

Tailoring the secondary coordination sphere: Impact of pendent groups on hydrogen evolution in  
palladium and nickel based calixpyrrole electrocatalysts

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## Abstract

The development of efficient and sustainable electrocatalysts for the hydrogen evolution reaction (HER) is essential for advancing clean energy technologies. While platinum-based systems exhibit near-zero overpotential and exceptional catalytic activity, their high cost and limited availability restrict large-scale applications. This work focuses on the rational design of calixpyrrole-based molecular catalysts, emphasizing the role of secondary coordination-sphere modifications in enhancing catalytic performance via proton relay and hydrogen-bonding interactions.

Chapter 2 investigates catalyst microenvironments by incorporating proton-shuttling and hydrogen-bond donor functionalities into palladium calixpyrrole complexes. Three complexes bearing pendant amine (2a), amide (2b), and carbamate (2c) groups were evaluated for HER using anilinium tetrafluoroborate as a mild proton source. All systems exhibit homogeneous catalytic behavior. Kinetic studies reveal a second-order dependence on acid concentration and significant H/D kinetic isotope effects, indicating hydrogen decoordination as the rate-limiting step. These catalysts demonstrate exceptional activity, with observed rate constants ( $k_{\text{obs}}$ ) and turnover frequencies of  $4.65 \times 10^6 \text{ s}^{-1}$ ,  $4.19 \times 10^6 \text{ s}^{-1}$ , and  $3.09 \times 10^6 \text{ s}^{-1}$  for complexes 2a–2c, respectively. These findings establish palladium calixpyrrole systems as benchmarks for ultrafast HER catalysis, rivaling the performance of highly efficient enzymatic systems.

Chapter 3 extends this strategy to nickel-based calixpyrrole complexes as cost-effective alternatives. Incorporation of pendant functional groups significantly enhances catalytic performance, lowering the overpotential from **0.96 V** in the unsubstituted system to **0.81 V** in functionalized complexes. These modifications improve reaction kinetics by facilitating proton-coupled electron transfer (PCET), highlighting the critical role of secondary coordination sphere engineering in optimizing catalytic efficiency.



Chapter 4 examines a nickel calixpyrrole complex with a pendant amine in a surface-associated, heterogeneous configuration. The catalyst was deposited on a glassy carbon electrode and evaluated under varying proton-donor strengths using triethylammonium tetrafluoroborate. Electrochemical studies show an increase in catalytic current with acid concentration, reaching an acid-independent regime above **0.075 M**, while scan rate analysis confirms a surface-confined process. Controlled-potential electrolysis demonstrates efficient hydrogen production with a Faradaic efficiency of **95.3%**, an overpotential of  **$0.896 \pm 0.014$  V**, and a turnover frequency of approximately  **$1775\text{ s}^{-1}$** . The pendant amine is proposed to function as a proton relay, facilitating PCET and efficient H–H bond formation. These results highlight the impact of proton-donor strength and interfacial confinement on catalytic behavior.

Overall, this work demonstrates that precise tuning of the secondary coordination sphere significantly enhances catalytic activity, lowers overpotential, and improves reaction kinetics in both homogeneous and heterogeneous HER systems. These findings provide important design principles for developing efficient, earth-abundant molecular electrocatalysts for sustainable hydrogen production.

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## **Dedication**

I dedicate this thesis to my beloved parents and my brother

Your unconditional love, endless sacrifices, and unwavering belief in me have been the foundation of all my achievements. You have been my constant source of strength, guiding me through every challenge with patience and encouragement. This accomplishment is as much yours as it is mine.

With deepest love and gratitude,

This work is for you.



## Chapter 1 - Introduction

Fossil fuels (such as coal, oil, and natural gas) continue to serve as the fundamental drivers of global energy systems. This is most attributed to the fact that they are easy to handle and transport, and relatively inexpensive. However, the consumption of fossil fuels creates greenhouse gases, which are a major contributor to global warming and related environmental issues. Global warming leads to rising temperatures, melting polar ice, rising sea levels, drought, extreme weather events (hurricanes, floods, wildfires, etc), loss of biodiversity, ocean warming and acidification, etc.<sup>1</sup> The consumption of fossil fuels also contributes to air pollution by emitting toxic gases (sulfur dioxide and nitrogen oxides among them) that cause acid rain, and it is harmful to ecosystem systems. Furthermore, the ongoing extraction worldwide is destroying natural habitats. Overall, these environmental impacts disrupt ecosystems, decrease biodiversity, and cause great destructive harm to the planet.<sup>2,3</sup>

Fossil fuels are a non-renewable energy source that were formed from the fossils of plants and animals over millions of years. A process that is not easily duplicated. Based on global energy data, fossil fuel resources include approximately 1.7 trillion barrels of oil, 7 trillion cubic feet of natural gas, and almost 1 trillion tons of coal. Depending on the usage, these sources could stay roughly 50 years for oil, 60 years for natural gas, and 130 years for coal.<sup>4-5</sup> Together, the limited supply of fossil fuels and their negative environmental impact pose a clear threat to the world's energy needs.

Towards this, cleaner, renewable energy sources are necessary to mitigate the growing effects of greenhouse gas emissions. Finding alternative energy sources will not only improve efficiency but also create paths to use existing carbon-based technologies while enhancing carbon-zero technologies.<sup>6-7</sup> This relates to challenge, specifically in energy systems which are environmentally green, economically viable, and reliable. Renewable energy sources such as solar, wind, geothermal, hydropower, and biomass are green and widely available.<sup>8-9</sup> These sources balance energy generation with minimal greenhouse gas emissions. However, their consistency can be affected by environmental factors such as wind patterns, sunlight availability, and land-use competition. Right now, these sources account for a relatively small share of global energy consumption, alongside a significant share from fossil fuels, while hydropower accounts for a notable fraction of power generation.<sup>10-14</sup> Although these energy sources are sustainable and green,

their inability to provide continuous, consistent power generation highlights the need to develop alternative green, renewable energy sources that can provide continuous, consistent energy.<sup>15</sup>

Hydrogen has achieved the place of a promising alternative energy to remove the inconsistency and continuity challenges related to solar, wind, etc., energy sources, as it is light and mostly available on the planet, burns without producing greenhouse gases, and water is the only by-product of its combustion to produce electricity or power.<sup>16,34</sup> It can be produced, stored, and used on demand, which ensures a continuous and consistent energy supply.<sup>17-21</sup> Normally, it can be produced by steam methane reforming, coal gasification, and water splitting. However, splitting or electrolysis using renewable energy sources (wind, solar, etc.) is considered “green hydrogen,” ensuring sustainability and carbon-zero emissions. In water splitting, water is split by an electrical force, producing hydrogen and oxygen. As electricity is generated from renewable sources, the whole system operates as a near-zero-emission greenhouse gas system.<sup>22-34</sup>

### **1.1. Hydrogen, as an alternative source of power generation**

Using hydrogen has shown a path to a sustainable alternative to fossil fuels. From Jules Verne’s early ideas about water as a future fuel source and technological developments, water splitting emerged as a convenient method for producing hydrogen.<sup>35</sup> In the modern energy world, hydrogen is considered a green and renewable power generation, but only when it is produced through solar and/or wind rather than fossil fuel-based approaches<sup>34</sup>. Hydrogen is chosen as an attractive energy carrier for several reasons. First, due to its environmentally friendly characteristics, hydrogen combustion emits no greenhouse gases. Another factor is recyclability: after combustion, it can be recycled. Hydrogen, being a light and abundant element in nature, has a gravimetric energy content (120 MJ/kg), almost 2 or 3 times that of traditional fuels.<sup>36</sup> Additionally, hydrogen shows easily portable behavior as it can be transferred as power lines or pipelines over long distances.<sup>37</sup> In addition, hydrogen production from abundant, clean water makes it lucrative for industries as a chemical fuel.<sup>38,39</sup>

Hydrogen production is expected to see high demand in the coming decades, especially as an essential starting material for ammonia synthesis, as a fuel for transportation and electricity

generation in industry, and as an important chemical in refining, among other uses. Hydrogen fuel cells help power conventional combustion engines and battery-operated electric vehicles, balancing zero carbon emissions with fast refueling and long driving range. By generating electricity through electrochemical reactions, hydrogen powers electric motors that move the vehicle forward. This emission-free hydrogen technology works to reduce air pollution and increase energy security in transportation. In a passenger vehicle, a hydrogen fuel cell improves performance and fuel capacity compared to a gasoline-powered vehicle, making it well-suited for daily and long-distance travel. Also, it paves the way for the decarbonization of heavy-duty and commercial vehicles (such as trucks and buses). As this vehicle is for long-distance travel and heavy loads, it benefits from hydrogen's high energy density and fast refueling. This fuel technology reduces maintenance and operating costs, air pollution in urban areas, and, overall, helps mitigate climate change. Electricity generation from hydrogen fuel cells supports grid stability, peak shaving, and off-grid applications, with maximum efficiency and low emissions. Additionally, this energy from hydrogen fuel cells supports distributed energy supply and backup power, reducing costs and enhancing capacity.

On an industrial scale, hydrogen is used in ammonia synthesis, petroleum refining, food processing, and steelmaking. Ammonia, a key ingredient in fertilizers and chemical products, is normally produced from natural gas (the Haber-Bosch process), which generates carbon dioxide emissions. But hydrogen helps to follow a green, sustainable way to produce ammonia, without carbon emissions. Ammonia produced by this green method supports global agriculture, enhancing food security and reducing the risk of environmental disasters.

Green hydrogen is used in refining processes such as hydrotreating and catalytic reforming to increase purity, enhance hydrocarbon and fuel quality, and improve petrochemical quality. For example, in metallurgy and steel processing, sustainable hydrogen serves as a reducing agent and a heating source to improve quality and yield while reducing energy use, advancing cleaner practices.<sup>40-42</sup>

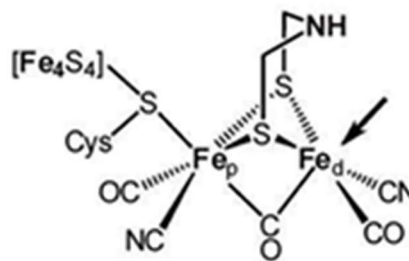
Given the importance of hydrogen, both in the areas of its utilization in food production and energy production, and its ease of production from water or a proton source via electrolysis, it has been deemed a “high priority” for investigation. From a chemical viewpoint, hydrogen generation

via water electrolysis occurs via two pathways: a hydrogen evolution reaction (HER) and an oxygen evolution reaction (OER). In HER, molecular hydrogen is formed at the cathode, where protons are reduced. Theoretically, 0 V is required for this process, but in practice, more than 0 V is needed to produce hydrogen via water splitting. This additional potential energy is called overpotential. Given that this overpotential is essential to hydrogen generation, maximizing the process's efficacy and/or yields means lowering the activation barrier and improving reaction kinetics, both of which are largely dependent on the catalytic materials.

Platinum-based catalytic materials showed excellent hydrogen production capacity at almost zero potential. However, the high cost (tens of dollars per gram-Platinum acetate \$195 per gram) and the scarcity reduce industrial-scale production and prompt the search for alternative catalysts.<sup>43-49</sup> Furthermore, research based on homogeneous and heterogeneous catalysts with high activity, selectivity, and long-term stability is also being pursued. Different methods, such as nanostructure formation, alloy formation, and ligand secondary coordination modification in organometallic compounds, are used to optimize catalytically active sites and enhance charge transfer. These strategies are designed to reduce overpotential and increase the overall efficiency of hydrogen production systems.<sup>50</sup>

## 1.2. Natural Hydrogenase Enzyme

Hydrogen production with the reduction of dioxygen from water splitting involves multiple electron-proton transfer, where charge buildup on the substrate is quite common, making the subsequent reductions less favorable.<sup>51</sup> To prevent the buildup and unfavorable reaction conditions that arise from the transfer of multiple electrons and protons to a substrate, nature gives inspiration for the catalyst design. The most well-known enzyme, Fe-Fe hydrogenase (**Figure 1.1**), enlightens the significance of proton relays.<sup>51,52</sup> [Fe-Fe] enzyme is the best example in nature for catalyzing hydrogen evolution, with a lower



**Figure 1.1.** Structures of [Fe-Fe] Hydrogenase enzyme

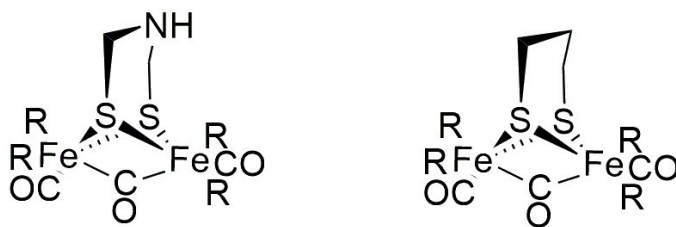
overpotential (100 mV) and a high turnover frequency (~10,000 hydrogen molecules per second per enzyme). It is found that this remarkable efficiency is related to the secondary coordination sphere (not directly attached to the metal active center). In the secondary coordination sphere, it has a bridging azadithiolate ligand,  $(-\text{SCH}_2\text{NHCH}_2\text{S}-)^{-2}$ , which helps to enhance proton transfer rates by acting as a proton shuttle (accepting or donating protons to or from the metal active center) and positioning a proton near the metal center to produce a metal hydride for hydrogen production and reducing the charge buildup. Also, these hydrogen-bonding groups, as proton shuttles, enhance stabilization of the intermediate, allowing the catalysts to efficiently participate in the hydrogen evolution reaction. Mainly, the mechanism involves simultaneous coupling of protons and electrons; it shuttles the proton to the metal center to reduce overpotential and increase the reaction rate.<sup>51-56</sup> While biologically superior and efficient, enzymes are often impractical for commercial use due to stability issues outside their native environments.<sup>52</sup> Taking inspiration from [FeFe]-hydrogenases, much work has been done for synthetic catalysts based on earth-abundant metals to mimic the structure of the hydrogenase enzyme's active site for HER.

### 1.3. Homogeneous Catalysts

Inspired by the hydrogenase enzyme, researchers often work with a homogeneous catalyst system, in which both the catalyst and the substrate are in the same phase. This catalyst offers greater scope to tune its structure and improve HER efficiency. Also, it does not depend on surface activity; it allows the reaction to occur throughout the entire solution. This system widens the range of structural and mechanistic modifications to increase control over catalyst capacity.<sup>57,58</sup> A lot of work has been done using homogeneous synthetic models to better understand reaction pathways and mechanisms. Transition metals have been given priority for these catalytically active centers because of their ability to interact with pi-electron systems through multiple oxidation states, coordinate with ligands, and participate in redox reactions. Besides these advantages, this system also suffers from disadvantages, such as low thermal stability and irreversibility after the reaction, which limit its use at an industrial level and make it economically inconvenient for large-scale applications.<sup>58-67</sup>

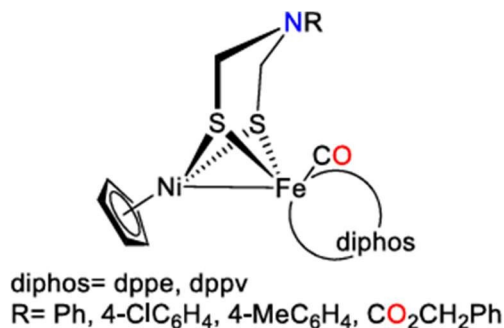
Given hydrogenase's benchmark for low overpotential and high turnover, many researchers have focused on modifying homogeneous catalysts for HER by drawing inspiration from the natural Fe-

Fe hydrogenase enzyme. Rauchfuss et al.'s work on diiron-based complexes (Figure 1.2) that mimic the active site of [Fe-Fe] hydrogenase with azadithiolate ligands to reproduce natural enzymes' structural and catalytic behavior is a notable contribution to the field of HER catalysis.<sup>65,68</sup> For this study, this group used chloroacetic acid and trifluoroacetic acid (TFA) as proton sources to produce hydrogen. To assess the importance of the proton relay of the adt ligand in hydrogenase enzymes, they analyzed another diiron-based complex with propanedithiolate (pdt) instead of azadithiolate (adt), because pdt ligands do not act as proton relays.



