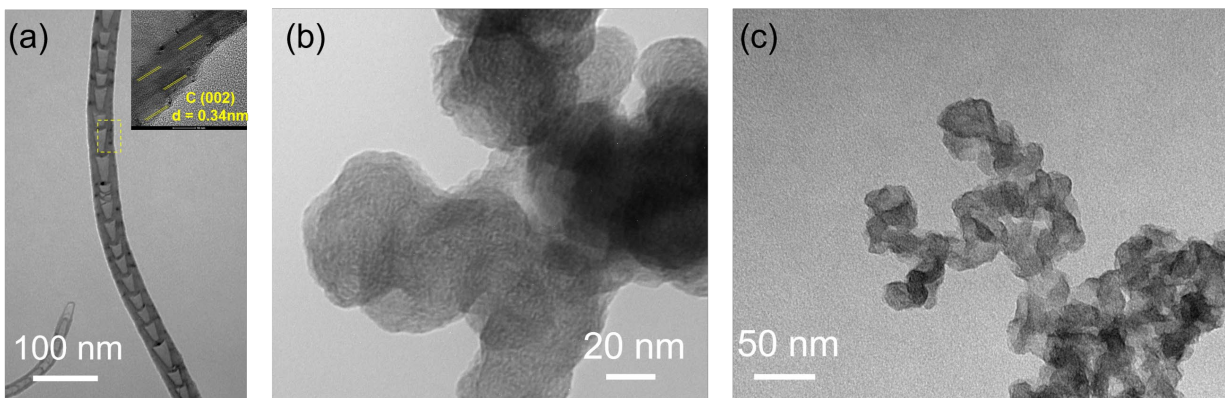


Figure B1: TEM image of (a) bare ONCNT and inset is the HRTEM image of highlighted yellow box showing the graphitic planes at edges and (b) bare Vulcan and (c) bare KB 600JD.

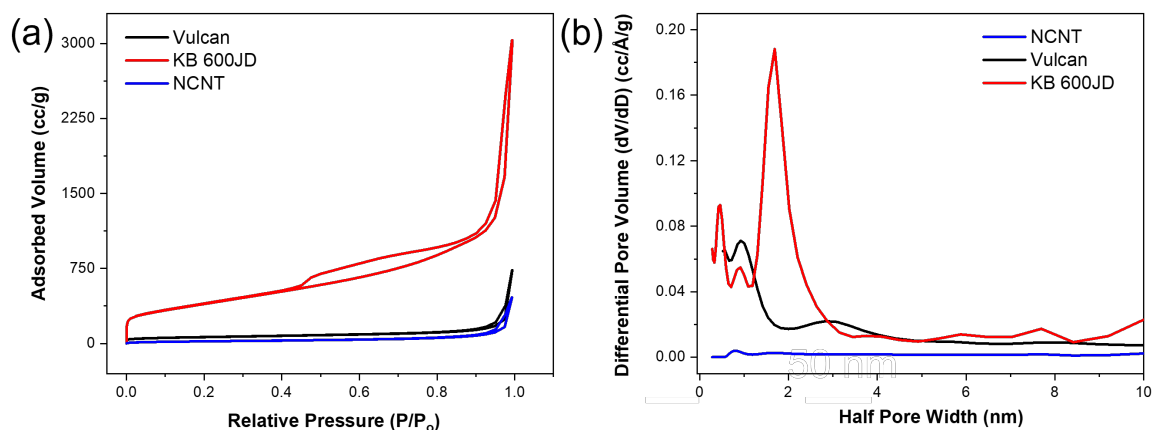


Figure B2: (a) BET N₂ adsorption-desorption isotherms and (b) corresponding pore size distribution curves of ONCNT, Vulcan and KB 600JD.

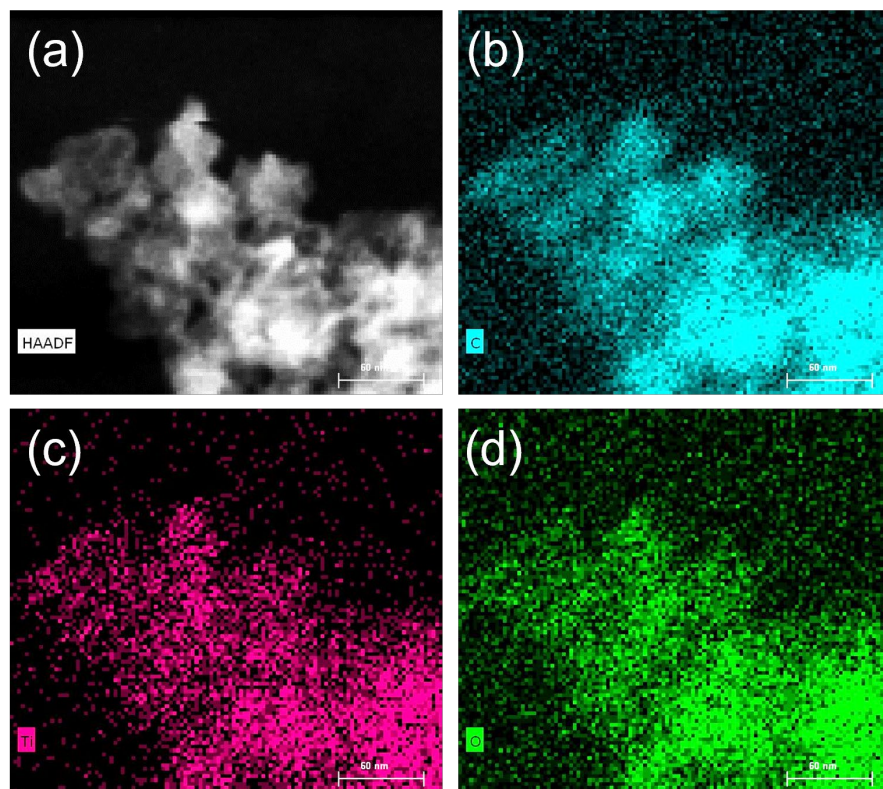


Figure B3: (a) HAADF-STEM image and (b–d) STEM-EDX elemental mapping of C, Ti, and O of TiO₂/KB 600JD.

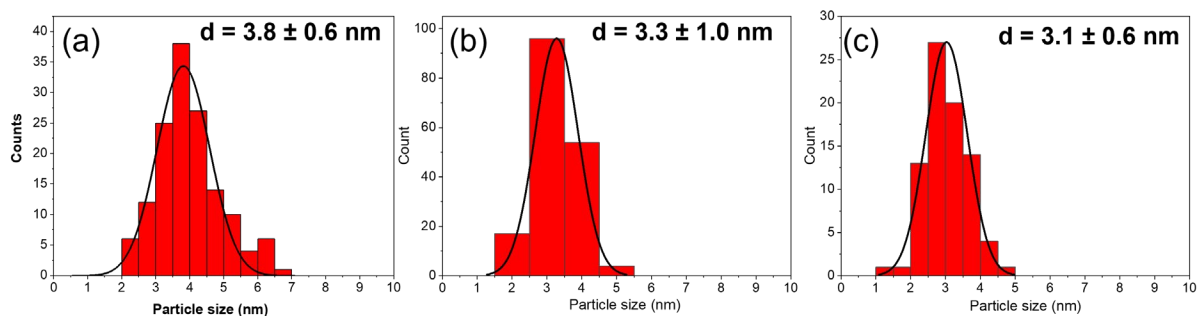


Figure B4: Particle size distribution histogram of (a) PtRu/TiO₂/ONCNT-400, (b) PtRu/TiO₂/Vulcan-400 and (c) PtRu/TiO₂/KB 600JD-400.

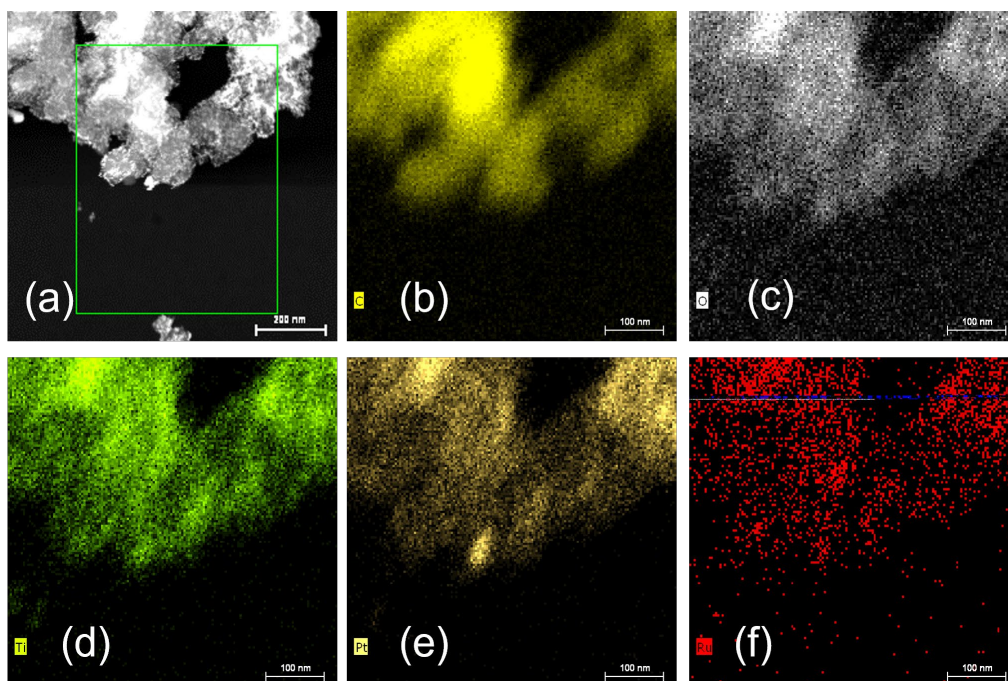


Figure B5: (a) HAADF-STEM image and (b–f) STEM-EDX elemental mapping of C, O, Ti, Pt and Ru of PtRu/TiO₂/Vulcan-400.