**Figure 1.2.** Structure of Rauchfuss et al. group diiron complexes, bearing a pendant adt ligand (left) and pdt ligand (right)

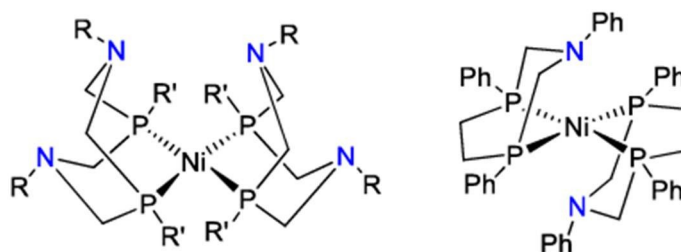
They found that adt ligand-based complexes operate at a lower overpotential of 510 mV in TFA, and pdt ligand-based complexes show a higher overpotential of 1032 mV using HBr<sub>4</sub>. Moreover, the reaction rate kinetics also differ: the adt complex shows a higher rate of 58,000 s<sup>-1</sup> than the pdt complex at 5 s<sup>-1</sup>. This comparison shows the importance of proton relays in increasing catalytic capacity.<sup>65,68</sup> Based on these examples, heterometallic [Ni-Fe] hydrogenase-based mimics have also been done. In these catalysts, tuning ligands show a crucial role in monitoring catalytic behavior. More recently, Song et al. reported a [Ni-Fe] hydrogenase-inspired complex (**Figure 1.3**), where the iron center shows pseudo-octahedral geometry and CO groups, and diphosphine ligands such as bis(dipehnylphosphino) ethane (dppe) or bis(diphenylphosphino)ethene (dppv) were ligands.<sup>69</sup>



**Figure 1.3.** Structure of Song et al. groups [Ni-Fe] hydrogenase-inspired catalysts

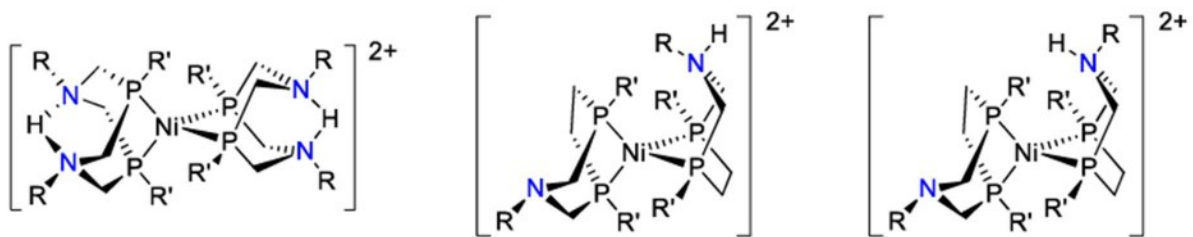
This work also had azadithiolate ligand, ensuring the presence of a pendant amine that acts as a proton shuttle within the secondary coordination sphere. The paper found that varieties of amine substituents tune the catalytic behavior. The carbobenzyloxy (Cbz)-substituted amine, which is more electron-withdrawing in nature compared to other amines, produced a higher normalized catalytic current ( $i_{cat}/i_p$ ) (where  $i_{cat}$  is catalytic current and  $i_p$  is current in the absence of acid). All complexes bearing a bridging amine had higher normalized current than the propanedithiolate (pdt)-bridged [Ni-Fe] analogs under identical conditions. In contrast, the NH-bridged complex, which has a more basic amine, showed lower overpotentials than the Cbz-substituted variant. This happened due to the more efficient protonation of the basic amine group.<sup>69</sup>

Another example of HER catalysts, Ni (II) bis(diphosphine) complexes, was established by Bullock, Dubis, and coworkers as electrocatalysts for HER.<sup>50, 66, 70-73</sup> They found that ligands containing phenyl-substituted amines showed TOF of approximately 350 s<sup>-1</sup>. However, these groups bearing benzyl functionalities showed a significant decrease in TOF to 5 s<sup>-1</sup>, underscoring the importance of pendant amines in proton transfer during catalysis. They further modified the structure from an eight-membered diphosphacyclooctane with two pendant amines to a seven-membered diphosphacycloheptane ring (**Figure 1.4**) with a single pendant amine, leading to improved catalytic behavior.



**Figure 1.4.** Structure of the diphosphacyclooctane (left) and diphosphacycloheptane (right) Ni (II) bis (diphosphine) complexes

Under these conditions, TOFs were found at  $33,000\text{ s}^{-1}$  for diphosphacyclooctane, and TOF was increased to over  $100,000\text{ s}^{-1}$  for diphosphacycloheptane in the presence of water. This may be due to water's role in facilitating the conversion of an inactive exo-protonated isomer to the catalytically active endo-protonated form (**Figure 1.5**). Though this system had high TOFs, it was also accompanied by a greater overpotential than in previously described phenyl-substituted eight-membered ring systems. The incorporation of a single pendent amine was done to prevent the formation of an inactive “pinched” isomer, where a proton is trapped between H-bond donors.

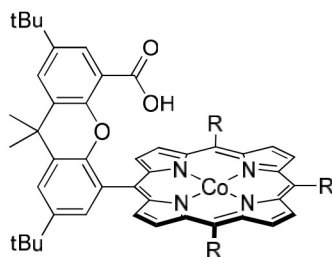


**Figure 1.5.** Structure of protonated “pinched” exo-exo isomer of Ni (0) bis(diphosphine) complex (left), exo protonated isomer of Ni(I) bis(diphosphine) with diphosphacycloheptane rings (middle), and endo protonated isomer of Ni(I) bis (diphosphine) (right)

Moreover, a high overpotential was observed for the seven-membered ring system due to its planarity, altering the complex's electronic structure. They also did comparative studies using anilinium buffer solution with previously reported phenyl-substituted complexes. They found that TOF with tertiary amines was higher than that of complexes with secondary amines. The reasons can be increased steric hindrance in tertiary amine systems, which facilitates exo-protonation paths, and the lower basicity of tertiary amines, which limits efficient protonation under mild acidic conditions.



Overall, these studies showed the significance of modifying both the pKa and steric environment of pendant amine proton relays within the secondary coordination sphere to optimize HER catalytic behavior.<sup>74</sup> Another important example of molecular electrocatalysts with pendant proton relays is the hangman porphyrins, corroles, and chlorins reported by Nocera and co-workers.<sup>58,75-85</sup> These systems had a pendant carboxylic acid (**Figure 1.6**) positioned within the secondary coordination sphere, which acts as an effective proton shuttle during processes such as the HER reaction, oxygen reduction, and carbon dioxide reduction. Cobalt complexes having this ligand structure were found to catalyze HER in the presence of benzoic acid (a relatively weak acid).



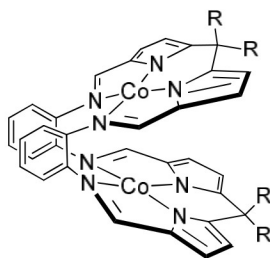
**Figure 1.6.** Structure of hangman porphyrin complexes.

Substitution of the pendant carboxylic acid group with a bromine substituent increased the overpotential by  $\sim 120\text{mV}$  for HER under the same conditions. Under weakly acidic conditions, the Co(I/0) redox couple was observed during catalysis in HER. After the addition of benzoic acid, this complex showed a shift in the redox potential of the Co(I/0) couple to the anodic region. But in the presence of carboxylic acid, a cathodic shift in the redox potential happened. This indicated proton transfer from the pendant carboxylic acid is facile and not rate-limiting in the catalytic cycle. In contrast, under stronger acid conditions, both the brominated and carboxylic acid-functionalized compounds showed catalytic waves at similar potentials, with catalytic onset closer to the Co (II/I) redox couple. These findings suggest that stronger acids can directly protonate the reduced Co(I) intermediate, thereby reducing the influence of the pendant proton relay and effectively suppressing the hangman effect.

Subsequent studies by Nocera and co-workers focused on modifying the spatial positioning of the pendant proton relay relative to the metal active center. In these systems, the xanthene backbone was replaced with a phenyl substituent at the meso position of the porphyrin, functionalized with a carboxylic acid group at either the ortho or para position. Electrochemical analysis revealed that both exhibited a reversible Co(II/I) redox couple at potentials like those

observed for the original xanthene-based complex, consistent with a catalytic mechanism involving protonation of a doubly reduced intermediate ( $\text{Co}^0$ ). However, significant differences were observed in the second redox feature corresponding to the  $\text{Co(I/0)}$  couple. The ortho-substituted compound showed an irreversible redox event, while the para-substituted system showed a reversible redox process shifted by 290mV more negative potential to the ferrocene/ferrocenium reference. These findings revealed that decreasing the distance between the pendant carboxylic acid and the metal center enhances catalysis by facilitating more effective proton transfer.<sup>58, 75-85</sup>

Schiff-base ligands are another commonly used chelating ligand in transition-metal catalysis. The main advantages of these ligands over porphyrin systems are the ease of synthesis and high yields, which allow modifications using a variety of functionalized amines and aldehydes/ketones.<sup>86,87</sup> One example of Schiff-based ligands is the binuclear macrocyclic  $\text{Co(II)}$  complex. These compounds adopt “pacman” shapes resembling cofacial diporphyrin complexes. Interestingly, these compounds were found to influence the reduction of dioxygen using reductants with potentials like those of cofacial diporphyrins. Here, the desired superoxol intermediate was observed only as a minor species during catalysis, leading to low selectivity for the four-electron reduction of oxygen to water. It was attributed to faster electron transfer, leading to a peroxo intermediate. This again underscores the need for proton shuttling to enhance the faster proton-coupled electron transfer (PCET) process.<sup>86-92</sup>



**Figure 1.7.** Structures of Pacman complexes

## 1.4. Heterogeneous catalysts

Though homogeneous catalysts are the subject of much more research, heterogeneous catalysts have advantages that make them economically feasible. Here, catalyst separation from the product is easier, and both liquid- and gas-phase substrates can be used in continuous-flow reactors. Moreover, catalyst deposition on the electrodes avoids the bimolecular decomposition pathway

associated with a homogeneous system. Electrode materials have attracted significant attention in heterogeneous electrocatalysis. This has led to increased research interest in developing novel electrode materials, such as metal alloys, chalcogenides, carbides, nitrides, borides, and phosphides.<sup>93-114</sup>

#### **1.4.1. Ni (Diphosphacyclooctane) complex on edge plane graphite (EPG)**

One of the classic examples of heterogeneous catalysis is the covalent immobilization of a [Fe-Fe] hydrogenase enzyme mimic on edge-plane graphite (EPG) via click chemistry, where the adt ligand was functionalized for anchoring. It showed a surface coverage of  $2.4 \times 10^{-10}$  mol/cm<sup>2</sup>, which is higher than that for physisorption. This catalyst's activity towards HER in 0.05 M Sulfuric acid, with an overpotential of 440 mV, TOF of 139 s<sup>-1</sup>, and Faradaic efficiency of 90.7%. The mechanism shows electrons being transferred from the electrode to the iron active center, followed by protonation to form H<sub>2</sub>. However, compared with homogeneous analogs, the catalytic rate was reduced due to restricted flexibility and slow electron/proton transfer at the electrode surface.<sup>115,</sup>

116

#### **1.4.2. Ni Diphosphacyclooctane complex on GC (Glassy carbon) Bullock system**

From a mimic of a homogenous proton relay, a Ni-based molecular electrocatalyst was developed through covalent attachment to a glassy carbon electrode. It had a TOF of 28 s<sup>-1</sup>, which is significantly lower than that of homogeneous analogs (1900 s<sup>-1</sup>), though the onset potential is in a similar range. It used an overpotential of about 700 mV in acetonitrile. In this catalysis towards HER, proton shuttling occurred via pendant amines, but due to covalent anchoring, conformational changes were restricted, and steric hindrance slowed electron transfer.<sup>116</sup>

#### **1.4.3. Ni Diphosphacyclooctane Complex on CNT (Carbon nanotube)**

The same Ni (previous example) complexes behaved as heterogeneous catalysts through immobilization on carbon nanotubes (CNTs). It showed a lower overpotential of 200 mV in 0.5 M sulfuric acid. But the reaction kinetics remained slow, with a TOF of 5.5 s<sup>-1</sup>, though the Faradaic efficiency was higher, around 94 %. This catalyst mechanism involved HER via proton-coupled

electron transfer (PCET), but steric hindrance hindered structural rearrangements, thereby decreasing reaction kinetics.<sup>117</sup>

#### **1.4.4. Co (II) Tetraphenylporphyrin (TPP) on GC**

These catalysts were immobilized on glassy carbon and exhibited solvent-dependent behavior. HER through these catalysts followed outer-sphere electron-transfer mechanisms, but in water, strong adsorption led to inner-sphere electron transfer via PCET. They found that catalysis over a wide pH range, with pH-dependent onset potentials, indicated proton involvement as the rate-determining step. This catalysis signified how electronic coupling through the electrode shifted the mechanism from molecular to surface catalysis.<sup>118</sup>

#### **1.4.5. Co(III) Diimine-Dioxime on MWCNT (Multi-walled carbon nanotubes)**

These complexes were covalently attached to multi-walled carbon nanotubes (MWCNTs). It had an onset overpotential of around 350 mV and 1 mA/cm<sup>2</sup> at 590 mV, along with TOF  $\approx 2.2$  s<sup>-1</sup> and a faradaic efficiency  $\approx 97\%$ . From this catalysis mechanism, it was found that ligand-assisted proton transfer occurred, but reaction rates were low due to reduced flexibility of the ligand backbone after covalent attachment, which is important for redox-based structural changes.<sup>119</sup>

#### **1.4.6. Pyrene-Anchored [FeFe] Mimic on CNT ( $\pi$ - $\pi$ Interaction)**

Based on [Fe-Fe] hydrogenase mimic, pyrene anchors on CNTs showed HER catalysis with faradaic efficiency around 99% at 490 mV overpotential, but with slower reaction kinetics, TOF  $\sim 1$  s<sup>-1</sup>. It went through electron transfer via  $\pi$  coupling, enhancing electronic characteristics and surface loading. But catalytic capacity is limited because of Fe-S bond degradation and slow proton delivery.<sup>120-122</sup>

#### **1.4.7. Cobaloxime Metallopolymer on MWCNT**

Another example of a heterogeneous catalyst is pyrene-functionalized cobaloxime metallopolymer immobilized on CNTs. It showed HER at onset overpotentials of 100 mV and 320 mV during electrolysis, with a TOF of 0.011 s<sup>-1</sup> and a faradaic efficiency of around 90%. The mechanism showed proton reduction at Co centers and improved stability from polymer cross-

linking and local proton-rich atmospheres, though the reaction kinetics remained slower than in homogeneous systems.<sup>123-125</sup>

#### **1.4.8. Co(II) Corrole on CNT**

Co-corrole complex, an example of a heterogeneous catalyst, was attached to CNTs via covalent bonding. It showed HER catalysis across pH 0 to 14 with overpotential  $\sim 510$  mV (pH-7). The mechanism showed that metal-centered proton reduction and catalytic behavior improved relative to homogeneous analogs ( $> 800$  mV), suggesting that thermodynamic enhancement can be achieved via immobilization.<sup>126-128</sup>

#### **1.4.9. Pyrrolide Ligands in Redox Catalysis**

Pyrrolide as an anionic donor ligand opens a new door in redox coordination catalysis, and it coordinates through deprotonated nitrogen atoms. It can act as an electron reservoir because of its high-energy pi orbitals. Normally, dipyrromethene derivatives are prone to oxidation, which leads to bond formation between the two  $\alpha$ -carbon atoms. Due to their electronic structure, these pyrrolide donors increase the reduction power of metal active centers, helping activate small molecules such as carbon dioxide and nitrogen. In calixpyrrole systems, meso-substituents play an important role. Although these do not directly show conjugation with the ligand backbone, they can have an impact on the bite angle and thereby affect metal coordination, as in Ni (II) dipyrromethane-phosphine complexes. The electron reservoir capacity of these ligands can be modified by extension of  $\pi$ -conjugation, such as coupling with pyridine rings. This type of conjugation shows a push-pull electronic effect, in which the lower-energy  $\pi^*$  orbitals of pyridine can accept electron density. However, some research found that pyridine-pyrrole conjugation imparts partial amide character to the pyridine nitrogen, making reduction more difficult than in simple pyridine systems. Some conjugations stabilize high-oxidation-state metals while simultaneously increasing the reduction capacity of lower-oxidation-state metals.<sup>129-132</sup>

### **1.5. Evaluation of catalytic behavior**

HER becomes successful after overcoming significant kinetic energy barriers. Here, catalysts lower the activation barrier for the HER reaction. The evaluation of catalysts for HER can be

determined by factors such as catalyst activity, stability, and efficiency. Overpotential exchange current density defines the activity of the catalysts. The stability of the catalysts is indicated by changes in catalytic current over time. The efficiency is denoted by the faradaic efficiency and turnover frequency, etc.,<sup>133</sup>

### **1.5.1. Overpotential & Tafel plot**

The overpotential of the catalyst is the energy gap between the theoretical and practical reduction potential of the redox couple  $H^+/H_2$  to drive HER. It depends on the catalyst's resistance, the proton source, the concentration, the solvent's pKa, and the wire and equipment resistance, which creates an ohmic drop in potential. Betterment of catalysts relies on lower overpotential.<sup>133,134</sup> Catalyst's activity is also denoted by the Tafel slope. It is based on the ratio of current density to exchange current density. Faster reaction kinetics are indicated by a low Tafel slope, which means a small overpotential is required to increase current density.<sup>133, 135</sup>

### **1.5.2. Stability**

It is an important factor in the design of HER catalysts. To find out the stability of catalysts, two methods are used: cyclic voltammetry or Linear sweep voltammetry (evaluating the current by cycling the potential through a potential range), and chronoamperometry (current is kept constant over the change of potential) or chronopotentiometry (potential is kept constant over the change of potential). If the current or potential change is nearly constant over time, the catalyst's stability can be determined from these experiments.<sup>133</sup>

### **1.5.3. Faradaic efficiency**

The efficiency of the catalysts is measured by faradaic efficiency during bulk electrolysis, which is the ratio of the moles of hydrogen quantified to the moles of hydrogen theoretically produced, expressed as a percentage. Experimental hydrogen production can be measured by the amount of hydrogen gas produced from the cell using the gas-displacement method, gas chromatography, or a hydrogen detector. This factor helps determine the catalysts' selectivity for hydrogen production. Values closer to 100% show the high efficiency of the catalysts.<sup>133</sup>

#### 1.5.4. Turnover frequency

Turnover frequency (TOF) is another parameter that helps determine the reaction kinetics of catalysts, i.e., the reaction rate per catalytic site. The number of reactants that can be converted to the desired products by the catalytic cycle of the redox-active compound in the solution per second. A homogeneous system is easier than a heterogeneous system, as it does not require specifying the number of active sites per electrode area.<sup>133</sup>

Overall, TOF is considered an effective way for comparing catalytic activity among different catalysts.