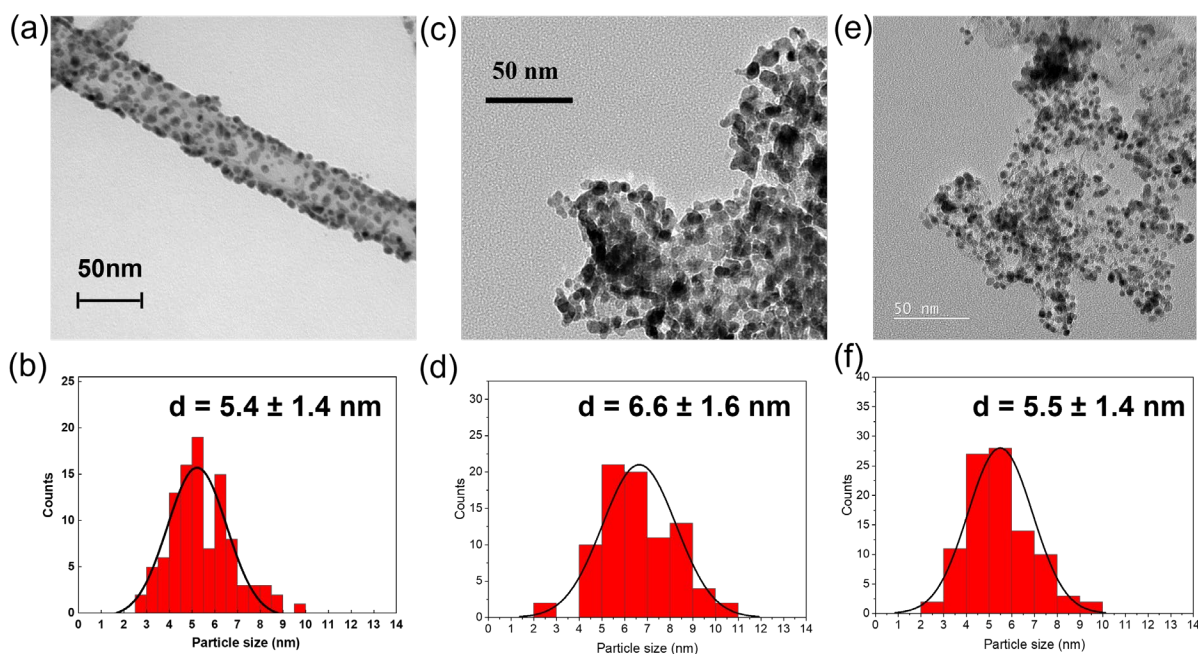


Figure B6: TEM image and corresponding particle size distribution of (a)-(b) PtRu/ONCNT-400, (c)-(d) PtRu/Vulcan-400 and (e)-(f) PtRu/KB 600JD-400.

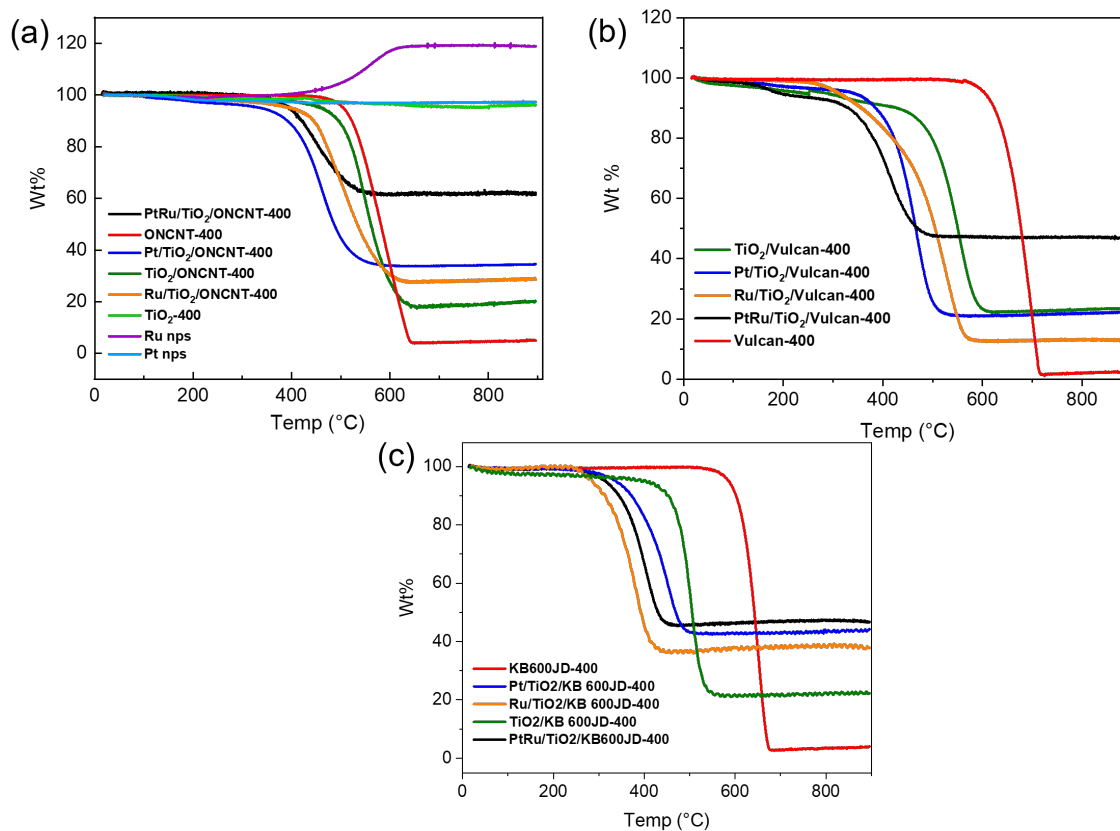


Figure B7: TGA curves comparing (a) PtRu/TiO₂/ONCNT-400 and control samples (b) PtRu/TiO₂/Vulcan-400 and control samples and (c) PtRu/TiO₂/KB 600JD-400 and control samples. °

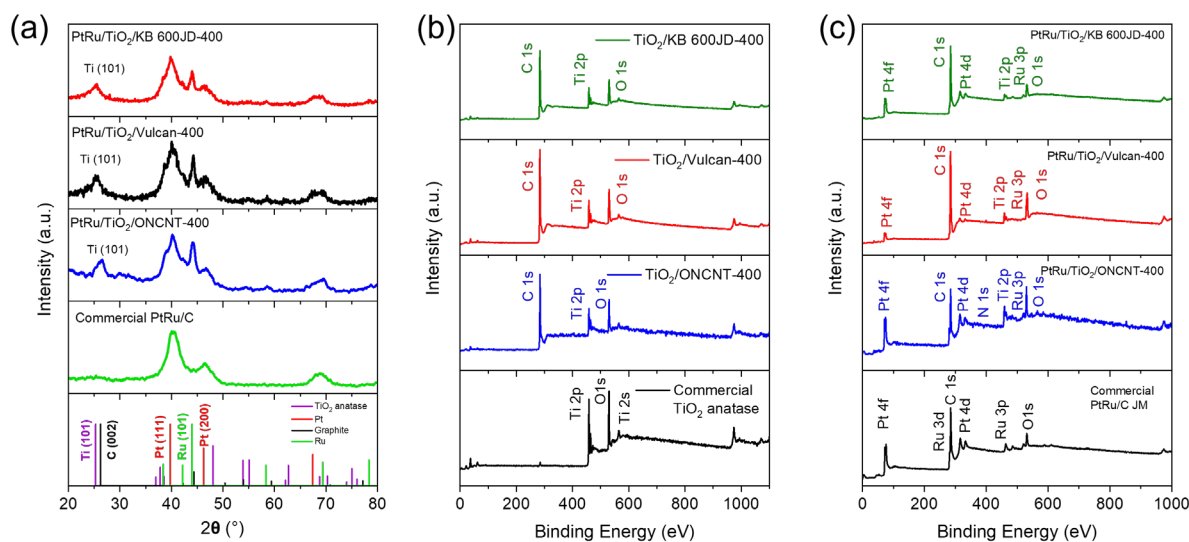


Figure B8: (a) XRD full range spectra of Ru reference (JCPDS # 06-0663), graphite reference (JCPDS# 75-1621), Pt reference (JCPDS# 04-0802), TiO₂ anatase reference (JCPDS# 21-1272) compared with commercial PtRu/C, PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/Vulcan-400 and PtRu/TiO₂/KB600JD-400. (b) and (c) XPS survey spectra of various catalysts.

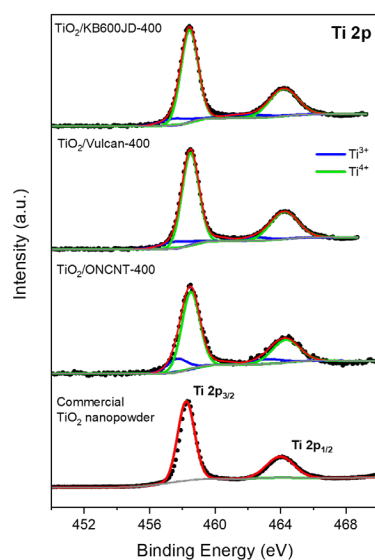


Figure B9: The comparison of Ti 2p XPS spectra of commercial TiO_2 anatase nano powder, $\text{TiO}_2/\text{ONCNT-400}$, $\text{TiO}_2/\text{Vulcan-400}$ and $\text{TiO}_2/\text{KB 600JD-400}$.

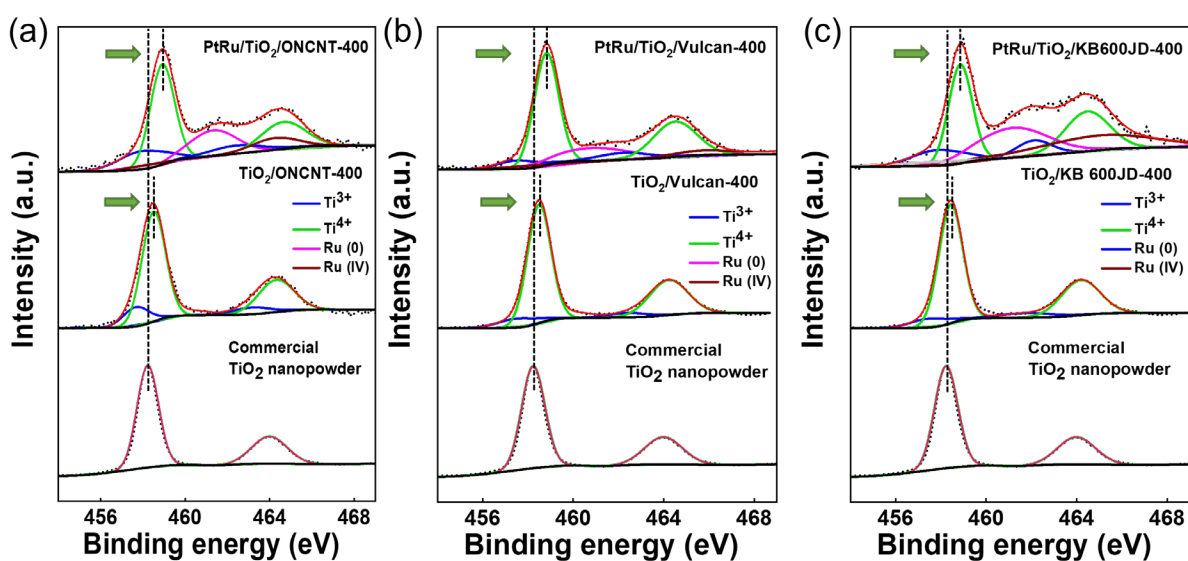


Figure B10: The comparison of Ti 2p XPS spectra of (a) $\text{PtRu}/\text{TiO}_2/\text{ONCNT-400}$ and its corresponding control samples; (b) $\text{PtRu}/\text{TiO}_2/\text{Vulcan-400}$ and its corresponding control samples; (c) $\text{PtRu}/\text{TiO}_2/\text{KB 600JD-400}$ and its corresponding control samples.