#### 1.5.5. Kinetic Isotope Effect (KIE)

The kinetic isotope effect is an important factor in determining reaction mechanisms and identifying rate-determining steps. It is the ratio of the rate of HER by hydrogen to the rate of HER by deuterium. ( $KIE = k_H/k_D$ ;  $k_H$  = rate constant based on hydrogen,  $k_D$  = rate constant based on deuterium). If the bond to hydrogen is broken or formed in the rate-determining step, it is called primary KIE in the range of 2-7. If the isotope is not related to bond breaking or forming, KIE is secondary in the range of 1-1.5.<sup>136</sup>

#### 1.5.6. Identification of excellent electrocatalysts for HER

To be an excellent catalyst for HER, it should have a combination of characteristics such as low overpotential, which means a low amount of potential will be needed to split the water into hydrogen, faster reaction kinetics, which denote high TOFs, meaning HER is happening at a high rate under operational conditions. For ensuring long-term performance, stability is important to consider. Catalyst must be stable under acidic or basic conditions in electrochemical water splitting. High current density and small Tafel slope define a catalyst's high performance. From an economic perspective, catalysts should be made from earth-abundant, inexpensive materials.<sup>133</sup> These characteristics should be kept in mind in designing excellent electrocatalysts for HER.

### 1.6. Intramolecular or Intermolecular proton transfer

Proton transfer in catalysts can occur in two ways: intra- or intermolecular. In an intramolecular system, it involves the transfer of a proton from a covalently attached pendant group to the

catalyst's active center within the same catalyst's structure. These pendant groups act as proton shuttles in the secondary coordination sphere, effectively transferring protons to metal hydrides. As the proton donor is in proximity, this reduces diffusion limitations and favors proton-coupled electron transfer (PCET) steps. So, this method lowers the activation energy barrier, increases reaction rates, and enhances catalytic efficiency. In contrast, intermolecular proton transfer involves transfer from external sources, such as acids and solvents, to the catalytic site. The secondary coordination sphere does not undergo direct protonation, but it helps organize and stabilize proton donors through hydrogen bonding. However, this system is based on molecular diffusion, orientation, and solvent; it is more dynamic and can be slower than intramolecular pathways.<sup>137-143</sup>

## 1.7. Sues group chemistry

From studies on cofacial pacman porphyrins, Love and Sessler separately developed analogous macrocyclic Schiff base calixpyrroles. The main advantage of this calixpyrrole is an easy synthetic route with high yield, enabling access to the ligand using inexpensive materials while still yielding macrocycles that adopt cofacial geometries. Moreover, Nocera and coworkers drew inspiration from cofacial porphyrin systems for their hangman porphyrin systems. They modified the system by including a proton-shuttling group in the secondary coordination sphere of the 2<sup>nd</sup> metal center.<sup>58,75-80, 88-90,91-92,144-150,151</sup> From taking inspiration from the Nocera group, the Sues group has also applied a similar method to the macrocyclic Schiff base calixpyrrole, as shown in hangman porphyrins. The approach focuses on “half “of the Love calixpyrrole macrocycles and keeps unreacted amine groups as the backbone to potentially behave as proton shuttles in the secondary coordination sphere in the place of a second metal center. The main difference of Sues group systems from other catalysts in the literature is that the calixpyrrole ligands with pendant functional groups (amine, amide, tertbutyl carbomate)<sup>151</sup>, which were structurally similar to the “hangman” porphyrin ligands from the Nocera group, but the facile synthetic route has been adapted from the Schiff-based calixpyrrole ligands. In these systems, the pendant functional groups are meant to control the secondary coordination system.



## 1.8. Thesis goals

The main goal of this thesis is to tailor the secondary coordination sphere of dipyrromethene-based Schiff base complexes with pendent hydrogen bonding groups and check the catalytic efficiency of these complexes in the hydrogen evolution reaction. This research highlights the synthesis, characterization, and detailed investigation of the electrochemical behavior of calixpyrrole ligand-based metal complexes.

Chapter 2 describes the investigating of electrochemical behavior of a Palladium calixpyrrole-inspired ligand architecture bearing pendant functional groups to modulate the secondary coordination sphere for enhanced hydrogen evolution. Three complexes with pendant amine, amide, and carbamate groups were used to investigate the roles of proton relays and hydrogen-bonding interactions in enhancing multi-electron-proton transfer processes. Based on prior studies demonstrating heterogeneous catalytic films under strong acidic conditions (para-toluene sulfonic acid), the present work investigates these systems using a milder proton source, anilinium tetrafluoroborate, to gain a better understanding of their intrinsic catalytic behavior. Electrochemical and kinetic analyses showed that under mild acidic conditions, the catalyst behaves as a homogeneous solution-phase catalyst. These systems revealed a second-order dependence on acid concentration, with larger kinetic isotope effects, consistent with the hydrogen-decoordination step. All these complexes exhibited exceptional catalytic performance, with observed rate constants and turnover frequencies on the order of  $10^6 \text{ s}^{-1}$ , approaching the diffusion-controlled limit. This study establishes palladium complexes with tailored secondary coordination spheres as benchmark systems for ultrafast hydrogen evolution catalysis.

Chapter 3 focuses on the influence of modifications to the secondary coordination sphere on the catalytic performance of nickel-based calixpyrrole compounds for hydrogen evolution. To probe the role of pendant functional groups in controlling catalytic activity and stability, a series of Ni(II) calixpyrrole complexes with amide, carbamate, and unsubstituted ligands was systematically evaluated. The use of nickel, as a more earth-abundant and cost-effective alternative to palladium, enables the economically feasible catalytic systems while preserving tunability in ligand design. Electrochemical studies with anilinium tetrafluoroborate as the proton source showed that inclusion of pendant groups enhances catalytic performance. The presence of amide and carbamate groups reduced the overpotential for hydrogen evolution from 0.98V (unsubstituted) to 0.81V (pendent group), while increasing TOF 3332891  $\text{s}^{-1}$  to 48,931  $\text{s}^{-1}$ , indicating faster reaction kinetics.

Chapter 4 builds upon these findings by investigating electrochemical behavior using the Ni(II) calixpyrrole complex with an amine pendant group, which was deposited on the glassy carbon electrode in the presence of anilinium tetrafluoroborate and electrochemical evaluation over a different pH range. In contrast to the previous chapter, this one aims to evaluate how a weaker acid, triethylammonium tetrafluoroborate, influences the capacity and interfacial activity of deposited Ni catalysts, particularly the role of proton relays in governing proton-coupled electron transfer (PCET) pathways. Additionally, this chapter seeks to determine how catalyst deposition on the electrode and local proton-transfer environments affect catalytic efficiency, stability, and hydrogen evolution kinetics under mild acidic conditions. These evaluations provide valuable insights into catalyst design, including proton availability, the secondary coordination sphere, and heterogeneous catalyst behavior.

Finally, Chapter 5 outlines future directions for advancing these ligand systems. Strategies are proposed to facilitate metal-centered reductions at more positive potentials, including the incorporation of electron-withdrawing substituents at imine positions and the introduction of charged functionalities within the ligand framework. Potential approaches include the formation of quaternary ammonium groups on pendant arms or the incorporation of crown ether units that bind mono- and divalent cations. Additionally, tuning the basicity of pendant amines by varying alkyl substituents is discussed. While such modifications may induce cathodic shifts in reduction potentials due to conjugation effects, these shifts can be mitigated by using aliphatic diamine backbones rather than aromatic systems.

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## Chapter 2. Hydrogen Evolution at the near Diffusion Limit: A

### Palladium Calixpyrrole Study

#### 2.1. Abstract

Working on catalyst microenvironments through proton shuttling and hydrogen-bond donors in the secondary coordination sphere is a promising strategy for facilitating multi-proton, multi-electron transfer processes. In this research, three palladium calixpyrrole complexes featuring pendant amine (2a), amide (2b), and carbamate (2c) groups were electrochemically analyzed for the hydrogen evolution reaction (HER) using the milder proton source anilinium tetrafluoroborate. All three systems showed a homogeneous nature. Kinetic analysis reveals a second-order dependence on acid concentration and large H/D kinetic isotope effects, revealing hydrogen decoordination as the rate-limiting step. The catalysts exhibit remarkable activity, with observed rate constants ( $k_{\text{obs}}$ ) and turnover frequencies of  $4.65 \times 10^6 \text{ s}^{-1}$ ,  $4.19 \times 10^6 \text{ s}^{-1}$ , and  $3.09 \times 10^6 \text{ s}^{-1}$  for complexes 2a-c, respectively. Accordingly, these palladium calixpyrrole systems establish a new benchmark for ultrafast HER catalysis and rival the performance of the fastest enzymatic systems.

#### 2.2. Introduction

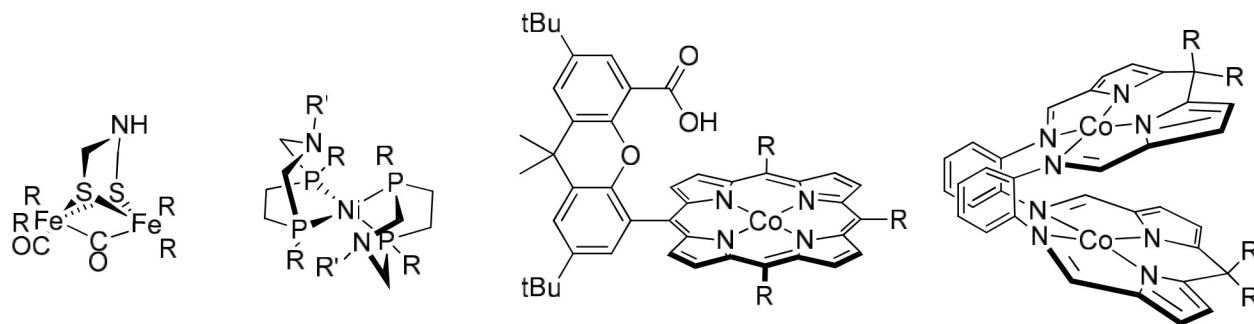
Over the next 25 years, global temperatures are going to experience a rise from 1.3 to 1.9<sup>0</sup>C, this global change will have profound effects on the environment.<sup>1</sup> The fossil fuel dependency for fuel is causing an increased amount of CO<sub>2</sub>, greenhouse gases, and environmental disasters.<sup>2</sup> This adverse impact on the environment from fossil fuel burning has shifted energy source search towards renewable energy sources such as wind, solar, tidal, and geothermal energy, etc. But these renewable sources have some limitations, such as intermittency, creating a need for a strategy for storing energy in a reliable and accessible form.<sup>3,4</sup>

Electrochemical-based fuel sources, such as hydrogen fuel cells, can offer a lucrative solution by enabling the conversion of renewable energy into fuels to reduce greenhouse gas emissions. To obtain hydrogen as a raw material for hydrogen fuel, water splitting for hydrogen generation offers a clean, sustainable approach.<sup>5</sup> To produce hydrogen from water splitting, it faces an activation

energy barrier or an overpotential. To overcome this activation barrier, hydrogen evolution reaction (HER)-based catalysts are needed. Platinum is the most efficient catalyst for hydrogen evolution, operating the reaction at minimal overpotential. But the high cost and scarcity of platinum pose major problems for large-scale industrial operations, which require the search for alternative catalytic systems.<sup>6</sup>

Another major problem comes from multiple proton and electron transfers in the HER reaction. From multiple proton and electron transfer processes, charge buildup occurs at the catalytic active center, slowing reaction kinetics. To solve this problem, one strategy is to work with the secondary coordination sphere, such as by incorporating proton shuttles or hydrogen bond donors, which activate proton-coupled electron transfer (PCET). By PCET, the high energy or charge buildup will be reduced.<sup>7</sup>

In Mother Nature, the hydrogenase enzyme provides compelling examples in the HER area, catalyzing with high efficiency using earth-abundant, cheap metals. Specifically, the [Fe-Fe] hydrogenase enzyme has azadithiolate ligands that act as proton relays, facilitating rapid PCET and high reaction kinetics at low overpotential. But these enzymes have some limitations outside their natural environment, which limit their industrial uses.<sup>8</sup>



**Figure-2.1.** General structure of the Rauchfuss di-iron complexes (left), the Bullock nickel diphosphacycloheptane complexes (middle left), the Nocera “hangman” porphyrin complexes (middle right), and the Love/Sessler macrocyclic calixpyrrole “pacman” complexes(right).

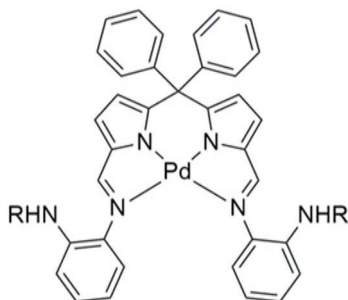
To develop an industrially applicable electrocatalyst, significant research has focused on synthetic catalysts with these functional features. Diiron-based complexes by Rauchfuss and co-workers (**Figure 2.1**) mimic the main features of hydrogenase active sites but still operate at high

overpotentials ( $> 700$  mV).<sup>9</sup> Another example where Nocera's "hangman" porphyrin shows how strategically placed proton donors can help proton transfer via hydrogen bonding, although the synthetic route suffers from complexation<sup>10,11</sup>

Based on this literature and nature inspiration, our group recently reported a nickel calixpyrrole-based electrocatalyst featuring pendant amine groups.<sup>12</sup> This system showed rapid kinetics and high turnover frequencies, outperforming many related nickel catalysts and approaching the activity of some platinum-based catalysts. Mechanistic findings revealed that PCET was rate-limiting and that protonation of the pendant amines offered an important role. But now an important question arises from this mechanistic research: does proton transfer occur intramolecularly or via intermolecular interactions, such as hydrogen bonding with an external proton source? Do both provide similar catalytic efficacy?

To find this question, we have electrochemically analyzed a series of palladium calixpyrrole complexes bearing pendant amine, amide, and tert-butyl carbamate and evaluated their efficacy as HER electrocatalysts (**Figure 2.2**). These catalysts are a combination of a "hangman" type framework and a synthetic route to Schiff-based calixpyrrole "pacman" complexes by the Love and Sessler groups.<sup>13,14</sup>

In this study, we examine the electrochemical behavior and catalytic performance of complexes **2a-c** for HER in the presence of the mild proton source anilinium tetrafluoroborate. Through kinetic and mechanistic analysis, we aim to elucidate how hydrogen-bonding interactions and proton shuttling in the secondary coordination sphere influence catalytic activity.

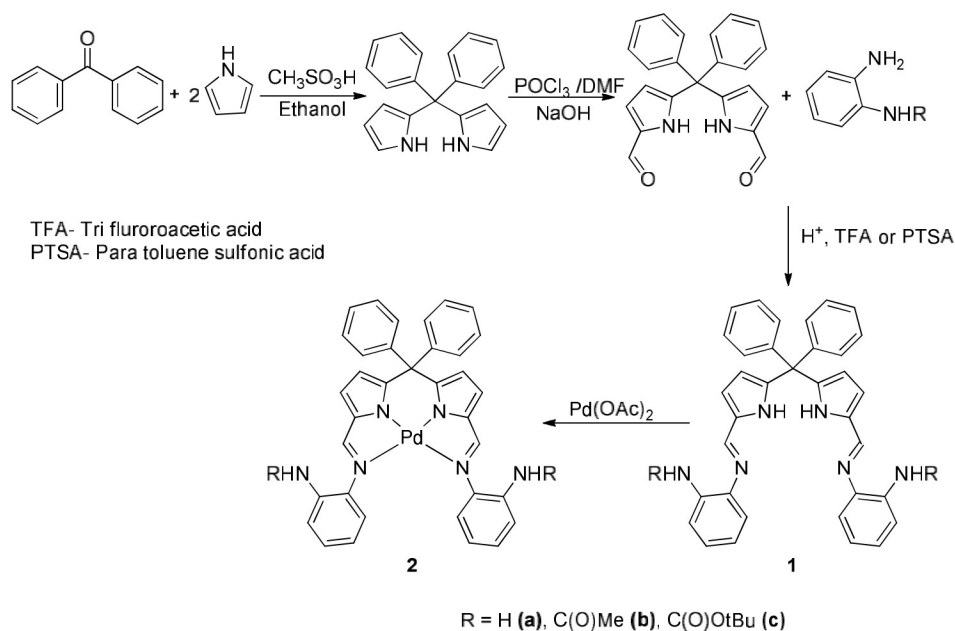


**Figure 2.2.** General structure of the Pd calixpyrrole complexes **2a-c** with different pendant groups in the secondary coordination sphere. R = H (a), C(O)Me (b), and C(O)OtBu (c).