Table B1 Binding energies and relative deconvoluted peak area % of individual chemical component from Ti 2p XPS spectra of various catalysts.

		TiO ₂ /ONCNT-400		TiO ₂ /Vulcan-400		TiO ₂ /KB 600JD-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ti	(III)	457.63	16.7 %	457.47	10.8 %	457.52	11.4 %
		462.30		462.41		462.09	
	(IV)	458.50	83.3 %	458.51	89.2 %	458.43	88.6 %
		464.32		464.22		464.19	
		PtRu/TiO ₂ /ONCNT-400		PtRu/TiO ₂ /Vulcan-400		PtRu/TiO ₂ /KB 600JD-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ti	(III)	458.02	27.0 %	457.49	14.0 %	457.78	20.63 %
		462.37		462.24		462.15	
	(IV)	458.92	73.0 %	458.80	86.0 %	458.85	79.37 %
		464.64		464.53		464.47	

Table B2 Binding energies and relative deconvoluted peak area % of individual chemical component from Pt 4f, Ru 3p and Ti 2p XPS spectra for various catalysts.

		PtRu/TiO ₂ /ONCNT-400		PtRu/TiO ₂ /Vulcan-400		PtRu/TiO ₂ /KB 600JD-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Pt	metallic	71.41	61.1 %	71.66	57.8 %	71.59	53.4 %
		74.77		75.02		74.88	
	(II)	72.26	23.7 %	72.68	20.1 %	72.42	25.3 %
		76.14		76.25		76.20	
	(IV)	73.50	15.3 %	73.89	22.1 %	73.86	21.3 %
		78.27		77.72		78.35	
		PtRu/TiO ₂ /ONCNT-400		PtRu/TiO ₂ /Vulcan-400		PtRu/TiO ₂ /KB 600JD-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ru	metallic	461.02	69.2 %	460.65	71.1 %	461.06	68.2 %
		483.80		484.09		484.01	
	(IV)	464.49	30.8 %	465.94	28.9 %	465.38	31.8 %
		485.81		487.77		487.32	
	(IV) hydrate	-	-	-	-	-	-
		-		-		-	
		PtRu/TiO ₂ /ONCNT-400		PtRu/TiO ₂ /Vulcan-400		PtRu/TiO ₂ /KB 600JD-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ti	(III)	458.02	27.0 %	457.49	14.0 %	457.78	20.6 %
		462.37		462.24		462.15	
	(IV)	458.92	73.0 %	458.80	86.0 %	458.85	79.4 %
		464.64		464.53		464.47	

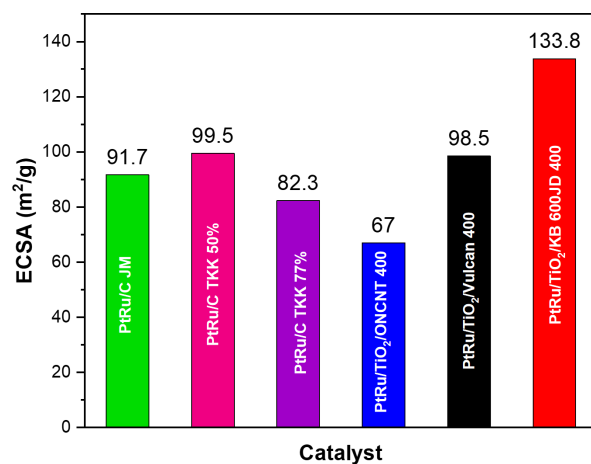


Figure B11: Comparison of ECSA values of different catalysts.

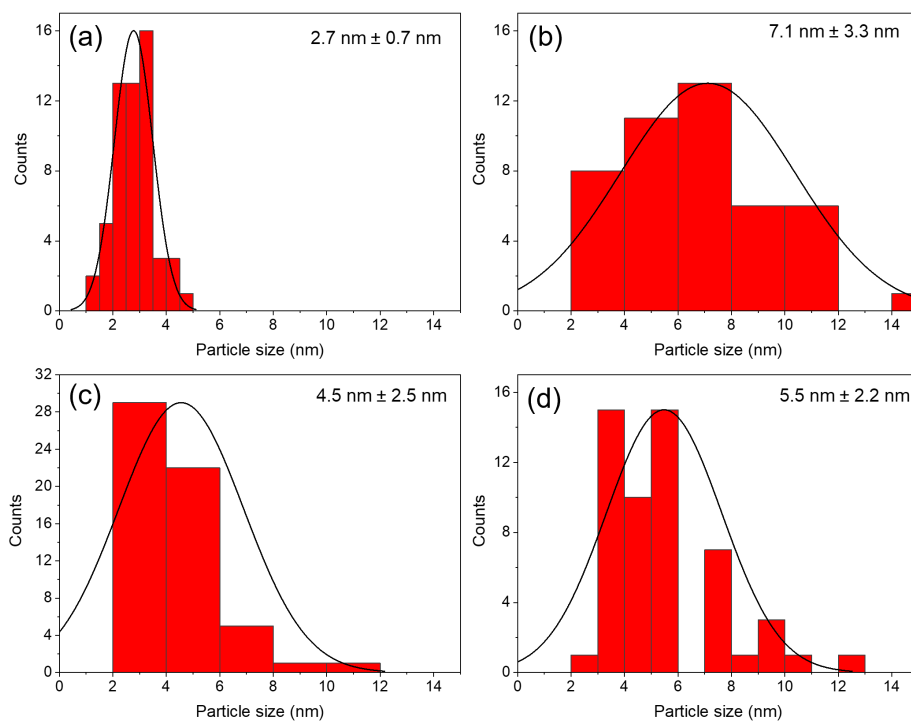


Figure B12: Particle size distribution of (a) fresh PtRu/C JM from Figure 3.10 (a); (b) PtRu/C JM after AST protocol 1 from Figure 3.10 (c); (c) fresh PtRu/C TKK 50% from Figure 3.10 (d); and (d) PtRu/C TKK 50% after AST protocol 1 from Figure 3.10 (e).

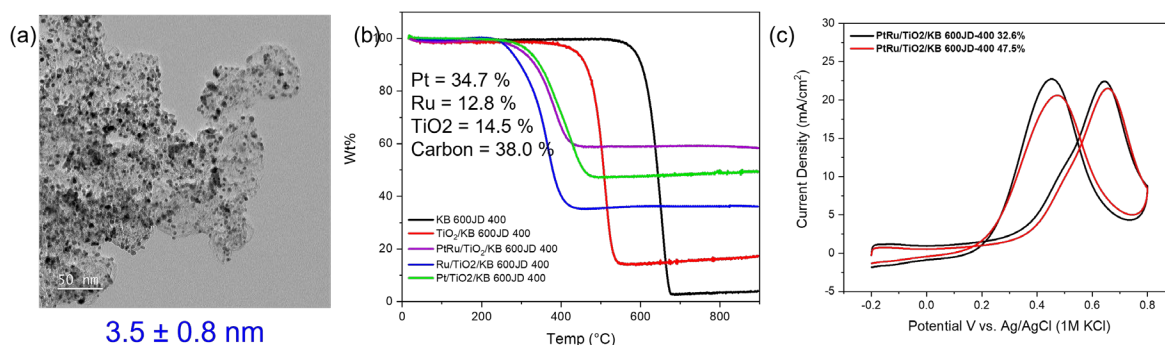


Figure B13: TEM image of PtRu/TiO₂/KB 600JD-400 (50% PGM), (b) Comparison of TGA curve of PtRu/TiO₂/KB 600JD-400 (50% PGM) and its control sample and (c) Comparison of MOR CV curve of PtRu/TiO₂/KB 600JD-400 (50% PGM) and PtRu/TiO₂/KB 600JD-400 (32.6% PGM).