### 2.3. Synthesis:

The calixpyrrole ligands and Pd complexes were synthesized as shown in Figure-2 by following the same procedures reported by Trowbridge *et al.*<sup>15</sup>

For the calixpyrrole ligand synthesis (named (1) and further differentiated according to the pendant groups (a) for amine groups, (b) for acyl-protected amines, and (c) for tert-butoxycarbonyl or Boc-protected amines), diphenyldipyrromethane was initially produced (according to a literature procedure).<sup>16</sup> A dialdehyde precursor was then prepared from diphenyldipyrromethane (Figure 3, also following a literature procedure).<sup>17</sup> With 5,5'-diformyl-2,2'-diphenyldipyrromethane in hand, it was mixed with aniline precursor in the presence of acid (Figure 2).<sup>15,16-21</sup> Pd(II) was then coordinated to the calixpyrrole ligands, partially because Pd complexes with pendent nitrogen groups were found to reduce oxygen and also because previous results from the group suggested that the Pd complexes were active for HER.<sup>22</sup> To install Pd, a salt metathesis reaction with Pd(OAc)<sub>2</sub> was performed to give the corresponding Pd complexes (named 2 and also differentiated according to pendant group a-c, as before, **Figure-2.3**). This procedure was developed by another member, Dr. Sachi, of the Sues group<sup>23</sup>

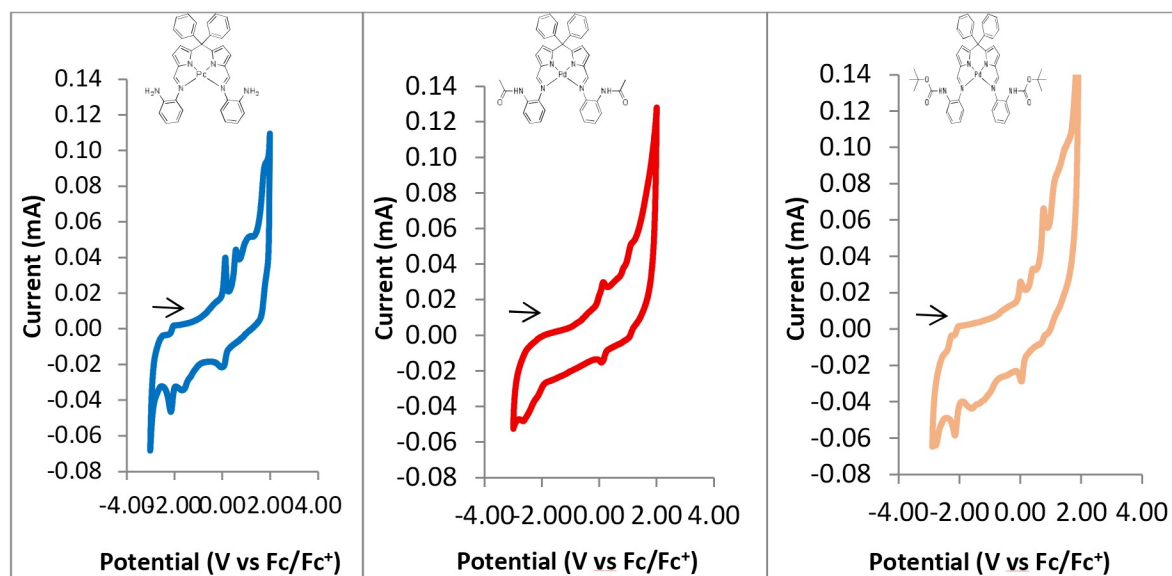


**Figure-2.3.** General synthetic procedure for the calixpyrrole ligands 1a-c and Pd complexes 2a-c<sup>15</sup>

## 2.4. Electrochemical Properties of 2a-c:

The electrochemical behavior of the Pd complexes 2a-c was studied by cyclic voltammetry (CV). The complexes were dissolved in acetonitrile, and tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte. As shown in Figure 2.4, for the unprotected complex 2a, two irreversible oxidation peaks around 0.097V and 0.542V vs ferrocene/ferrocenium redox couple ( $\text{Fc}/\text{Fc}^+$ ) were found along with two irreversible reductions at -2.06V and -1.49 V. A redox couple can also be observed around 0V vs  $\text{Fc}/\text{Fc}^+$ . For the acyl-protected complex 2b, we observe two irreversible oxidation peaks at 0.441V and 0.782 V vs  $\text{Fc}/\text{Fc}^+$  and two irreversible reduction peaks around -2.02 V and 1.41V vs  $\text{Fc}/\text{Fc}^+$ . There was also a redox couple around 0V vs  $\text{Fc}/\text{Fc}^+$ . For the Boc-protected complex 2c, there were two irreversible oxidations at 0.37V and 0.722 V vs  $\text{Fc}/\text{Fc}^+$ , a redox couple around 0V, and two irreversible reductions around -2.04V and -0.944 V vs  $\text{Fc}/\text{Fc}^+$ .

In the unprotected complex, the irreversible reduction and oxidation peaks occurred at slightly more negative potentials than those of the acyl- and Boc-protected species. It is likely said that the electron-rich nature of the pendant aniline group caused the observed shifts in potential.

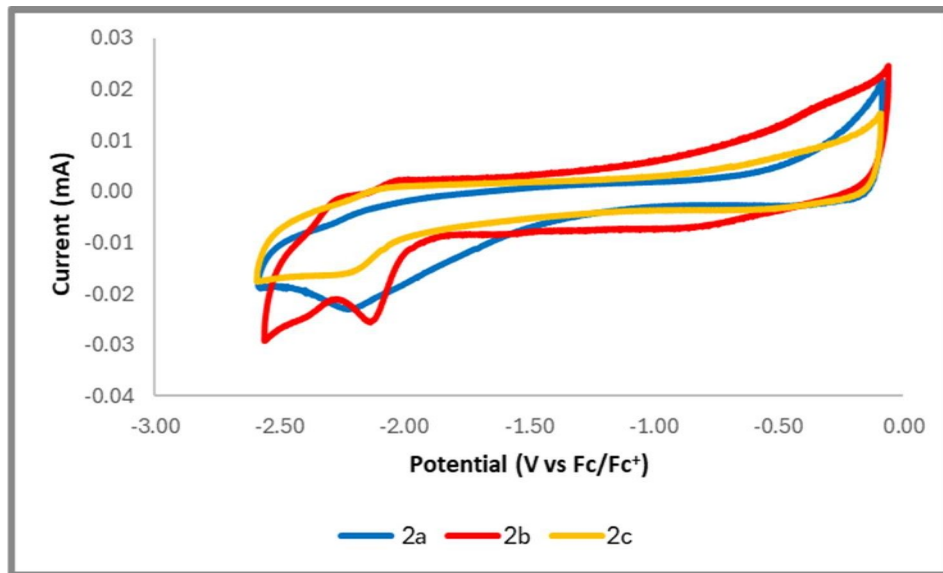


**Figure-2.4.** Cyclic Voltammograms of 2a-c (0.25mM) in acetonitrile (0.1M TBAP, glassy carbon working electrode, platinum wire counter electrode, 0.01M  $\text{Ag}/\text{AgNO}_3$  reference electrode, scan rate= 800 mV/s).

### 2.4.2. Electrochemical Characterization of 2a-c

Complexes **2a-c** were previously synthesized and investigated as catalysts for the hydrogen evolution reaction (HER) in the presence of *p*TSA as the proton source.<sup>15</sup> Their electrochemical studies were done through cyclic voltammetry (CV) in acetonitrile with tetrabutylammonium hexafluorophosphate (TBAP) as the supporting electrolyte; however, these experiments were completed over wide scanning windows with both positive and negative potentials. In more recent research, a nickel analog of 2a was also explored as an HER catalyst under similar conditions<sup>12</sup>. The CV experiments were done using a narrower potential window to negative potentials, two quasi-reversible redox events were found for the Ni<sup>II/I</sup> and Ni<sup>I/0</sup> couples.

Therefore, the electrochemical characterizations of **2a-c** were reinvestigated. Upon limiting the scan window to negative potentials, redox couples were found around -2.33 V, -2.26 V, and -2.35 V vs. Fc/Fc<sup>+</sup> for **2a**, **2b**, and **2c**, respectively (**Figure 2.5**). According to the literature, these redox couples are identified as Pd<sup>(II/I)</sup>. Furthermore, given the relatively modest...

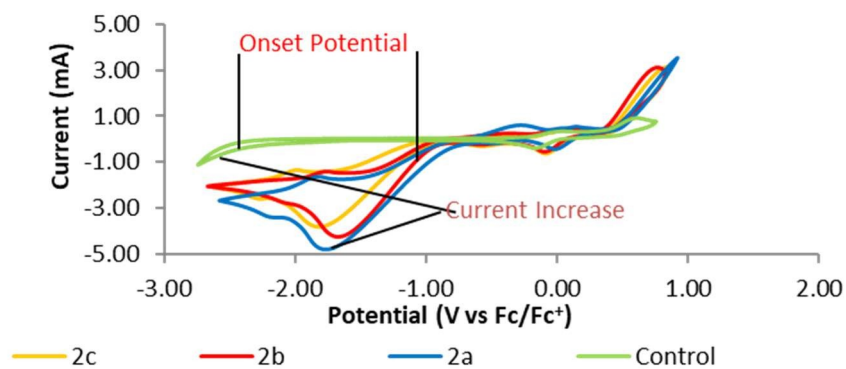


**Figure 2.5.** CVs showing the redox couples for **2a-c** when only negative potentials were scanned (0.1 M TBAP, 0.25 mM **2a-c**, glassy carbon working electrode, platinum wire counter electrode, 0.0 1M Ag/AgNO<sub>3</sub> reference electrode, scan rate = 800 mV/s).



### 2.4.3. Electrocatalytic Hydrogen Evolution:

From the previous study, it was found that Pd calixpyrrole complexes **2a-c** showed heterogeneous HER catalysts in acetonitrile when utilizing *p*TSA as the proton source.<sup>15</sup> These systems, however, were not very active and ill-defined, as they were producing high background current. Also, it was found that the high acidity of *p*TSA may have caused the unwanted decomposition of **2a-c**, potentially leading to the deposition of catalytically active HER species on the electrode surface. A related nickel calixpyrrole complex, on the other hand, also generated a heterogeneous HER catalyst, but the catalytic activity was significantly higher using a much milder acid, anilinium tetrafluoroborate ( $pK_a = 10.62$ )<sup>12</sup>. As such, the catalytic activity of **2a-c** was revisited using anilinium tetrafluoroborate as the proton source.



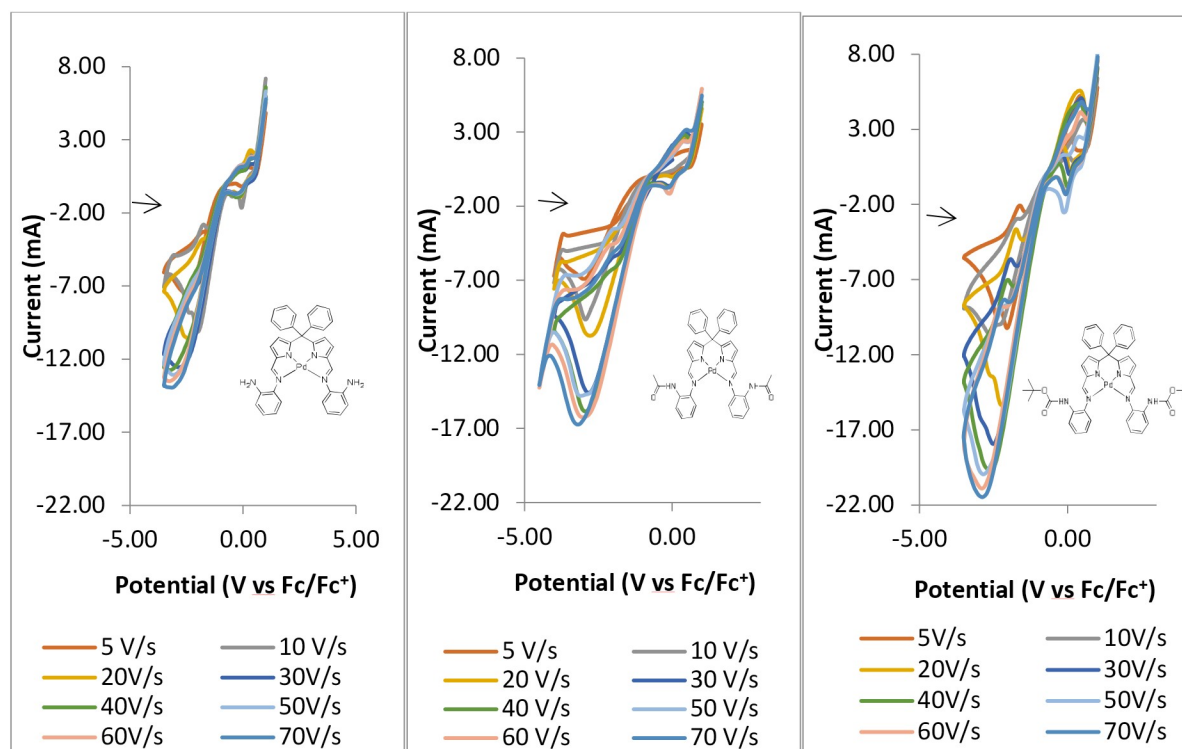
**Figure 2.6.** CVs of HER using **2a-c** (0.1 M TBAP, 0.25 mM catalyst, 0.25 M anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.0 1M Ag/AgNO<sub>3</sub> reference electrode, scan rate = 800 mV/s).

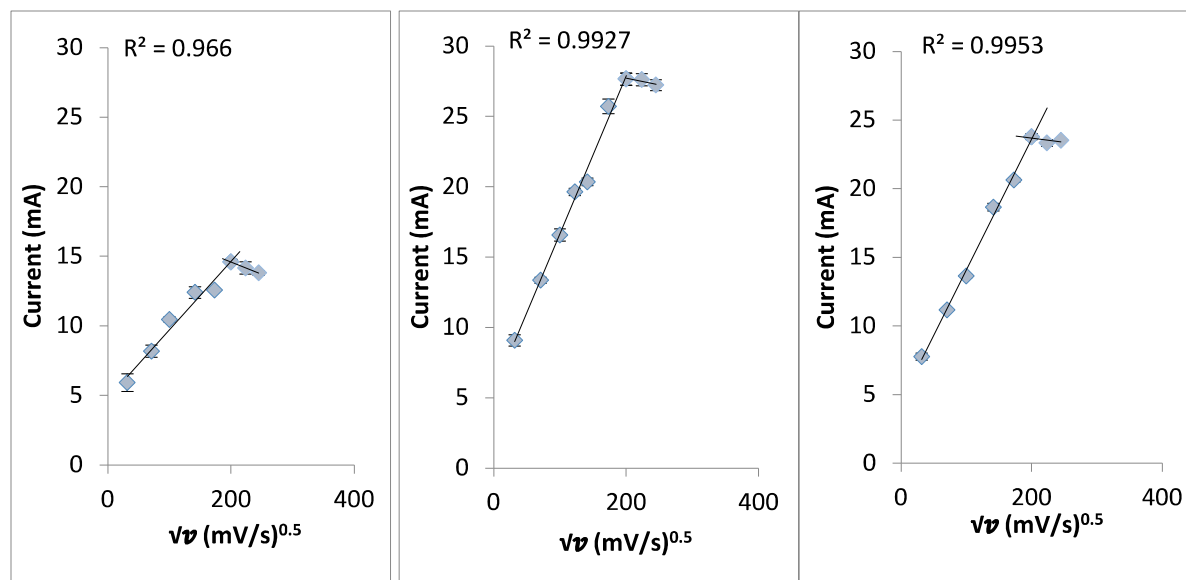
This figure illustrates the catalytic behavior of the Pd calixpyrrole complexes in the presence of the milder acid. The onset of catalysis (potential at which the catalytic current starts to increase or shows catalysis) of the Pd complexes **2a-c** was more positive (0.4-0.5V) than the glassy carbon control and showed a greater increase in current, meeting the requirement for HER electrocatalysts. An irreversible catalytic current ( $i_{cat}$ ) was apparent, indicative of electrocatalytic HER.

## 2.5. Kinetic Studies

### 2.5.1. Scan Rate Dependence

After establishing the catalytic competence of **2a-c**, kinetic studies were carried out. To examine the heterogeneous or homogenous nature of catalysis, the scan rate dependence of HER using **2a-c** was carried out. We can see from **Figure 2.7** that scan rates ranging from 1000 mV/s to 60000 mV/s have been used, and the catalytic currents at each scan rate were analyzed. It was observed that the change in catalytic current was directly proportional to the square root of the scan rate. Therefore, this suggested that the catalysts were most likely homogeneous in nature and that HER was a diffusion-controlled process,<sup>23</sup> which was in direct contrast to the results obtained with *p*TSA as the proton source.





**Figure-2.7(a, top three graphs)** Catalytic CVs of HER in acetonitrile using different scan rates starting from 1000mV/s to 60000mV/s (0.1M TBAP, 0.25mM 2a-c, glassy carbon working electrode, platinum wire counter electrode, 0.01M AgNO<sub>3</sub> reference electrode)

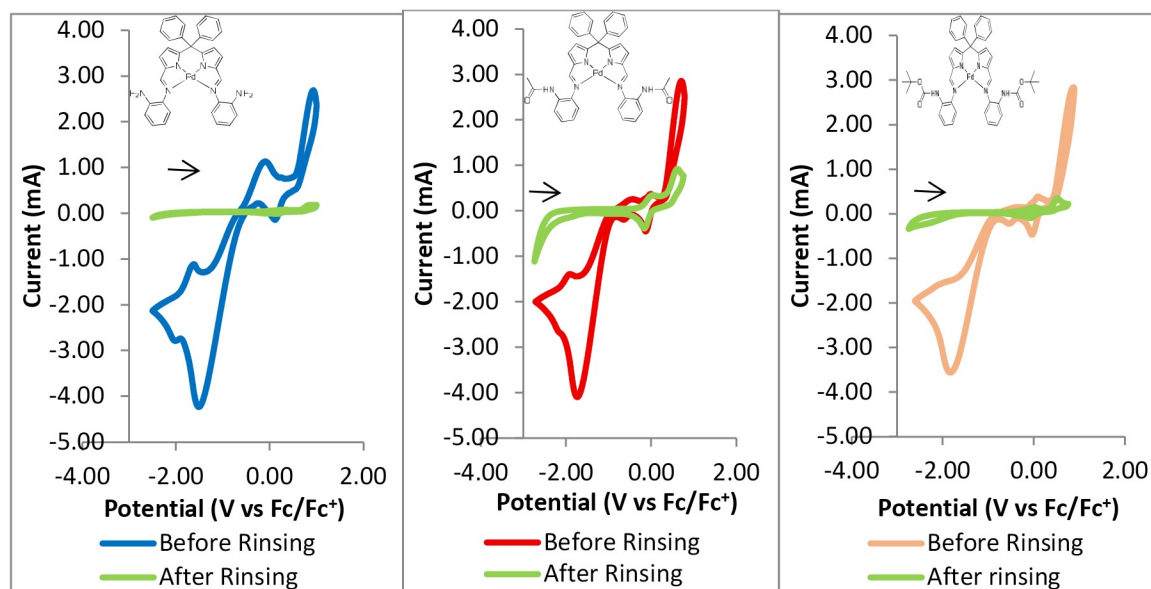
**Figure 2.7 (b. lower three graphs)** General plot of catalytic current vs. the square root of scan rate.

Additionally, from **Figure 2.7**, we can see that for all three complexes, the scan rate independence point was around 40 V/S. At higher scan rates, the current change began to plateau, indicating that the HER kinetics were purely under catalyst control. Moreover, a scan rate independence point of 40 V/s indicates faster reaction kinetics.

### 2.5.2. Other Tests of Heterogeneity:

To confirm the homogeneous nature of catalysis, rinse tests were performed for 2a-c. For a rinse test, if activity persists after catalysis and rinsing the working electrode, catalysis is likely heterogeneous.<sup>23</sup> For the experiments, first a CV was done with 0.25mM of complex in acidic acetonitrile, and after that, the working electrode was rinsed with TBAP solution in acetonitrile, and then again a CV was done with a fresh solution of acid in acetonitrile, without complex in the solution. From **Figure 2.8**, we can see that before rinsing, catalysis was present, with high catalytic

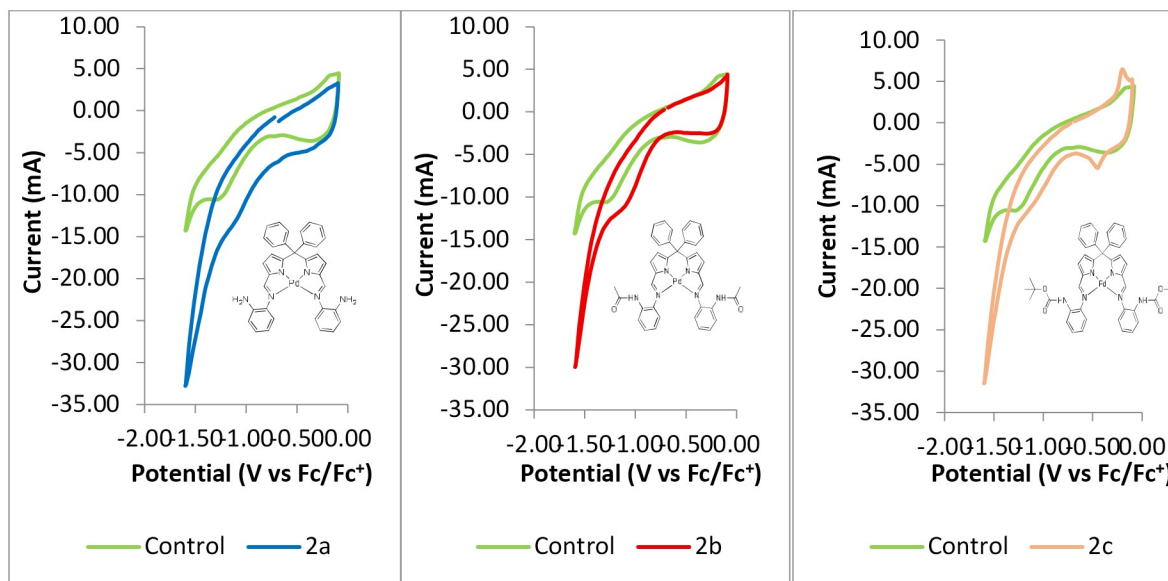
peak currents, but after rinsing, catalysis was absent. This suggests that HER did not work without complexes in solution, thus confirming their homogenous nature.



**Figure-2.8.** Rinse test results using acetonitrile as the rinsing media (0.1M TBAP in acetonitrile, 0 or 0.25mM of 2a-c, 0.25M anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01 M Ag/AgNO<sub>3</sub> reference electrode, scan rate= 800 mV/s)

### 2.5.3. Mercury Pool Test

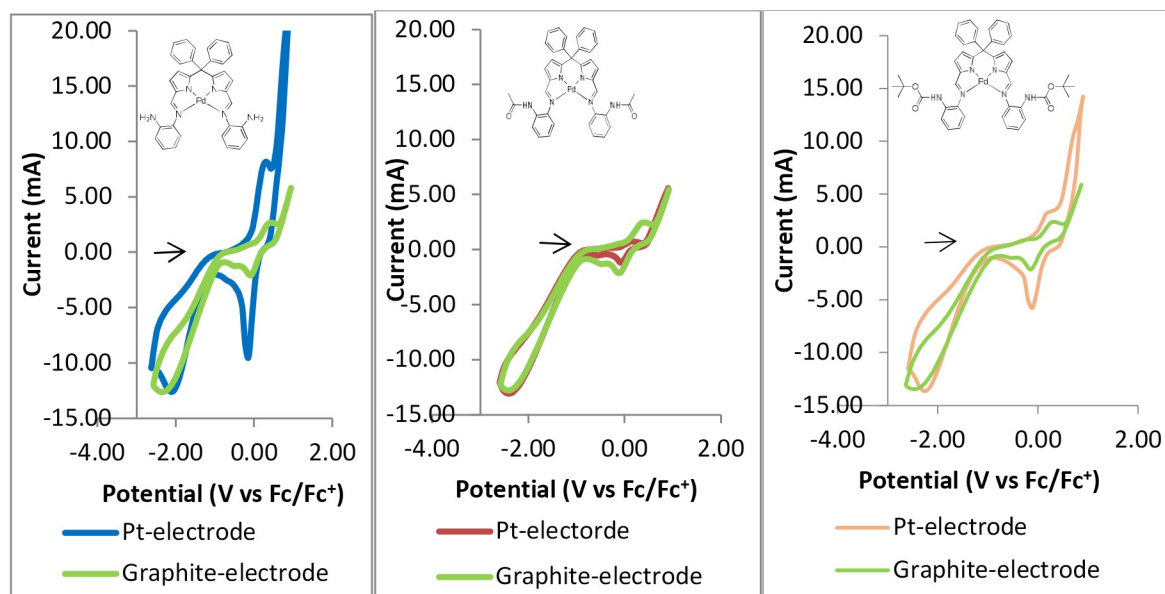
Mercury pool tests were also performed to assess whether soluble nanoparticles formed during HER. In a mercury pool test, the mercury pool serves as the working electrode. The idea is that if Pd particles were catalyzing HER, they would be deactivated by forming an amalgam with the mercury electrode or by adsorbing onto it, thereby inhibiting catalysis.<sup>32, 33</sup> From **Figure 2.9**, we can see that catalysis remained present in the region from 0 to -2V, and there was no inhibition of catalysis. This further supports the conclusion that 2a-c were homogeneous systems and that no nanoparticle formation occurred.



**Figure-2.9** CVs of the mercury pool tests for HER using 2a-c (0.25mM or 0mM) in acetonitrile (0.1M TBAP, 0.25M anilinium tetrafluoroborate, mercury pool working electrode, platinum wire counter electrode, scan rate=40V/s)

#### 2.5.4. Effect of Counter Electrode:

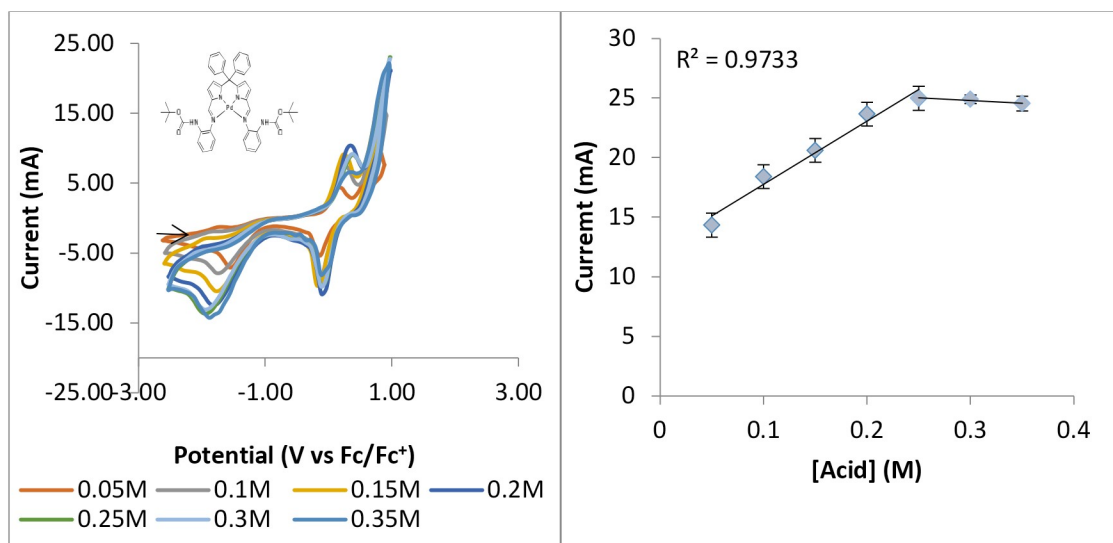
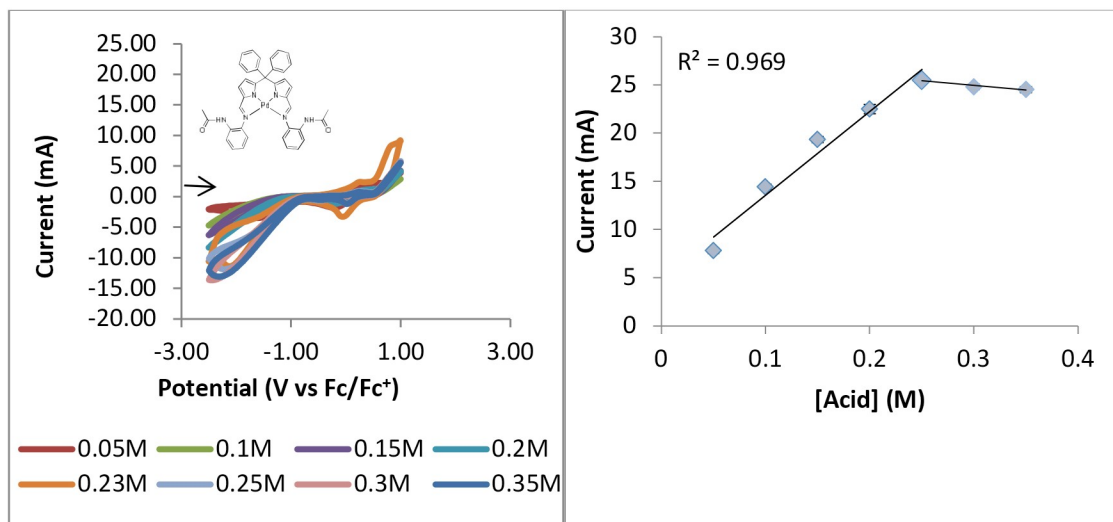
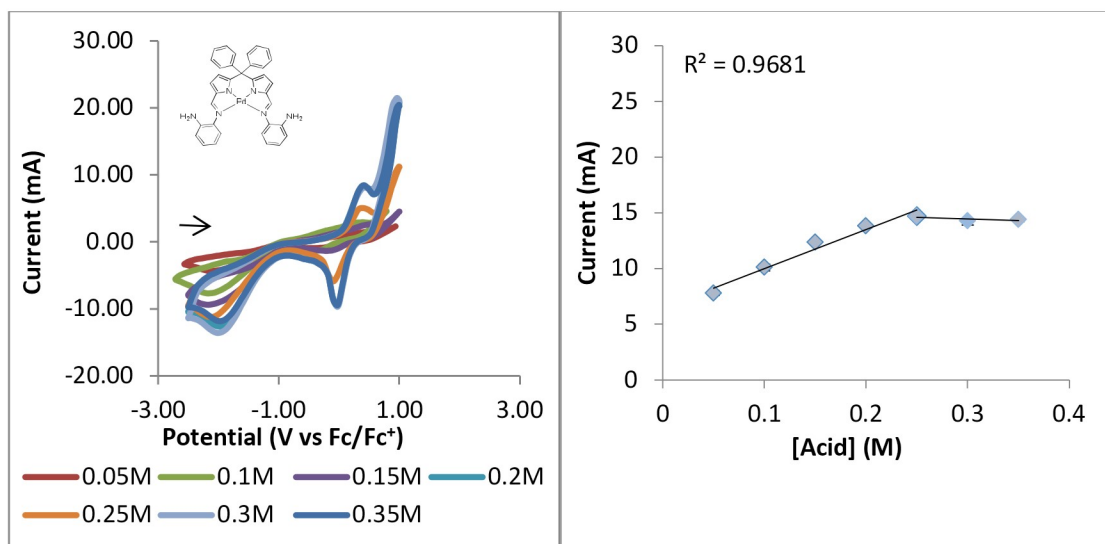
For all of the CVs discussed so far, platinum wire was used as the counter electrode. We know that platinum is considered the benchmark catalyst for HER, so it is important to perform a control reaction to determine whether the platinum counter electrode has an impact. Therefore, to check that, the counter electrode is not contributing to the catalytic current, a graphite electrode was also used as the counter electrode.<sup>15</sup> All the conditions were kept the same, such as 0.25mM of 2a-c in acetonitrile, 0.1M TBAP as the supporting electrolyte, glassy carbon was used as the working electrode, and Ag/AgNO<sub>3</sub> was used as the reference electrode. From **Figure-2.10**, CV plots both with and without a platinum wire counter electrode were similar. This means there was no impact from the platinum electrode; our catalysts 2a-c were performing as catalysts.



**Figure-2.10** CVs of 2a-c(0.25mM) in acetonitrile using platinum wire and graphite rod as the counter electrode (0.25M anilinium tetrafluoroborate, glassy carbon working electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=40V/s)

### 2.5.5. Acid Dependence:

The acid dependence of HER using 2a-c was also examined, and concentrations from 0.05M to 0.35M of anilinium tetrafluoroborate were used. From **Figure-2.11**,





**Figure-2.11** (a) CVs with different acid concentrations (starting from 0.05M to 0.25M anilinium tetrafluoroborate) using 2a-c(0.25mM) in acetonitrile, (glassy carbon working electrode, platinum wire electrode, 0.01M AgNO<sub>3</sub> reference electrode, scan rate=40V/s)  
(b) General plot of normalized catalytic current vs acid concentration.

From **2.11b**, it was found that catalytic current has linear relationship with acid concentration, which indicated that the reaction is second order dependence on acid according to Equation 1, where  $n$  is the number of electrons transferred (2 for HER),  $F$  is Faraday's constant,  $A$  is the surface area of the electrode,  $D$  is the diffusion coefficient, and  $x$  is the order with respect to acid.

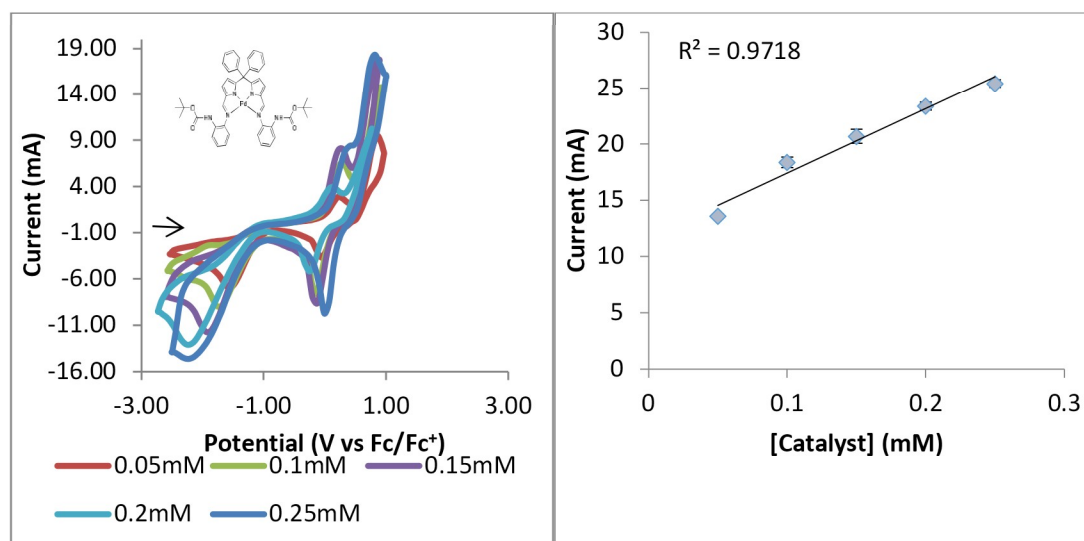
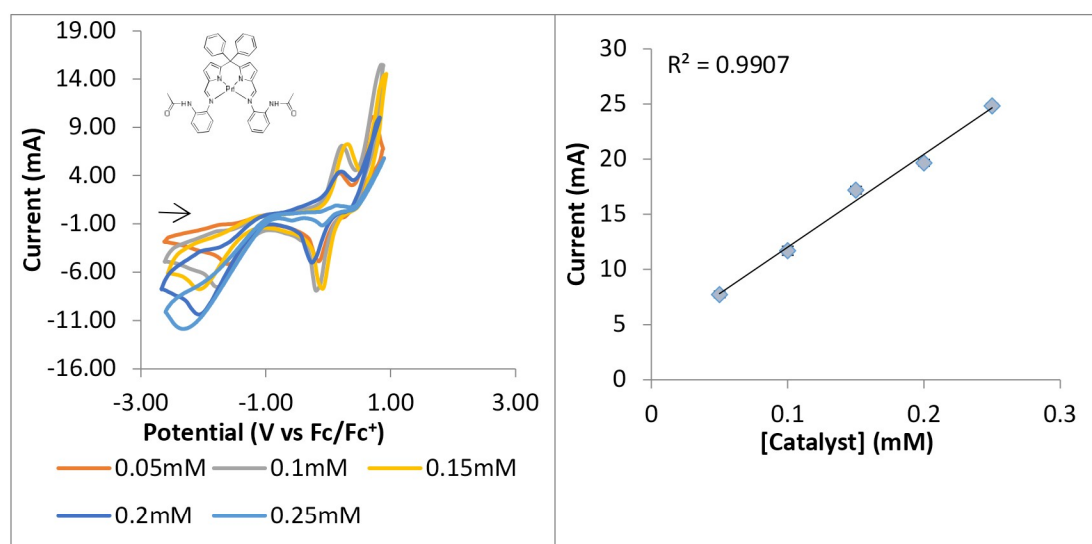
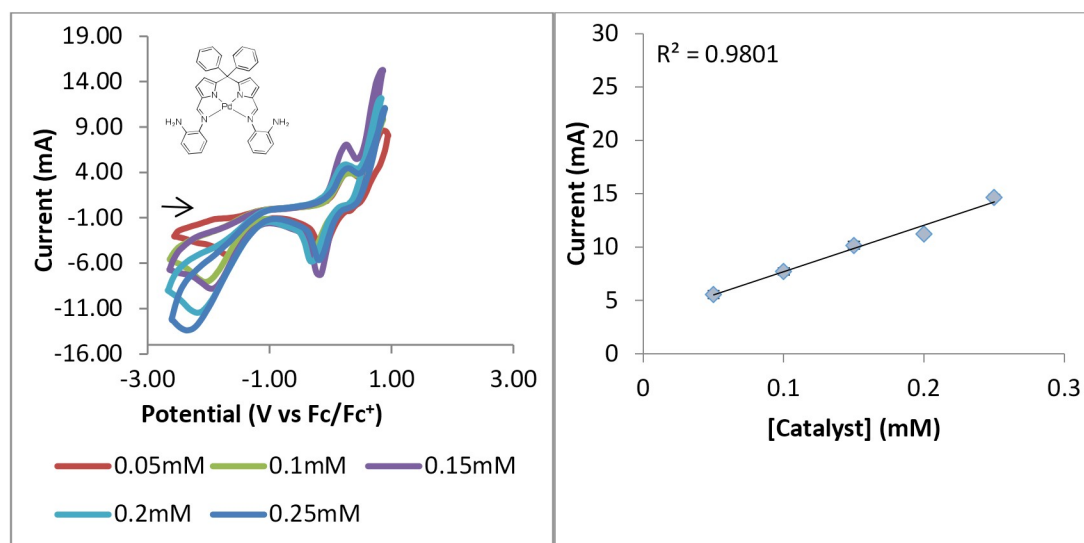
$$i_{cat} = nFA[cat]\sqrt{Dk[H^+]^x} \quad (1)$$