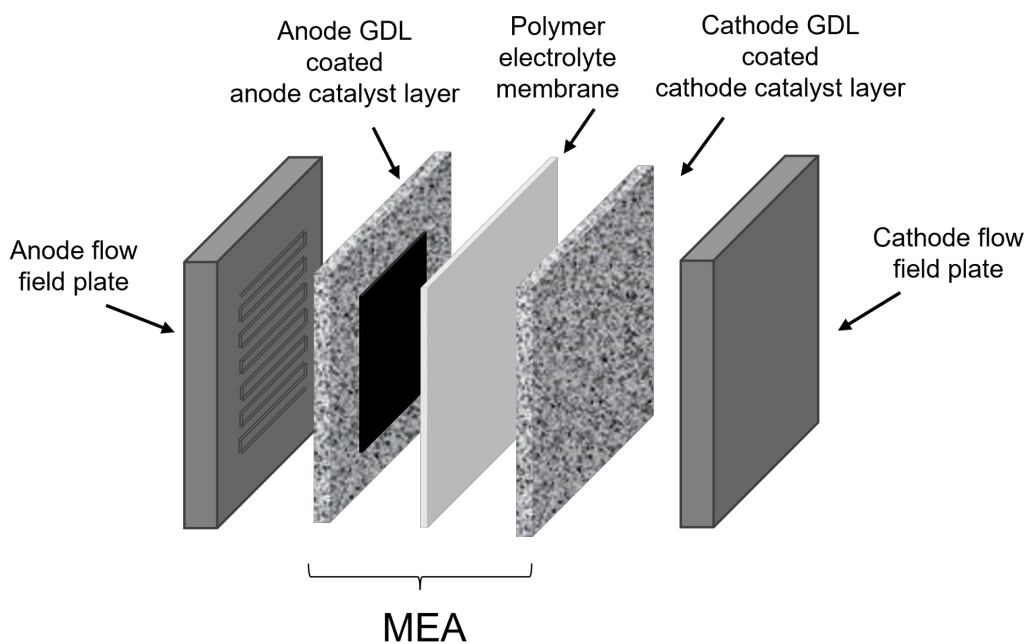


Figure B14: Schematic of MEA with its components

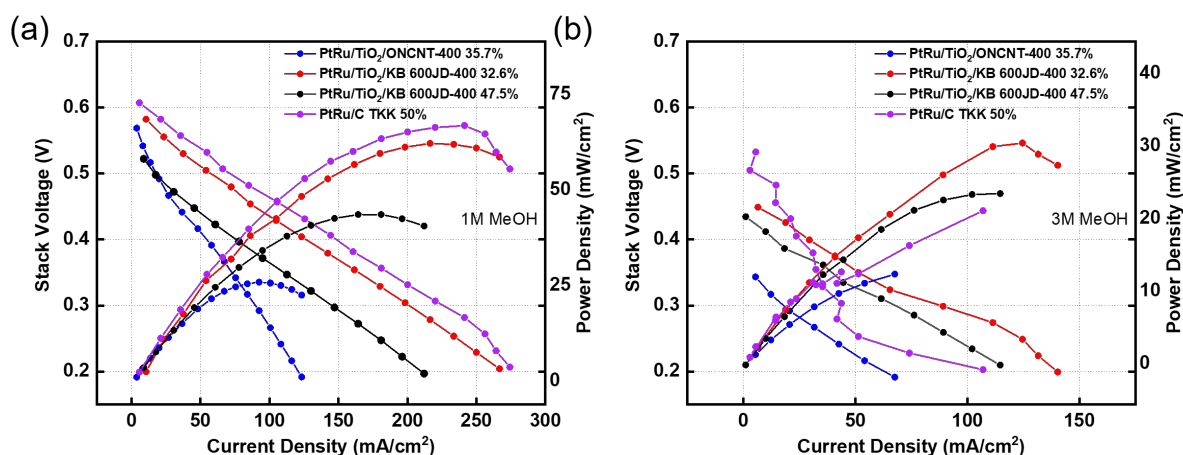


Figure B15: DMFC performance curves of PtRu/TiO₂/KB 600JD-400 (50% PGM) compared with PtRu/TiO₂/ONCNT-400, PtRu/TiO₂/KB 600JD-400 and PtRu/C TKK 50% catalysts in (a) 1.0 M methanol solution and (b) 3.0 M methanol solution with Pt/C JM 60% cathode. The anode and cathode catalyst loadings were 4.5 mg_{PtRu}/cm² and 1.5 mg_{Pt}/cm², respectively. Test conditions: cell temperature at 80.0 °C, at 1 mL/min methanol and 0.1 L/min air flow rate with 0.5 bar back pressure. Nafion 212 membrane was used and ionomer/carbon ratio of 1.0 and ionomer/Pt of 0.2 was maintained at anode and cathode, respectively, in all the fuel cell tests. Credits: DMFC tests were done by Nathan at Dr. Xianglin Li's lab from KU.

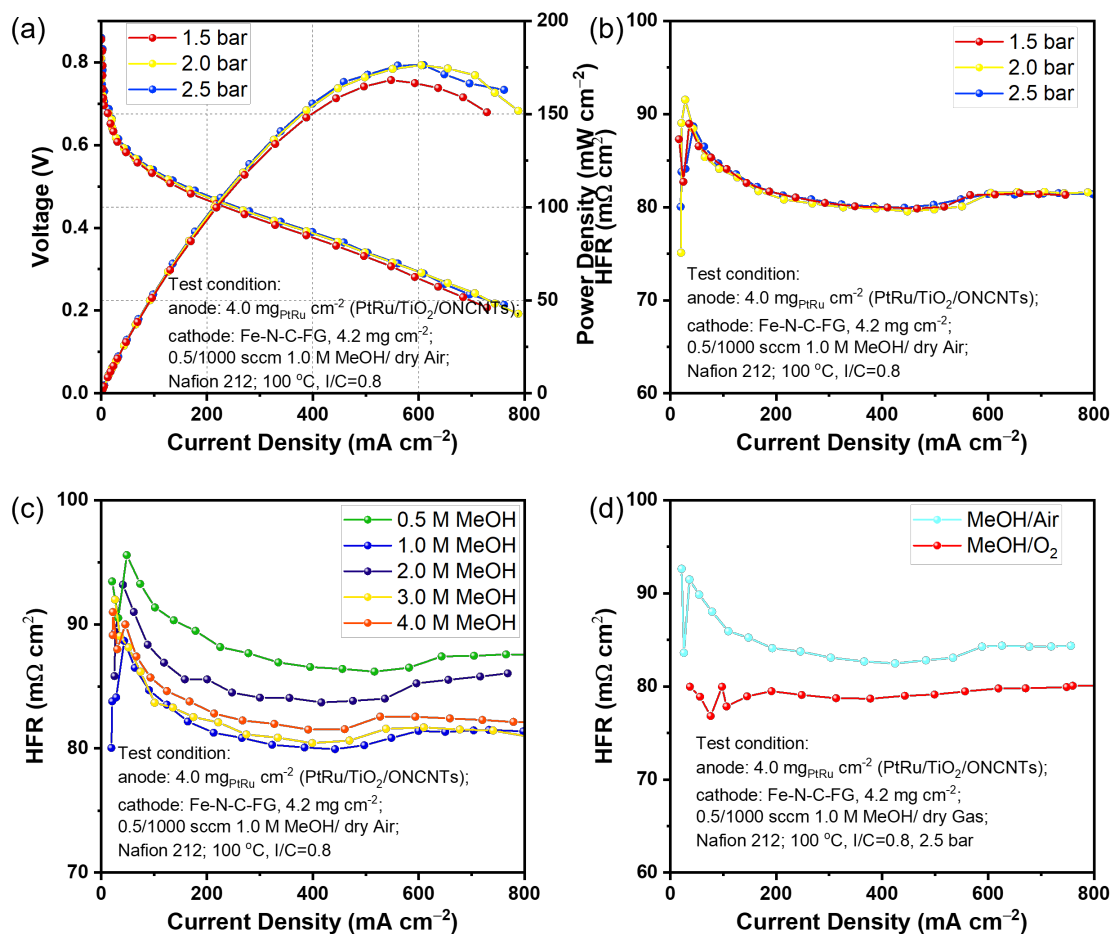


Figure B16: (a) Comparison of DMFC polarization curves of MEA with PtRu/TiO₂/ONCNT-400 anode and Fe-N-C-FG cathode at different cathode backpressures. (b) Comparison of high frequency resistance (HFR) of MEA at different back pressures. (c) Comparison of HFR of MEA at different methanol concentrations. (d) Comparison of HFT at different cathode feed. The anode and cathode catalyst loadings were $4.0 \text{ mg}_{\text{PtRu}}/\text{cm}^2$ and $4.2 \text{ mg}/\text{cm}^2$, respectively. Test conditions: cell temperature at 100.0 °C, at 0.5 mL/min methanol and 0.5 L/min air or oxygen flow rate. Nafion 212 membrane was used and ionomer/carbon ratio of 0.8 was maintained for anode and cathode in all the fuel cell tests. Credits: DMFC tests were done by Dr. Yachao Zeng at Dr. Gang Wu's lab from SUNY, Buffalo.

Appendix C - Supplementary Information for Chapter 4

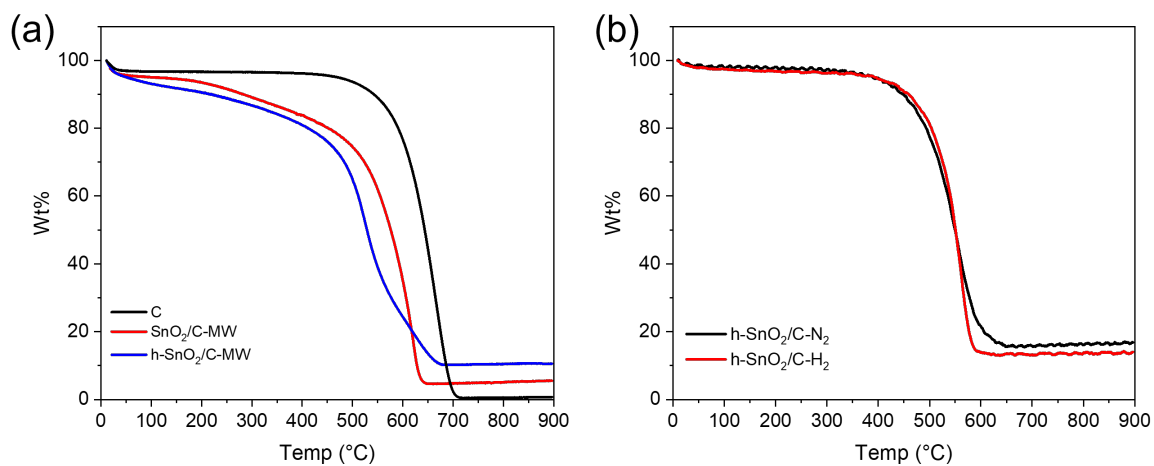


Figure C1: TGA curves of (a) control C, SnO₂/C-MW and h-SnO₂/C-MW; (b) h-SnO₂/C-H₂ and h-SnO₂/C-N₂ collected in air atmosphere from room temperature to 900 °C.

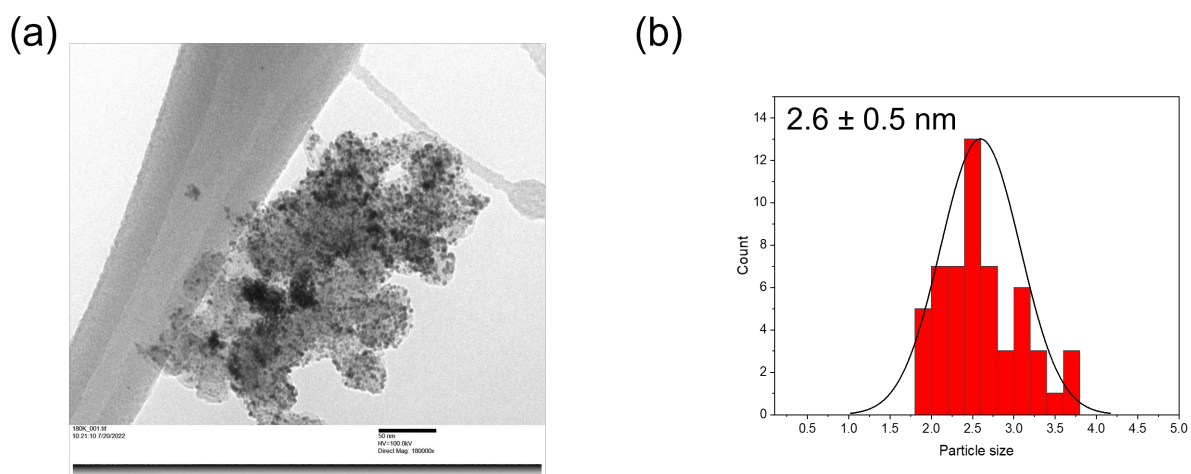


Figure C2: (a) TEM of PtRu/SnO₂/C-MW and (b) its corresponding particle size distribution.