Notably, for the calixpyrrole catalyst with unprotected amines in the secondary coordination sphere, an anodic shift in  $i_{cat}$  was observed with increasing concentrations of acid in solution (**Figure 2.11a**). This could suggest either direct protonation of the catalyst prior to electron transfer, or, alternatively, an electron transfer coupled to a chemical transformation/protonation, such as a PCET process. For **2a** and **2b**, on the other hand, with acyl- and boc-protected amines in the secondary coordination sphere, direct protonation of pendant groups by anilinium tetrafluoroborate is not possible. This was reflected in their catalytic behavior, where  $i_{cat}$  shifted to more cathodic potentials with increasing concentrations of acid (**Figure 2.11a**), which suggested initial electron transfer prior to proton transfer.

#### 2.5.6. Catalyst Dependence:

The catalyst dependence for HER using 2a-c was also investigated, with concentrations ranging from 0.05 mM to 0.25 mM. From **Figure 2.12**, it can be observed that the catalytic current was linearly dependent on catalyst concentration, indicating that the reaction was first order in catalyst, as shown in equation 1. At catalyst concentrations above 0.25 mM, these three complexes did not dissolve properly. Therefore, these catalytic systems were found to be second-order in acid, first-order in catalyst, and a third-order process overall.





**Figure-2.12** (a, graphs on the left) CVs with different concentrations of Pd complexes **2a-c** (0.05mM to 0.25mM) in acetonitrile (0.25M anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=40V/s)  
(b, graphs on the right) General plot of catalytic current vs concentration of catalyst

### 2.5.7. Calculating catalytic performance factors

Once optimized conditions for the HER were achieved, where  $i_{\text{cat}}$  was independent of scan rate and acid concentration, the turnover frequencies (TOFs) of **2a-c** were calculated using Equation 3, where  $\nu$  is the scan rate, and  $i_p$  is the peak current for the calixpyrrole catalyst in the absence of acid. Equation 3 is a simplified form of Equation 2 (where  $R$  is the ideal gas constant) when  $T = 298 \text{ K}$  and  $n = 2$  (the number of electrons transferred for HER)<sup>28-31</sup>.

$$\frac{i_{\text{cat}}}{i_p} = \frac{n}{0.4463} \sqrt{\frac{RTk[H^+]^x}{F\nu}} \quad (2)$$

$$k_{\text{obs}} = \text{TOF}_{\text{max}} = (1.94 \text{ V}^{-1})\nu \left(\frac{i_{\text{cat}}}{i_p}\right)^2 \quad (3)$$

It should be noted that Equation 3 is best suited for calculating the TOFs of scan rate independent, S-shaped catalytic waves, which are operating under “pure kinetic conditions”. For systems that exhibit a distinct peak rather than a plateau current, however, Dempsey and co-workers have noted that Equation 3 remains suitable for assessing catalytic performance.<sup>24-26</sup> Moreover, they found that using this method to calculate TOFs for non-ideal systems was inherently conservative, as it underestimated rate constants. As such, Equation 3 was utilized for the Pd calixpyrrole systems.

The TOFs and  $k_{\text{obs}}$  of **2a**, **2b**, and **2c**, were calculated to be  $4.65 \pm 0.17 \times 10^6 \text{ s}^{-1}$ ,  $4.19 \pm 0.13 \times 10^6 \text{ s}^{-1}$ , and  $3.09 \pm 0.09 \times 10^6 \text{ s}^{-1}$ , respectively. For context, these remarkably high reaction rates are over an order of magnitude higher than the fastest nickel diphosphocycloheptane HER catalysts reported in the literature (by Bullock and co-workers), which had TOFs and  $k_{\text{obs}}$  around  $1.0 \times 10^5 \text{ s}^{-1}$ . Therefore, to the best of our knowledge, the Pd calixpyrrole catalysts represent the fastest

known systems to date and now act as a benchmark for rapid HER catalysis. In fact, **2a-c** are so fast that they approach the diffusion rate limit and compare favorably to the fastest known enzymatic systems. In addition, it is important to note that the calixpyrrole complex with the unprotected amines in the secondary coordination sphere exhibited the fastest reaction kinetics, followed by the acyl- and boc-protected species. To achieve such impressive catalytic rates,

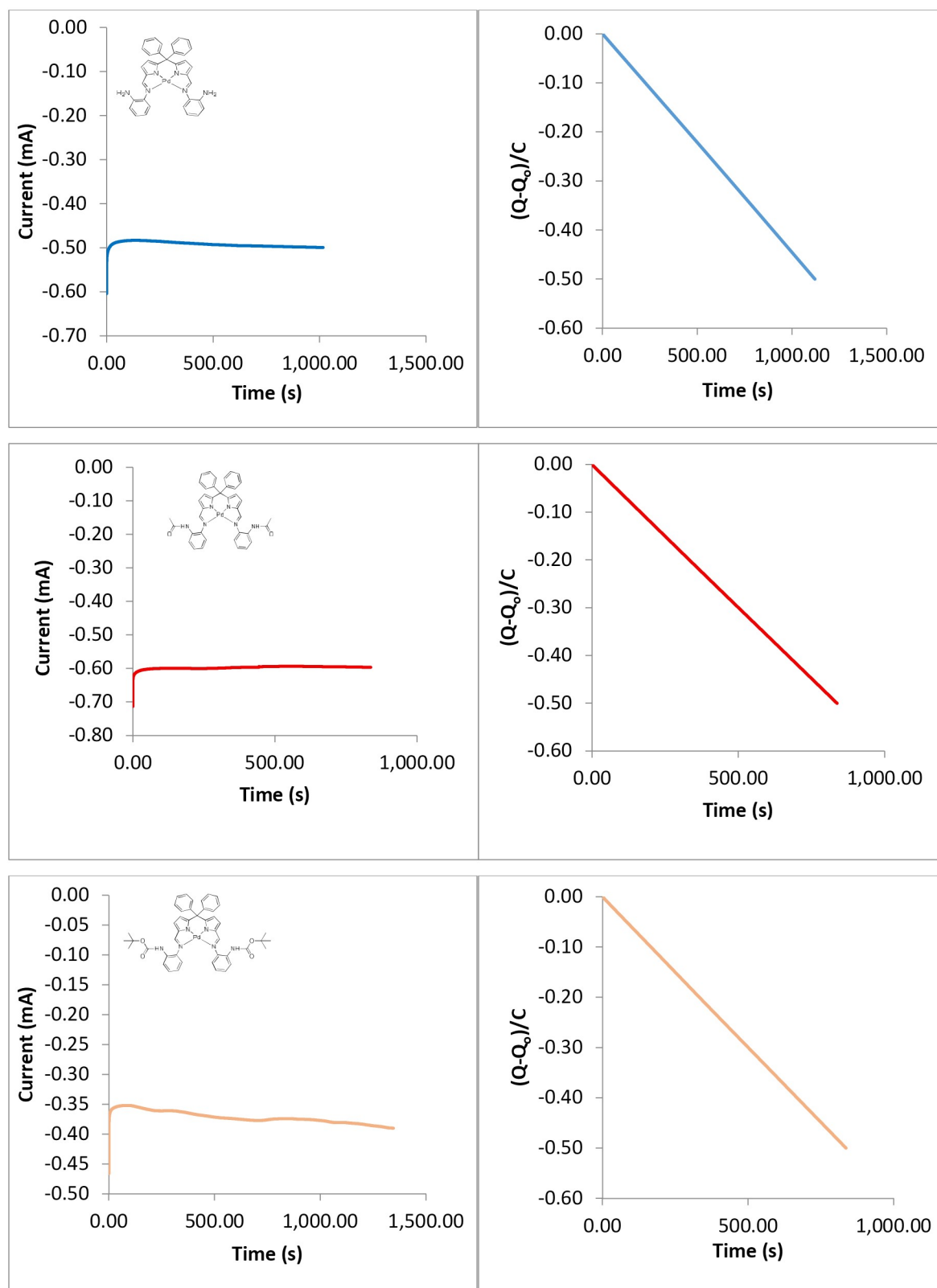
overpotentials of  $0.79 \pm 0.10$ ,  $0.79 \pm 0.03$ , and  $0.87 \pm 0.09$  V were required for **2a**, **2b**, and **2c**, respectively (equations 4 and 5).

$$\text{Overpotential} = [E_H^+ - E_{\frac{cat}{2}}] \quad (4)^{34}$$

$$E_H^+ = E_H^{+0} - 0.05961V * pKa \quad [E_H^{+0} = -0.028V, pka = 10.62] \quad (5)^{20,21}$$

The overpotentials seen for **2a-c** were similar to those reported by the Rauchfuss group for their biomimetic di-iron HER catalysts (overpotentials  $> 0.70$  V), as well as those reported by Bullock and co-workers for their nickel diphosphocycloheptane systems (overpotentials around 0.625 to 0.700 V). Although the overpotentials for **2a-c** are somewhat high, their similarity to the Bullock systems, which are dicationic, whereas the calixpyrrole complexes are neutral and very electron-rich, suggests opportunities to minimize these values in the future. In particular, the incorporation of positively charged functionalities into the calixpyrrole ligand framework should induce a dramatic positive shift in reduction potentials.

Controlled potential electrolysis (CPE) studies were also carried out using the Pd calixpyrrole complexes. The catalyst with pendant amines in the secondary coordination sphere once again demonstrated the most desirable properties and displayed the highest faradaic efficiency (FE) of  $97.7 \pm 5.3$  %.



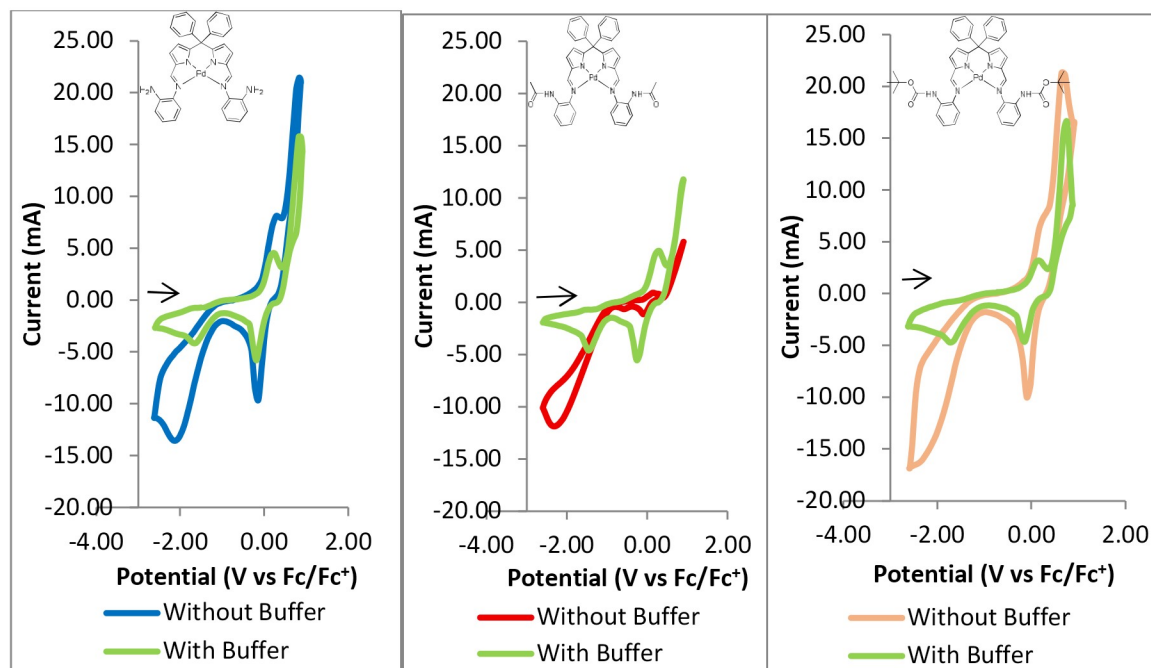
**Figure-2.13** Controlled potential electrolysis results in acetonitrile (0.1M TBAP, 0.25 mM of 2a-c in acetonitrile), 0.25M anilinium tetrafluoroborate, 6mm glassy carbon rod working electrode,

0.01M Ag/AgNO<sub>3</sub> reference electrode and 0.1MTBAP, 0.25M ferrocene, 6mm graphite counter electrode, 0.5C of charge passed) (1) current vs time (2) charge passed vs time

Moreover, a linear increase in charge transferred over time was observed for 2a, and the CPE current response remained stable for approximately 14 min (**Figure 2.13**). This provided evidence that 2a was relatively stable under the reaction conditions explored and did not undergo large structural changes during the catalytic cycle. Similar behavior was observed with the acyl-protected system, **2b** (**Figure 2.13**), except that the FE was slightly lower at  $95.7 \pm 7.6$  %. The boc-protected analog, **2c**, on the other hand, exhibited the lowest FE of  $95.3 \pm 3.7$  %, and also displayed a slight drop in catalytic current over time during CPE studies (approximately 24 min, **Figure 2.13**). This indicated that structural changes were occurring during catalysis. This is likely due to the very slow deprotection of the carbamate moiety under the acidic conditions used for HER.

## 2.6. Mechanistic Studies:

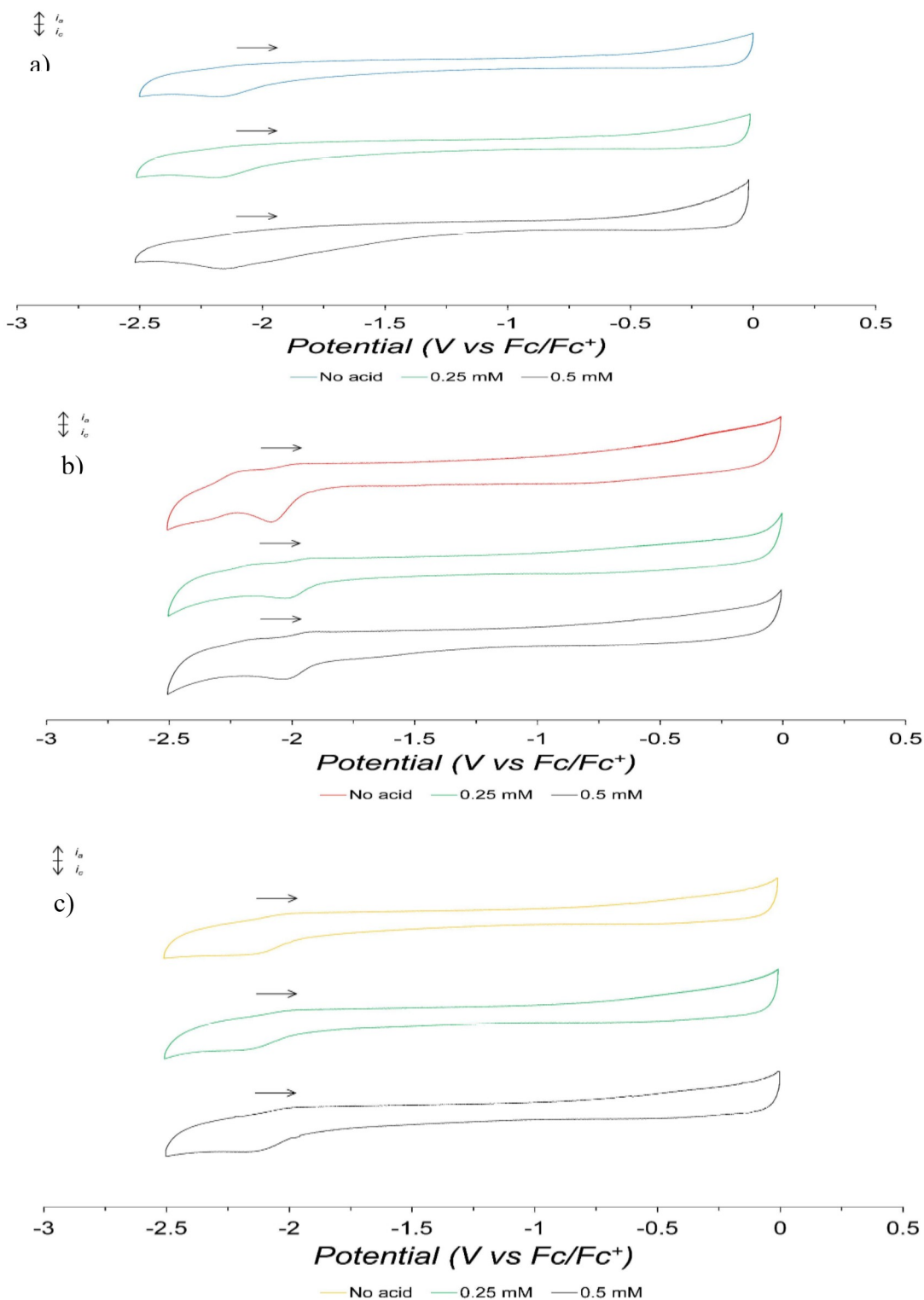
Whenever conducting HER in non-aqueous solvents, it is best practice to perform a control experiment using a 1:1 buffer solution of the acid being utilized and its conjugate base in order to rule out homoconjugation or pairing effects, which increase the apparent acidity of the proton source in low dielectric constant solvents. Homoconjugation or pairing effects of the proton source have also been investigated. As such, homoconjugation would be expected to lead to catalytic rates higher than expected and enhanced HER activity <sup>19</sup>. To test homoconjugation, a buffer solution containing a 1:1 ratio of aniline to anilinium tetrafluoroborate was used. In **Figure 2.14**, we can see that with only anilinium tetrafluoroborate in solution, the catalytic peak current was around 12mA for all three complexes. For the buffer solution, in contrast, the catalyst peak current decreased to around 4 mA, indicating that a large pairing is affecting and inhibiting catalysis. This revealed that aniline in solution was acting as a competitive inhibitor during that catalytic cycle.



**Figure-2.14** CVs of HER in buffered solution as well as without buffer solution ( 0.1M TBAP, 0.25mM of Pd complexes 2a-c, 0.25M anilinium tetrafluoroborate as non-buffered solution, 0.25M of anilinium tetrafluoroborate and 0.25 M aniline as buffered solution, glassy carbon working electrode, platinum wire electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=40V/s)

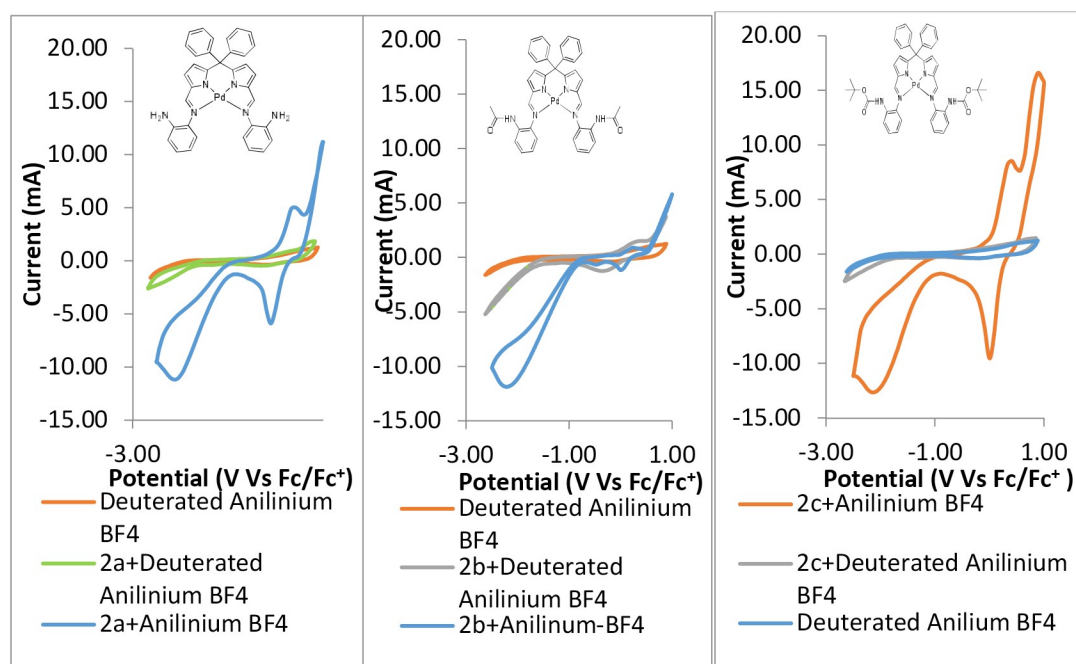
In order to gain further insight into the mode of action for **2a-c**, their behavior in the presence of small amounts of acid was explored. When the concentrations of anilinium tetrafluoroborate were increased from 0 to 0.25mM to 0.5mM (0 to 1 or 2 equivalents with respect to the catalyst concentration), minimal change was visible for the three Pd calixpyrrole systems (**Figure 2.15**). This showed that direct protonation of 2a-c did not occur with this small change in the concentration of the proton source. With 1 or 2 equivalents of acid, no positive shifts were found, and the presence of 2a-c peaks around -2.26V to -2.35V revealed the unprotonated 2a-c solution in solution. For **2b** and **2c**, with acyl- and Boc-protected amines in the secondary coordination sphere, respectively, direct protonation of pendant groups by the proton source was not expected due to hydrogen-bond donating behavior. For 2a, on the other hand, the absence of direct protonation was not expected, given the anodic shift in *i*<sub>cat</sub> observed with increasing acid concentration, as well as in analogs of 2a in Ni, which showed direct protonation of the catalyst

by anilinium salts. This can be rationalized by the more electronegative nature of Pd relative to Ni, which would lower the  $pK_a$  of the pendant groups through inductive effects. As such, it is thought that protonation of **2a** by anilinium tetrafluoroborate is only possible at higher acid concentrations. This would explain the positive shift in  $i_{cat}$  that was seen during the kinetic studies (where 0.05 to 0.35 M anilinium tetrafluoroborate was utilized), but not in the stoichiometric studies discussed above.



**Figure 2.15.** CVs in the absence and presence of acid (0.1 M TBAP, 0.25 mM catalyst, 0, 0.25, and 0.5 mM anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.0 1M Ag/AgNO<sub>3</sub> reference electrode, scan rate = 800 mV/s) for: 2a; 2b; and 2c.

To further probe the catalytic mechanism and the rate-determining step for the Pd calixpyrrole catalysts, kinetic isotope effect (KIE) studies were performed using anilinium-d<sub>3</sub> tetrafluoroborate as the deuterium source (**Figure 2.16**).



**Figure-2.16.** CVs of H/D (KIE) studies in acetonitrile (0.25 mM 2a-c, 0.25M anilinium or deuterated anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=40V/s)

For **2a**, **2b**, and **2c**, H/D KIE values of  $5.2 \pm 0.1$ ,  $4.2 \pm 0.1$ , and  $5.4 \pm 0.8$  were obtained, respectively. These results provided strong evidence that proton/deuteron transfer is involved in the rate-determining step for all three Pd catalysts. Furthermore, such large values may indicate PCET processes. A very similar KIE of 5.7 was seen for the nickel analog of **2a**, which was thought to proceed through a rate-limiting PCET nickel-hydride formation step. The rate law for the nickel



species, however, was found to be first order in acid concentration. This contrasts with the Pd calixpyrrole catalysts, which are second order in anilinium tetrafluoroborate. Therefore, it is unlikely that palladium-hydride formation is rate-limiting for **2a-c**.

## 2.7. Mechanistic Implications.

A careful examination of the electrocatalytic HER behavior of 2a-c complexes reveals several key design principles for future catalyst development. One important finding is the exceptionally high catalytic activity of these Pd calixpyrrole catalysts. The TOF values were found to be the fastest for homogeneous HER catalysts, surpassing even the well-established nickel diphosphacycloheptane by more than an order of magnitude.

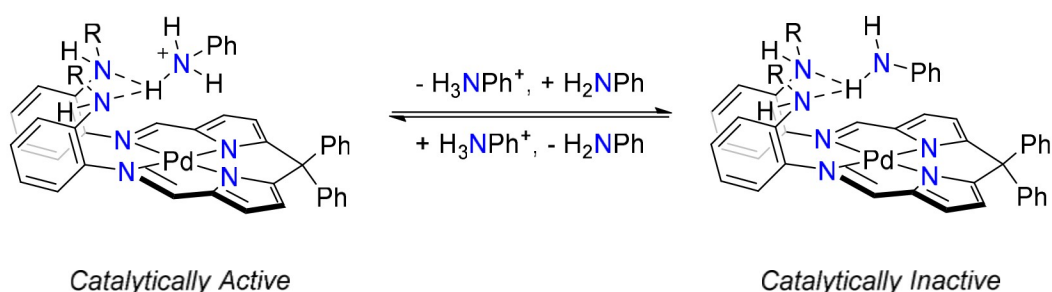
Though both systems have pendant functional groups in the secondary coordination sphere, a key difference was found in the rigidity of the ligand structure. In nickel diphosphacycloheptane catalysts, they have flexible methylene linkers that allow the pendant amine to move freely, adopting conformations both close to and far from the active center. This flexibility has been shown to negatively affect catalytic performance, especially when the directing groups are not properly positioned. In comparison, systems that restrict these groups near the active center tend to exhibit enhanced catalysis.

These Pd complexes do not have this issue entirely due to their rigid phenylene backbone; this backbone enforces an ortho geometry that keeps the pendant groups in a fixed position relative to the active center. As a result, the directing functionalities stay ideally positioned throughout the whole catalysis. Their structural constraints play an important role in facilitating the extremely fast reaction rates observed for 2a-c.

Another important observation is that all three systems show very similar catalytic behavior. While 2a has slightly higher TOF and Faradaic efficiency (FE) than 2b and 2c, the differences are minimal compared to what is expected. It was assumed initially that the amine-containing 2a complex would significantly outperform the amine and carbamate analogs due to its ability to behave as a proton shuttle. However, only modest improvements were found.

This verifies that, in cases 2b and 2c, the pendant groups do not function as a true proton shuttle but instead organize the proton source (anilinium tetrafluoroborate) via hydrogen bonding. Several

findings support this idea. No clear evidence of direct protonation was observed with 1-2 equivalents of acid, and with increasing acid concentration, a cathodic shift in the catalytic current was observed. Additionally, the catalytic current decreased when used in buffered solutions, suggesting that aniline acts as an inhibitor. This showed the consistency of a mechanism in which hydrogen bonding is important; aniline competes for these interactions, inhibiting the active catalytic assembly and decreasing catalysis without stopping the reaction (**Figure 2.17**). In this, 2a shows slightly different behavior. Anodic shift in the catalytic current with increasing acid concentration suggests that proton transfer precedes electron transfer, consistent with the proton-coupled electron transfer (PCET) mechanism.



**Figure 2.17.** The proposed hydrogen bonding interactions between **2a-c**, anilinium, and aniline.

Again, the strong inhibitory effect of aniline points to competition for hydrogen-bonding interactions. Considering these results together, they suggest that 2a may proceed along two parallel pathways. One likely includes a neutral species, similar to 2b and 2c, where the pendant amines act as hydrogen-bonding directing groups. The second one likely includes a protonated form of 2a, which is only available at higher acid concentrations, and in this case, pendant amines function as true proton relays. These dual characteristics may explain why 2a reveals slightly higher catalytic activity than other complexes.

Despite these differences, all three complexes led to the following similar mechanisms. This is supported by the same rate law and the comparable kinetic isotope effect. While it is not wise to propose a complete mechanism in this context, the requirement for two proton transfer steps prior to the rate-determining step, along with the large KIE, strongly supports that hydrogen release is the rate-determining step (slow step).

Overall, these results show that extremely fast HER catalysis does not require classical proton relays. Well-positioned hydrogen-bonding interactions in the secondary coordination sphere can be sufficient to achieve rates approaching the diffusion limit. However, these interactions are sensitive to disruption by competing hydrogen-bond acceptors, such as aniline, which must be considered when designing the catalyst.

Catalyst stability also depends on the reaction conditions. When pTSA was incorporated as the proton source, the Pd systems showed slower heterogeneous species. In comparison, the weaker acid, anilinium tetrafluoroborate, enabled homogeneous catalysis and operated at higher rates. The difference mainly depends on the calixpyrrole's susceptibility to protonation under strongly acidic conditions, especially at the pyrrolide donors. Though ligand hydrolysis appears unlikely based on stability studies, the basic nature of the ligand limits its compatibility with very strong acids. Ongoing studies are exploring how proton source pKa influences catalytic behavior.

## 2.8. Conclusions

In summary, 2a-c, Pd complexes are highly active homogeneous electrocatalysts for the HER in the presence of anilinium tetrafluoroborate. They show first-order dependence on catalyst concentration and second-order dependence on acid concentrations. Altogether, third-order and large H/D kinetic isotope effects (5.2, 4.2, and 5.4 for 2a, 2b, and 2c, respectively) show that hydrogen release is the rate-limiting step.

The catalytic rates found are exceptionally high, with high TOFs values of  $4.65 \times 10^6 \text{ s}^{-1}$ ,  $4.19 \times 10^6 \text{ s}^{-1}$ , and  $3.09 \times 10^6 \text{ s}^{-1}$  for 2a, 2b, and 2c, respectively. These values exceed those of previously reported HER catalysts by more than an order of magnitude and approach the diffusion-controlled limit. Controlled potential electrolysis experiments further show high Faradaic efficiencies (97.7% for 2a, 95.7% for 2b, and 95.3% for 2c), along with good catalyst stability.

These findings highlight the importance of ligand design for achieving high catalytic performance. The rigid calixpyrrole structure ensures that pendant functional groups remain properly positioned relative to the metal active center, eliminating the negative effects of conformational flexibility. At the same time, hydrogen-bonding interactions between the catalyst and the proton source play an important role in enhancing catalytic efficiency.

Most importantly, this research shows that proton shuttles are not the only way to get fast HER. Under optimum conditions, hydrogen bonding interactions can also show similar performance. While the overpotentials remain high, the calixpyrrole framework provides a strong foundation for future modifications. Future modifications may focus on tuning the electronic properties of the systems, such as incorporating charged groups to reduce overpotential.

Overall, complexes 2a-c demonstrate that carefully designed ligand frameworks can facilitate enzyme-like performance in homogeneous HER catalysis and open a new era of possibilities for advancing next-generation electrocatalysts.

## **2.9. Experimental part**

### **2.9.1. General Considerations.**

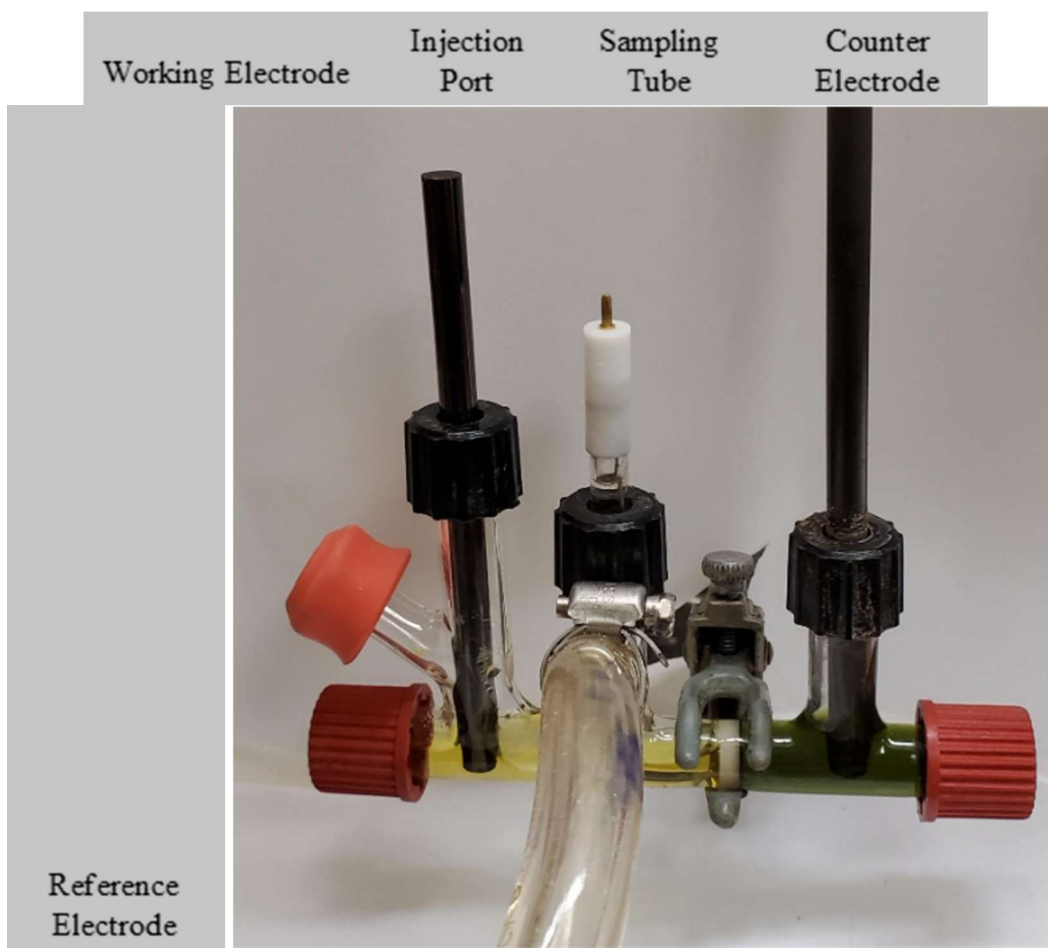
All procedures and manipulations were performed under a nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using an LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. Complexes **2a-c** and anilinium tetrafluoroborate-*d*<sub>3</sub> were synthesized according to literature procedures and spectroscopic characterization matched reported data.<sup>12,15</sup> All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. NMR spectra were recorded at ambient temperature and pressure using a Bruker 400 MHz spectrometer (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C, and 61 MHz for <sup>2</sup>H) or a Bruker 600 MHz spectrometer (600 MHz for <sup>1</sup>H and 151 MHz for <sup>13</sup>C). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane (TMS). Cyclic voltametric measurements were recorded using a Bio-Logic model SP-50 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer (-30 °C). The working electrode was a glassy carbon electrode or a mercury pool electrode; the reference electrode was a Ag/AgNO<sub>3</sub> non-aqueous electrode (0.01 M in CH<sub>3</sub>CN with 0.1 M TBAP); and a platinum

wire or graphite rod was used as the counter electrode. The glassy carbon electrode was polished with 0.05  $\mu\text{m}$  alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature under an argon or nitrogen atmosphere and processed using EC-Lab V11.21. Ohmic drop was accounted for using the current interrupt method available in EC-Lab V11.21. Reported half-wave potentials were referenced to the  $\text{Fc}/\text{Fc}^+$  redox couple by adding high purity ferrocene to the sample solution. Controlled potential electrolysis experiments were also performed with a Biologic SP-50 model potentiostat and processed using EC-Lab V11.21. The working electrode was a 6 mm glassy carbon rod, the counter electrode was a 6 mm graphite rod, and the reference electrode was a 0.01 M  $\text{Ag}/\text{AgNO}_3$  non-aqueous electrode (0.01 M in  $\text{CH}_3\text{CN}$  with 0.1 M TBAP). The amount of hydrogen produced was quantified using an ATO Inc. model ATO-SKY2000- $\text{H}_2$  handheld gas detector (0 to 500 ppm) and a calibration curve derived from known volumes of ultra-high purity hydrogen gas (Airgas).