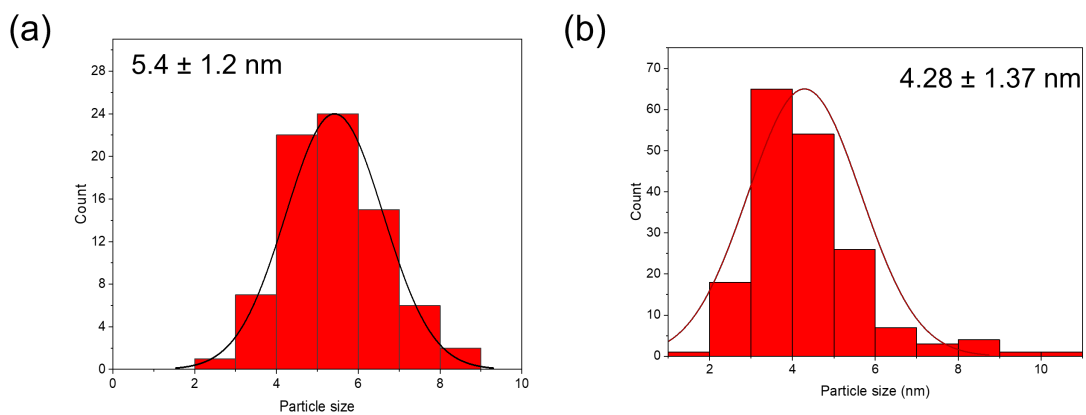


Figure C3: Particle size distribution of (a) PtRu/SnO₂/C-H₂ and (b) PtRu/h-SnO₂/C-H₂.

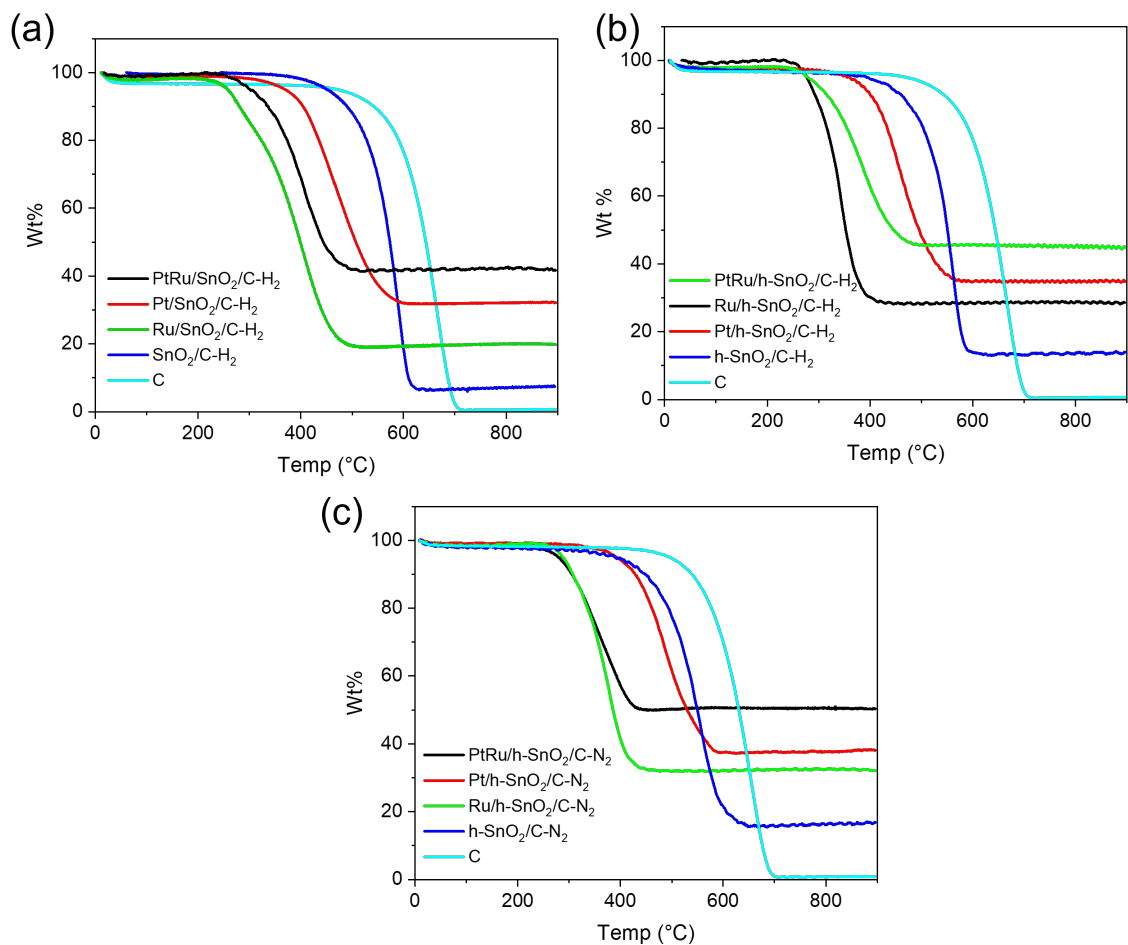


Figure C4: TGA curves of (a) PtRu/SnO₂/C-H₂ and its corresponding control samples; (b) PtRu/h-SnO₂/C-H₂ and its corresponding control samples; (c) PtRu/h-SnO₂/C-N₂ and its corresponding control samples collected in air atmosphere from room temperature to 900 °C.

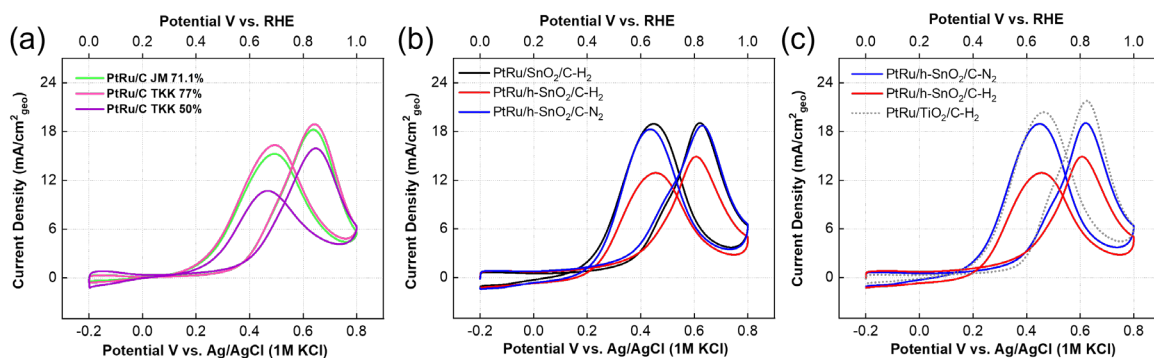


Figure C5. Comparison of 100th MOR CV curve of (a) PtRu/C TKK 77%, PtRu/C TKK 50% and PtRu/C JM 71%, (b) PtRu/SnO₂/C-H₂, PtRu/h-SnO₂/C-H₂ and PtRu/h-SnO₂/C-N₂, (c) PtRu/h-SnO₂/C-H₂, PtRu/h-SnO₂/C-N₂ and PtRu/TiO₂/C-H₂ collected in Ar-purged 0.50 M H₂SO₄ solution containing 0.75 M methanol at a scan rate of 50 mV/s. All the catalysts were tested at 54 $\mu\text{g}/\text{cm}^2$ at I/carbon ratio of 0.4.

Appendix D - Supplementary Information for Chapter 5

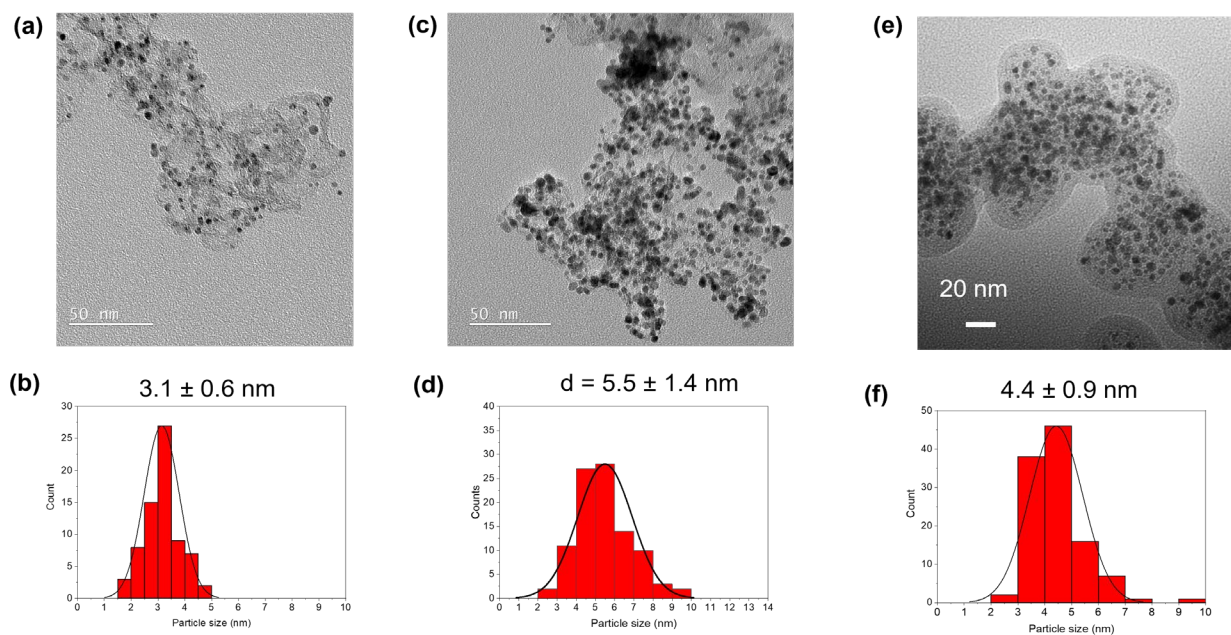


Figure D1: TEM image and corresponding particle size distribution of (a) – (b) PtRu/TiO₂/C-400, (c) – (d) PtRu/C-400 and (e)-(f) commercial PtRu/C.

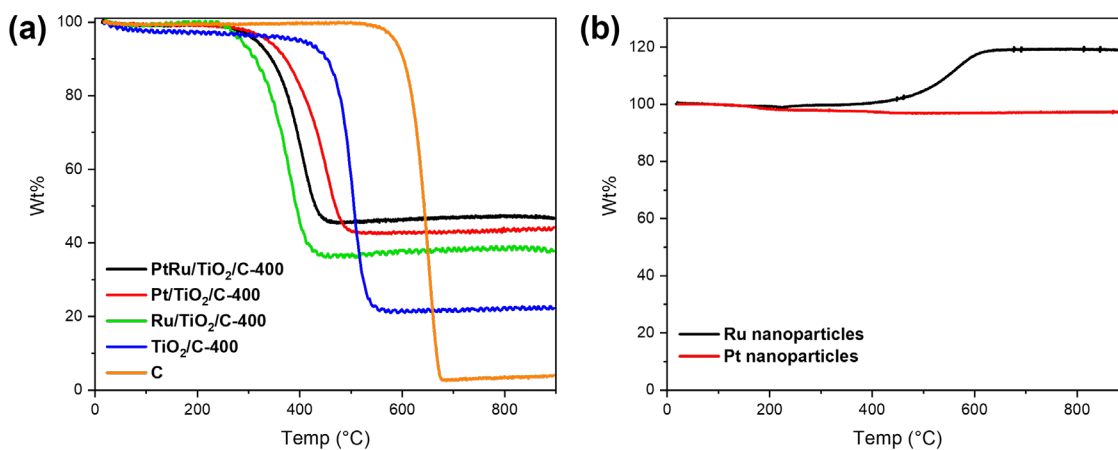


Figure D2: TGA curves comparing (a) PtRu/TiO₂/C, Pt/TiO₂/C, Ru/TiO₂/C, TiO₂/C and C & (b) Pt and Ru nanoparticles in air atmosphere from room temperature to 900 °C.

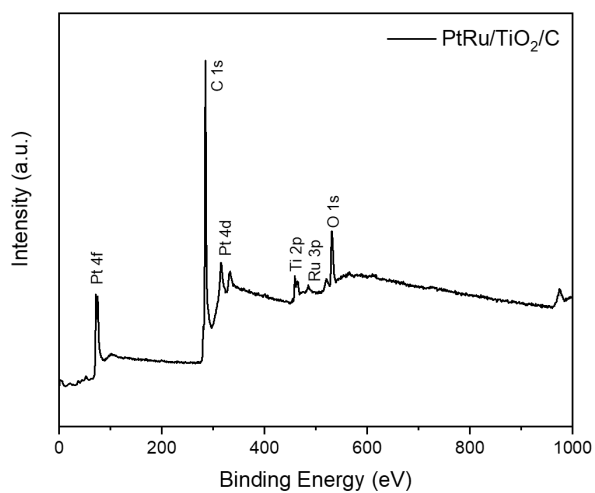


Figure D3: (a) XPS survey spectra of PtRu/TiO₂/C-400.

Table D1 Binding energies and relative deconvoluted peak area % of individual chemical component from Pt 4f, Ru 3p and Ti 2p XPS spectra for various catalysts.

		PtRu/TiO ₂ /C-400		Commercial PtRu/C	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Pt	metallic	71.59	53.4 %	71.82	50.6 %
		74.88		75.26	
	(II)	72.42	25.3 %	72.70	23.2 %
		76.20		76.86	
	(IV)	73.86	21.3 %	74.22	26.2 %
		78.35		76.94	
		PtRu/TiO ₂ /C-400		Commercial PtRu/C	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ru	metallic	461.06	68.2 %	462.43	64.0 %
		484.01		484.83	
	(IV)	465.38	31.8 %	465.97	18.3 %
		487.32		488.41	
	(IV) hydrate	-	-	469.27	17.7 %
		-		494.70	
		PtRu/TiO ₂ /C-400		TiO ₂ /C-400	
Element	Species	BE (eV)	% of elemental state	BE (eV)	% of elemental state
Ti	(III)	457.78	20.6 %	457.52	11.4 %
		462.15		462.09	
	(IV)	458.85	79.4 %	458.43	88.6 %
		464.47		464.19	

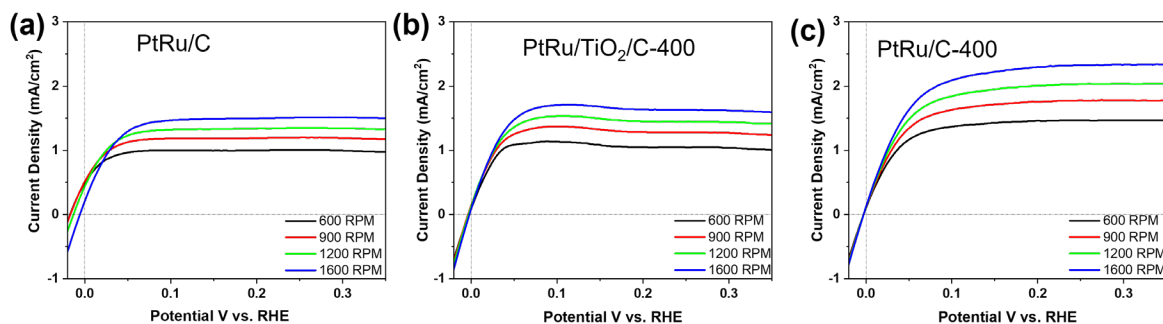


Figure D4: HOR RDE LSV curves of (a) commercial PtRu/C, (b) PtRu/TiO₂/C and PtRu/C-400 at different rotation speeds collected in H_2 -saturated 0.1 M KOH with 1600 rpm at a scan rate of 5 mV s^{-1} . Credits: These tests are done by Dr. Ramesh at Dr. Dario's lab from Israel Institute of Technology, Israel.

Appendix E - Supplementary Information for Chapter 6

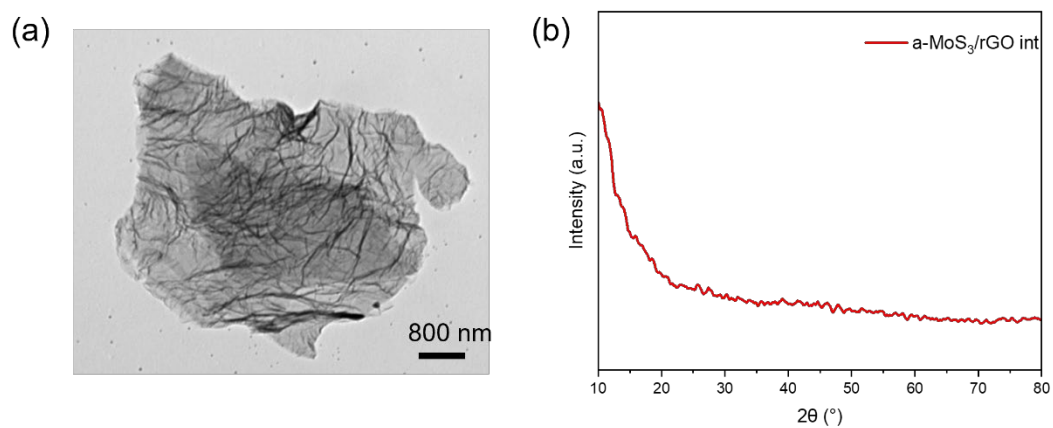


Figure E1: (a) TEM image of graphene oxide. (b) XRD for a-MoS₃/rGO int.

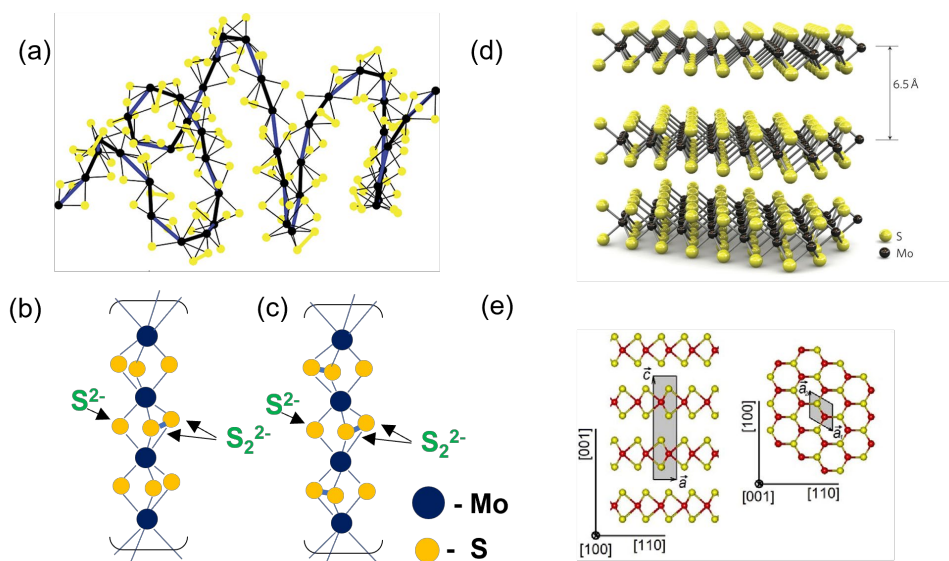


Figure E2: (a) 1D MoS₃ structure. Reprinted (adapted) with permission from J. Am. Chem. Soc. 2004, 126, 3, 959–965. Copyright 2004 American Chemical Society. (b) Schematic drawing of 1D MoS₃ chain structure with S₂²⁻ bond in alternate S₃ links, resulting in the formula Mo^V(S²⁻)₂(S₂²⁻)_{0.5}. (c) Schematic drawing of 1D MoS₃ chain structure with S₂²⁻ in every link with the formula Mo^{IV}(S²⁻)(S₂²⁻). (d) 2D 2H MoS₂ structure, Adapted with permission from Radisavljevic, B., Radenovic, A., Brivio, J. et al. Single-layer MoS₂ transistors. Nature Nanotech 6, 147–150 (2011)., Copyright 2011 Nature Publishing Group. (e) Crystal structure of the bulk 2H-MoS₂ (space group P63/mmc) from the side and top views (along [100] and [001] directions).¹

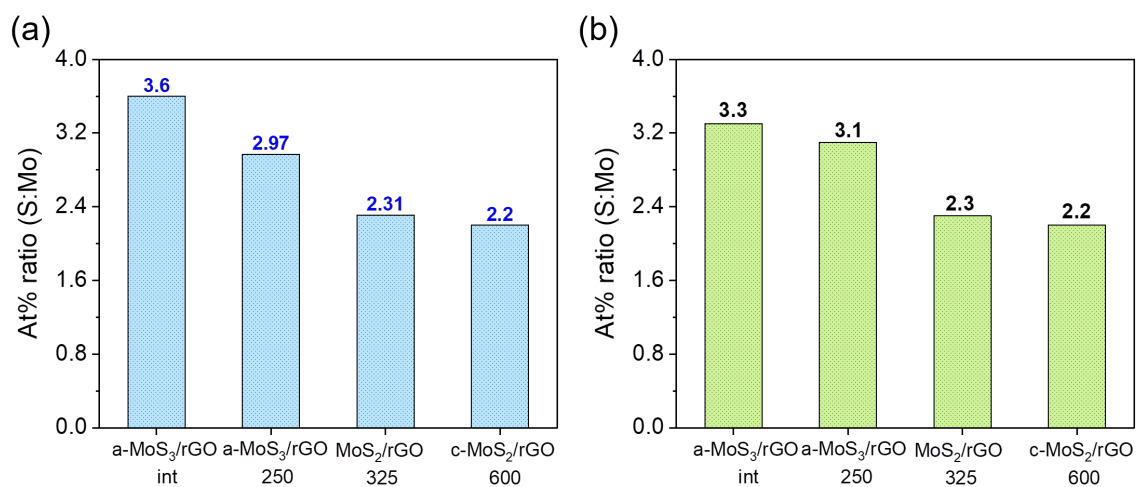


Figure E3: Bar graph comparison of ratio of S to Mo determined from (a) XPS analysis and (b) elemental CHNS analysis.

Table E1: Binding energy positions and relative at% of each Mo and S species of MoS_x/rGO hybrids.

		a-MoS ₃ /rGO int		a-MoS ₂ /rGO-250		MoS ₂ /rGO-325		c-MoS ₂ /rGO-600	
		B.E. (eV)	Relative at%	B.E. (eV)	Relative at%	B.E. (eV)	Relative at%	B.E. (eV)	Relative at%
Mo ⁴⁺	3d _{5/2}	229.16	33.3 %	228.97	55.3 %	229.13	61.0 %	229.27	79.6 %
	3d _{3/2}	232.26		232.07		232.23		232.37	
Mo ⁵⁺	3d _{5/2}	230.41	35.1 %	229.88	36.5 %	230.25	16.0 %	-	0 %
	3d _{3/2}	233.51		232.98		233.35		-	
Mo ⁶⁺	3d _{5/2}	232.49	31.6 %	232.07	8.2 %	232.50	23.0 %	232.54	20.4 %
	3d _{3/2}	235.59		235.17		235.60		235.64	
S ²⁻	2p _{3/2}	162.65	52.4 %	161.60	55.2 %	161.94	72.2 %	162.08	100 %
	2p _{1/2}	163.96		162.56		163.11		163.32	
S ₂ ²⁻	2p _{3/2}	165.42	47.6 %	163.23	44.8 %	162.90	27.8 %	-	0 %
	2p _{1/2}	166.69		164.27		163.72		-	
Mo:S At%	1 : 3.6			1 : 2.97		1 : 2.31		1 : 2.0	

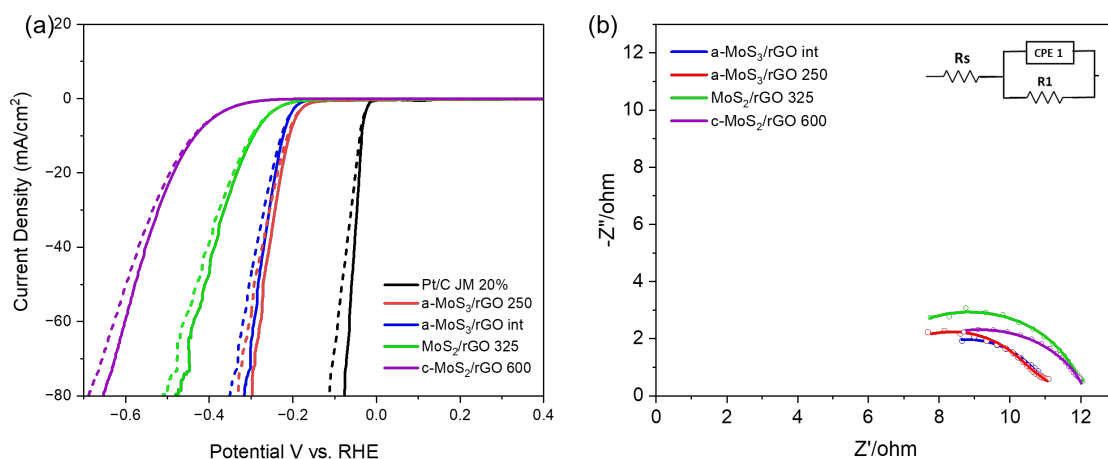


Figure E4: (a) Comparison of HER polarization curve before and after iR compensation of a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600. Dotted lines represent polarization curve before iR compensation. 100% iR compensation was done for all polarization curves. (b) EIS spectra of all the catalysts done at OCV. The EIS circuit fitting was done to determine the R_s value to perform iR compensation. Details can be found in experimental section.

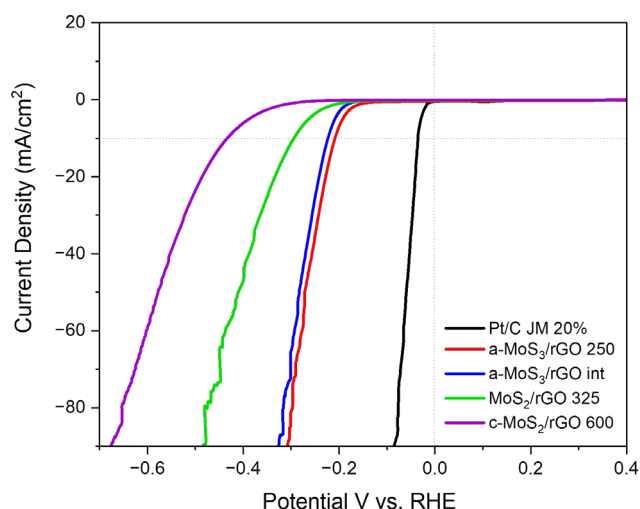


Figure E5: Comparison of full range HER polarization curves of a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600 till 90 mA/cm² current density.

Turnover Frequency Calculations:

It was calculated using the equation^{192, 193} given below,

$$TOF (s^{-1}) = \frac{j \times N_A}{n \times F \times \Gamma}$$

where j is the current density (mA/cm^2). In our work, the current density at $10 \text{ mA}/\text{cm}^2$ was considered to calculate the TOF for the best performing HER catalyst, a-MoS₃/rGO 250. Then the overpotential of 208 mV, required to reach $10 \text{ mA}/\text{cm}^2$ for a-MoS₃/rGO 250, is chosen as a metric to find the corresponding current density of other MoS_x/rGO hybrids to calculate its TOF. Hence, the TOF of all the electrocatalysts in this study are calculated from the HER current density at 208 mV HER overpotential.

N_A is the Avogadro constant, F is the Faraday constant, n is the number of electrons transferred to generate one molecule of H₂, Γ is the surface concentration of electrocatalytic active sites. The surface concentration of MoS₂ active sites is calculated by the equation below,

$$\Gamma = N_{\text{MoS}_2} \times \text{ECSA}$$

where N_{MoS_2} is the number of MoS₂ units/ cm^2 which is equal to $1.164 \times 10^{15} \text{ MoS}_2/\text{cm}^2$ and ECSA is the electrocatalytic active surface area.^{192, 193} The ECSA of MoS_x based materials is determined by dividing the non-faradaic capacitance (C_{dl}) associated with the double layer charging of MoS_x/rGO and the specific capacitance ($60 \mu\text{F}/\text{cm}^2$) of flat monolayer MoS₂ standard. The C_{dl} is determined using CV, which is done in non-faradaic potential region at different scan rates. The difference in anodic and cathodic current density at the center of the CV curves (Δj) is plotted vs. different scan rates. A linear curve is observed. The magnitude of C_{dl} was calculated from the slope of resulting linear curve.

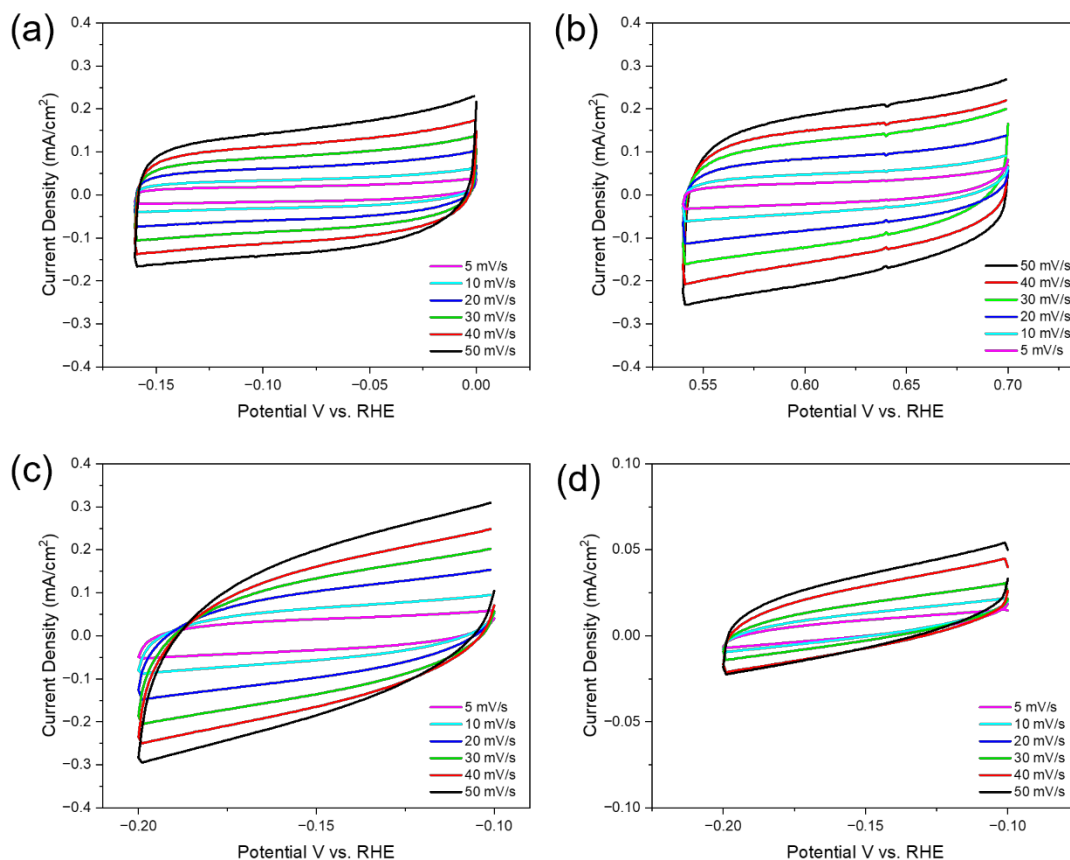


Figure E6: Cyclic voltammograms of (a) a-MoS₃/rGO int, (b) a-MoS₃/rGO 250, (c) MoS₂/rGO 325 and (d) c-MoS₂/rGO 600 collected at different scan rates where no faradic processes were observed to measure the capacitive current from double layer charging. The scan rates used are 5, 10, 20, 30, 40 and 50 mV/s.

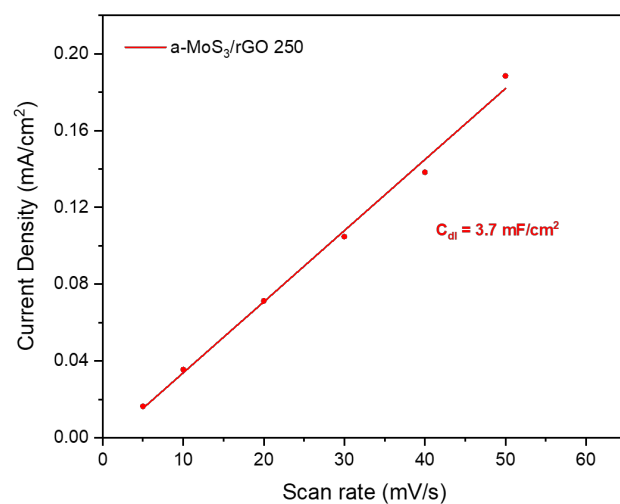


Figure E7: Linear fitting of the capacitive currents of a-MoS₃/rGO 250 vs scan rates. Calculated double layer capacitance is 3.7 mF/cm².

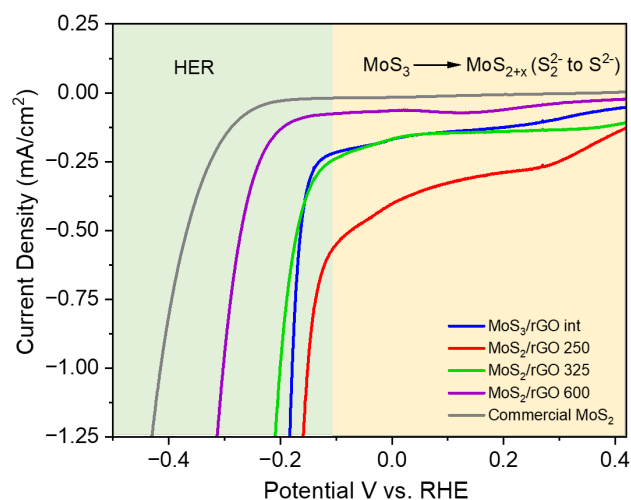


Figure E8. Enlarged region of polarization curve (a) from 0.5 to -1.25 mA/cm² to highlight the reduction of S₂²⁻ to S²⁻ sites before HER region on MoS_x/rGO samples.

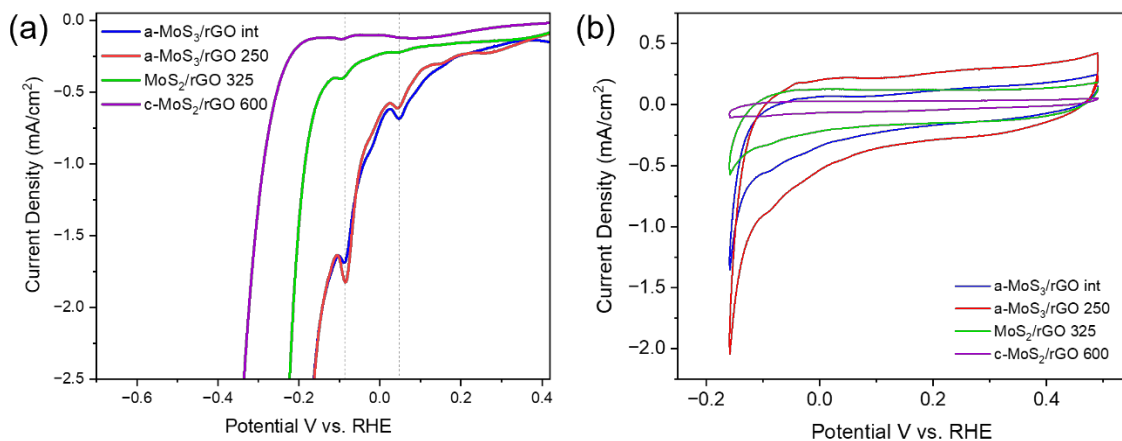


Figure E9: (a) First HER LSV curve of fresh catalyst surface of a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600. (b) CV after the first LSV curve of a-MoS₃/rGO int, a-MoS₃/rGO 250, MoS₂/rGO 325 and c-MoS₂/rGO 600.

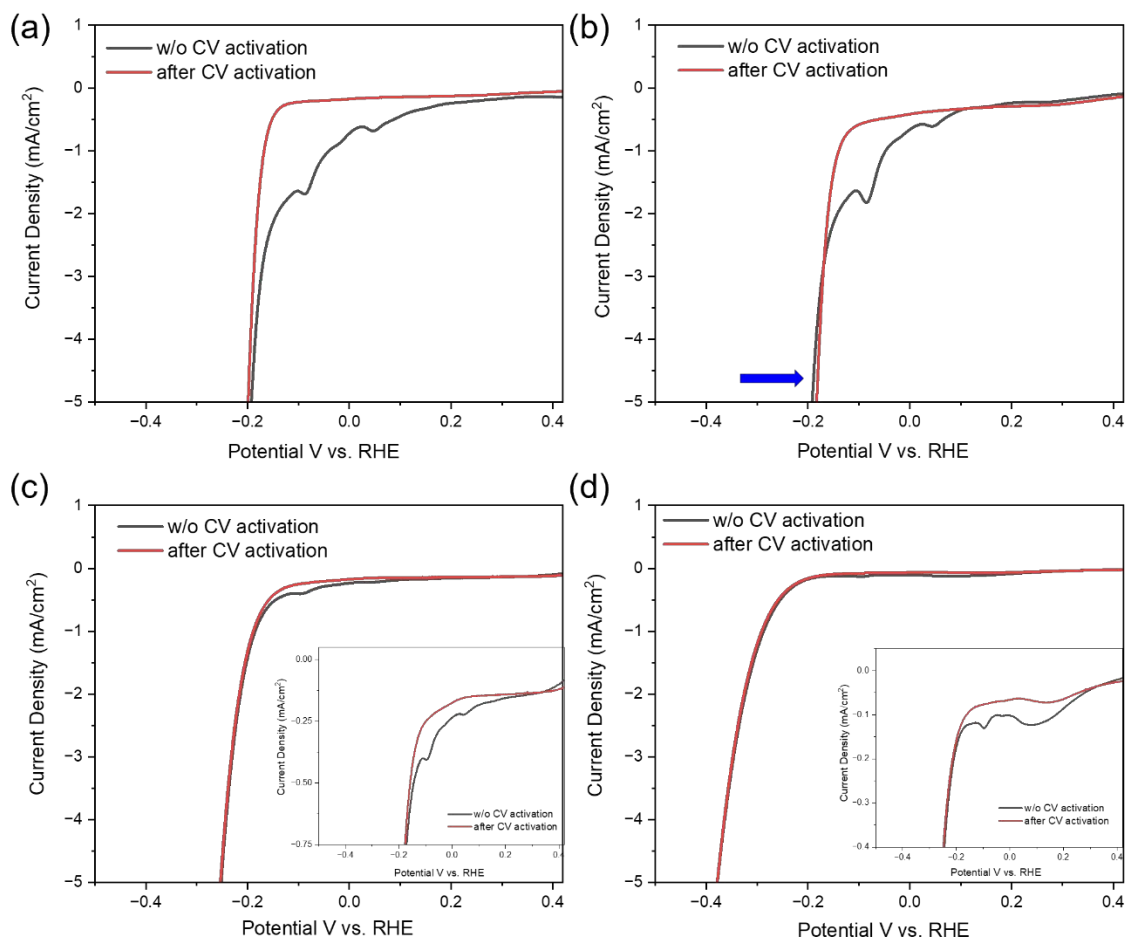


Figure E10: Comparison of first HER polarization curve of fresh catalyst surface and polarization curve after CV activation of (a) $\text{a-MoS}_3/\text{rGO int}$, (b) $\text{a-MoS}_3/\text{rGO 250}$, (c) $\text{MoS}_2/\text{rGO 325}$ and (d) $\text{c-MoS}_2/\text{rGO 600}$.

Appendix F - Publications and Presentations

Publications: (* Equally contributing authorship)

1. **Sekar, A.***; Douglin, J.C.*; Singh, R.K.; Li, J.; Dekel, D.R.; Hydrogenated TiO₂ Modified Carbon Supports for PtRu Bimetallic Alloys as a HOR Electrocatalyst for High-Performance AEMFC. **(Manuscript in Preparation)**
2. Rajendran, S.; **Sekar, A.**; and Li, J., Mechanistic Understanding of Lithium Plating/Stripping Processes in a 3D Conductive Host Based on Vertically Aligned Carbon Nanofibers for Li Metal Anodes. **(Submitted)**.
3. Mayyahi, A.A.; **Sekar, A.**; Rajendran, S.; Sigdel, S.; Lu, L.; Wang, J.; Wang, G.; Li, J.; Amama, P.; Hierarchical TiO₂-g-C₃N₄ Heterojunction Photocatalyst with Purification Effect for NO_x Oxidation Under Cyan Light. **(Submitted)**.
4. Syed, S.H.Z.; Rajendran, S.; **Sekar, A.**; Elangovan, A.; Li, J.; Li, X.; Binder-free Li-O₂ battery cathodes using Ni- and PtRu-coated vertically aligned carbon nanofibers as electrocatalysts for enhanced stability. *Nano Research Energy*, 2023.
5. Kumar, K.; Rajendran, S.; **Sekar, A.**; Chen, Y.; Li, J., Synthesis of V₂O₅ Nanoribbon–Reduced Graphene Oxide Hybrids as Stable Aqueous Zinc-Ion Battery Cathodes via Divalent Transition Metal Cation-Mediated Coprecipitation. *ACS Sustainable Chem. Eng.* 2023, 11, 6, 2670–2679.
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Patents:

1. Li, Jun and **Sekar, Archana**. 2022. Microwave-assisted Synthesis of Electrocatalysts on Modified Carbon Catalyst Supports for Methanol Oxidation in Direct Methanol Fuel Cells. U.S. Provisional Patent Application No.: 63/377,916, filed September 30, 2022. U.S. Provisional Patent.

Conferences/ Summit Presentations:

1. Poster: **Sekar, A.**; Metzger, N.; Zeng, Y.; Wu, G.; Li, X.; and Li, J., Enhancing the Activity and Durability of PtRu Electrocatalysts for Methanol Oxidation in DMFC by Metal Oxide Modified Carbon Supports. *Gordon Research Conference – Fuel cells* 2022, Bryant University, RI, USA.
2. Poster: **Sekar, A.**; Metzger, N.; Li, X.; and Li, J., Development of Durable Anode Electrocatalysts for Direct Methanol Fuel Cells. *Capitol Graduate Research Summit*, 2022, Topeka Capitol Building, KS, USA
3. Oral: **Sekar, A.**; Metzger, N.; Li, X.; and Li, J., Enhancing the Methanol Oxidation Reaction of Precious Metal Catalysts on Carbon Nanotube Support with a Thin Hydrogenated TiO₂ Shell. *Electrochemical Society 240th meeting* 2021, Virtual: Live, USA.
4. Oral: **Sekar, A.**; Metzger, N.; Li, X.; and Li, J., PtRu Nanoparticles on Nitrogen-Doped Carbon Nanotubes as Efficient Anode for High Performance Direct Methanol Fuel Cells. *Electrochemical Society 238th meeting* 2020, Virtual, USA.

Awards and Scholarships:

1. 2023 Phi Lambda Upsilon (PLU) Award winner, Phi Lambda Upsilon, Dept. of Chemistry, Kstate (2023)
2. Meloy Award for Outstanding Research in Analytical Chemistry, Dept. of Chemistry, KState (2022)
3. Travel Award from KSU graduate school (2022)
4. Travel Scholarship from KSU college of Arts and Sciences (2022)
5. Travel Award from Phi Lambda Upsilon (2022)
6. Research and the State Poster Competition Winner, KSU graduate school (2021)
7. Travel Award from Phi Lambda Upsilon (2021)