**2.9.2. Electrocatalytic  $\text{H}_2$  evolution.** The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte in acetonitrile, 0.05 mM to 0.25 mM of **2a**, **2b**, or **2c**, 1 to 1400 equivalents of anilinium tetrafluoroborate (0.25 mM to 0.35 M), and scan rates between 800 mV/s to 70 V/s. The three-electrode setup consisted of a glassy carbon working electrode or mercury pool electrode, a platinum wire or graphite rod counter electrode, and a 0.01 M  $\text{Ag}/\text{AgNO}_3$  reference electrode. All CVs were referenced versus the  $\text{Fc}/\text{Fc}^+$  redox couple. All CVs were recorded under a nitrogen atmosphere in dry acetonitrile. For the “rinse” test results, the working electrode was removed from the cell following catalysis, rinsed with either acetonitrile or acetone solvent, and then placed in a fresh electrolyte solution without **2a**, **2b**, or **2c** present (0.1 M TBAP, 0.25 M anilinium tetrafluoroborate). To determine the kinetic isotope effect (KIE), anilinium tetrafluoroborate- $d_3$  (0.25 mM) in acetonitrile- $d_3$  was utilized (0.1 M TBAP, 0.25 mM **2a**, **2b**, or **2c**). For buffered solutions, a 1:1 mixture of 0.25 M anilinium tetrafluoroborate and 0.25 M aniline were used (0.1 M TBAP, 0.25 mM **2a**, **2b**, or **2c**).

**2.9.3. Controlled potential electrolysis.** The glassy carbon working electrode was placed into a sealed bulk electrolysis cell filled with a solution of 0.1 M TBAP in acetonitrile, 0.25 mM **2a**, **2b**, or **2c**, and 0.25 M anilinium tetrafluoroborate, along with a 0.01 M

Ag/AgNO<sub>3</sub> reference electrode (**Figure 2.18**). The graphite counter electrode, separated by a porous frit, was submerged in a solution of 0.1M TBAP in acetonitrile and 0.25 M ferrocene. Bulk electrolysis experiments were carried out at a controlled potential of -2.2, -2.3, or -0.24 V vs. Fc/Fc<sup>+</sup> for **2a**, **2b**, or **2c**, respectively, until 0.5 C of charge was passed. The solution in the cell was then stirred for 1 hour to ensure equilibration between the solvent and headspace before sampling.



**Figure 2.18.** Image of the electrolysis cell utilized for controlled potential electrolysis after 0.5 C of charge had been passed.

### 2.3.0. Sample Calculations

Overpotential Calculations<sup>34,20,21</sup>

$$\text{Overpotential} = [E_H^+ - E_{cat}]^{\frac{34}{2}}$$

$$\begin{aligned} E_H^+ &= -0.028V - 0.05961V * 10.62 [E_H^{+0} = -0.028V, pka = 10.62]^{20,21} \\ &= -0.6568V \end{aligned}$$

$$\begin{aligned}\text{Overpotential} &= -0.6568 - (-1.4454) \\ &= 0.789V\end{aligned}$$

Sample Turnover Frequency Calculation<sup>37</sup>

$$\frac{i_{\text{cat}}}{i_{\text{p}}} = \frac{n}{0.4463} \sqrt{\frac{RTk[H^+]^x}{Fv}}$$

$$k_{\text{obs}} = TOF_{\text{max}} = (1.94 \text{ V}^{-1})v \left( \frac{i_{\text{cat}}}{i_{\text{p}}} \right)^2$$

$$\begin{aligned}k_{\text{obs}} = TOF_{\text{max}} &= (1.94 \text{ V}^{-1})40 \left( \frac{11.53}{0.0477} \right)^2 \\ &= 4529041.271 \text{ s}^{-1}\end{aligned}$$

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# **Chapter 3. Stabilizing Hydrogen Evolution: Secondary Coordination Sphere Effects in Heterogeneous Nickel Calixpyrrole Electrocatalysts**

## **3.1. Abstract**

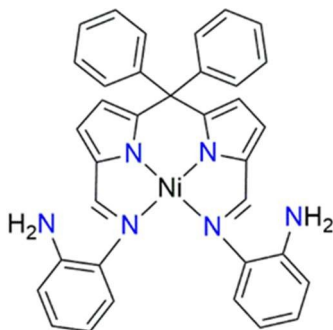
Supporting transition metal catalysts on electrode surfaces is a promising approach for developing next-generation electrocatalysts that retain molecular-level control in interfacial environments. More research is needed, however, to uncover the underlying principles governing the elementary steps of the hydrogen evolution reaction (HER) in these systems. In view of this, three nickel-based calixpyrrole complexes, 2a-c, were prepared; two of which (2a and 2b) had protected amines in the secondary coordination sphere, and one of which (2c) had no groups in the secondary coordination sphere. Electrochemical investigations using anilinium tetrafluoroborate as a mild proton source showed that all three systems are catalytically active for HER via a heterogeneous pathway, as evidenced by scan-rate dependence and rinse experiments. The inclusion of pendent amide and carbamate groups enhanced catalytical behavior resulting in lower overpotentials ( $0.83 \pm 0.03$  V for 2a,  $0.86 \pm 0.04$  V for 2b, and  $0.95 \pm 0.05$  V for 2c), higher turnover frequencies ( $17,700 \pm 700$  s<sup>-1</sup> for 2a,  $16,794 \pm 569$  s<sup>-1</sup> for 2b, and  $12,031$  s<sup>-1</sup> for 2c), and enhanced Faradaic efficiencies ( $95.9 \pm 0.02\%$  for 2a,  $95.6 \pm 0.05\%$  for 2b, and  $91.1 \pm 0.01\%$  for 2c). Based on the FE study, pendant groups (2a and 2b) showed high selectivity for hydrogen production and minimal catalyst degradation or side reactions. Mechanistic investigations confirmed a heterogeneous catalytic pathway and revealed that proton-coupled electron transfer (PCET) is involved in the rate-determining step, as supported by kinetic isotope effect (KIE) values of 4.9-5.6. This increased FE and enhanced catalytic behavior suggest that pendant groups play an important role in stabilizing the catalyst during HER, by reducing structural decomposition and suppressing competing pathways. The combination of enhanced stability and catalytic behavior, along with the use of an earth-abundant metal, signifies the nickel system for practical and scalable HER.

### 3.2. Introduction

Rapidly rising worldwide energy demand, coupled with escalating greenhouse gas emissions, has underscored the need for sustainable energy technologies to avoid the catastrophic consequences of rising global temperatures. While renewable power sources are currently available (solar panels, wind turbines, etc.), they are heavily dependent on geographic and temporal factors, which often create a mismatch between electricity generation and demand.<sup>1</sup> This has driven extensive research in the field of energy storage, particularly small molecule activation and the hydrogen evolution reaction (HER).<sup>2</sup> With zero carbon emissions and a wide variety of uses, hydrogen gas, H<sub>2</sub>, is both a clean fuel and a commodity chemical. Currently, the vast majority of H<sub>2</sub> is generated from hydrocarbons (mainly methane) through the steam reforming process.<sup>3</sup> Using an electrolysis cell to generate H<sub>2</sub> from a proton source like water would therefore be a promising solution to renewable energy storage, as well as a potential avenue for dramatically reducing greenhouse gas emissions in other areas.<sup>4</sup> One of the current barriers to the widespread application of these technologies, however, is a reliance on platinum-based catalysts.<sup>5</sup>

Taking inspiration from natural systems (specifically the active site of [FeFe]-hydrogenase), which can efficiently generate H<sub>2</sub> using earth-abundant metals,<sup>6-8</sup> a large number of synthetic HER catalysts have focused on placing proton shuttles in the secondary coordination sphere close to a catalytically active metal center.<sup>9</sup> Primary examples of this are the nickel diphosphacycloheptane electrocatalysts developed by Bullock and co-workers, which displayed turnover frequencies (TOFs) greater than 100,000 s<sup>-1</sup>.<sup>10-13</sup> There have also been examples, however, of small molecule activation catalysts with hydrogen bond donors/acceptors in the secondary coordination sphere (in place of proton shuttles) that exhibited enhanced catalytic efficiencies.<sup>14-29</sup> For example, Chang et al. found that catalytic rates were influenced by the location of hydrogen bond donors and acceptors within the secondary coordination sphere when investigating iron-based porphyrin CO<sub>2</sub> reduction catalysts.<sup>30</sup> As such, a fundamental question remains with respect to catalyst design and pendant groups: when are proton shuttles necessary, and when will hydrogen bond donors/acceptors suffice? Moreover, while there has been more extensive research on the effects of secondary coordination sphere in homogeneous systems, less is known about surface-supported heterogeneous species, especially with respect to utilizing pendant groups to influence small molecule activation reactions and control catalyst microenvironments. Therefore, more research is

needed to provide a deeper fundamental understanding of which directing groups are required to achieve high catalytic efficiency, especially in interfacial environments.



**Figure 3.1.** Structure of the nickel-based Schiff-based calixpyrrole HER electrocatalyst with pendant amine groups.

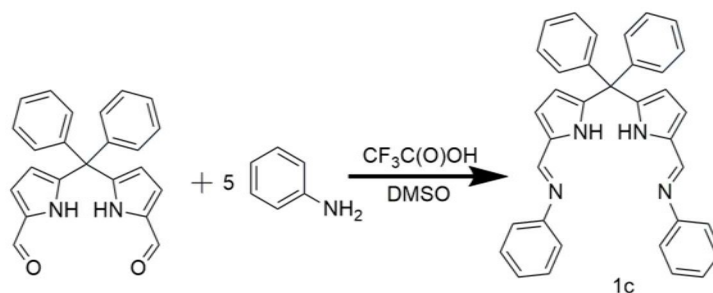
Recently, our group reported the synthesis and HER activity of a supported nickel calixpyrrole electrocatalyst with pendant amine groups (**Figure 3.1**).<sup>31</sup> The heterogeneous system displayed incredibly fast reaction kinetics with TOFs up to 25,900 s<sup>-1</sup> or 366,000 s<sup>-1</sup>·cm<sup>-2</sup>,<sup>31</sup> which were several orders of magnitude larger than known supported nickel diphosphacycloheptane catalysts,<sup>32-37</sup> and were even competitive with some of the fastest reported platinum nanoparticle catalysts.<sup>38</sup> Moreover, a proton-coupled electron transfer (PCET) process was found to be rate-limiting for the nickel calixpyrrole system, and evidence suggested that protonation of the pendant amine groups was key for enabling catalytic performance. Still, the question of whether intramolecular proton transfer from groups in the secondary coordination sphere was needed for HER lingers. Could proton transfer occur in an intermolecular process where hydrogen bond donors/acceptors in the secondary coordination sphere position the proton source through hydrogen bonding?

In this context, electrochemical properties, and catalytic performance of a selection nickel calixpyrrole complexes were examined. These species were modelled after the co-facial “pacman” complexes developed by Love and Sessler,<sup>39-47</sup> as well as the “hangman” porphyrins from the Nocera group.<sup>48-60</sup> The nickel systems that were investigated included calixpyrroles with protected amine groups in the secondary coordination sphere (which could not act as proton shuttles, but could function as both hydrogen bond donors and acceptors), as well as an analogue with no pendant functionalities. With respect to nomenclature, throughout this paper the calixpyrrole ligands (1) will be named according to their pendant groups (a for acyl; b for tert-butoxycarbonyl

or Boc; and c for no pendant groups), while the nickel complexes will be named according to the bound calixpyrrole ligand (2a-c for 1a-c, respectively).

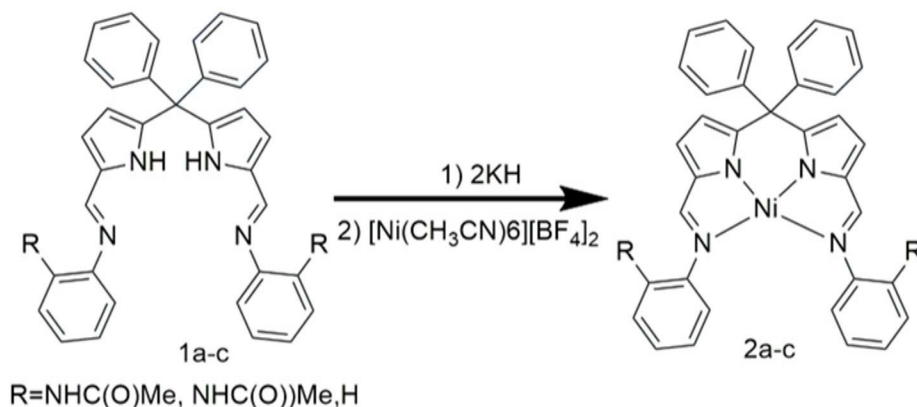
### 3.3. Synthesis

Compound 1c (**Scheme 3.1.1**) was synthesized using an acid-catalyzed Schiff-base reaction, in a similar manner reported for 1a and 1b<sup>61</sup>



**Scheme 3.1.1** General synthetic procedure for generating calixpyrrole ligand 1c.<sup>61</sup>

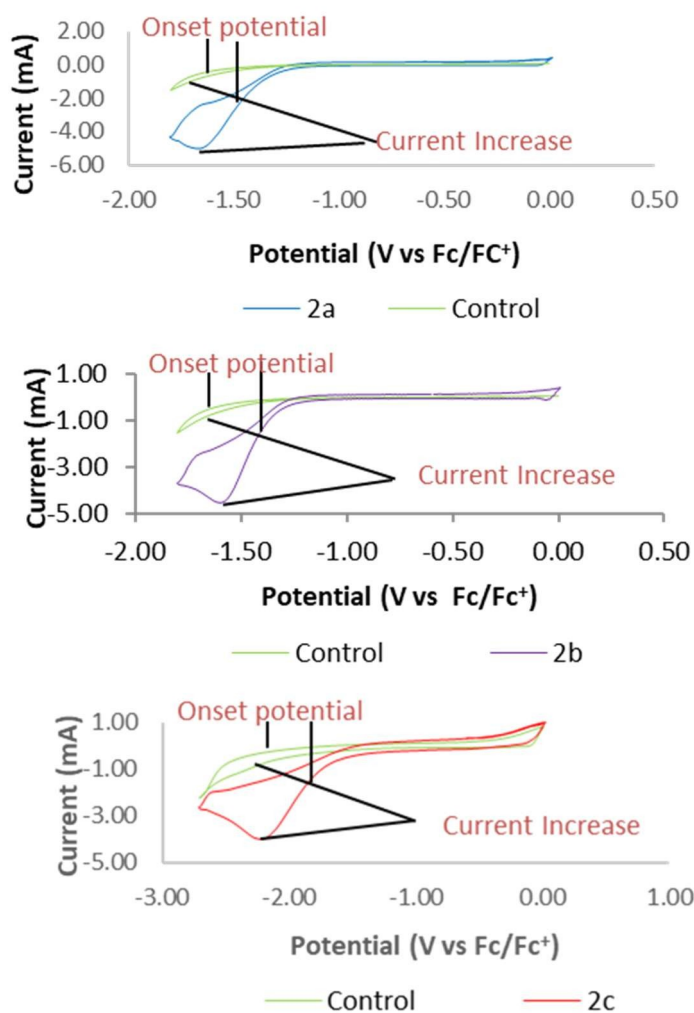
One equivalent of 5,5'-diformyl-2,2'-diphenyldipyrromethane was combined with excess aniline in the presence of catalytic amounts of trifluoroacetic acid, and the resulting calixpyrrole ligand 1c was obtained as a brown/yellow solid in moderate yields (65%). Complexes 2a-c were synthesized using the same synthetic procedure developed for the previously reported nickel calixpyrrole HER electrocatalyst with pendant amine groups (**Scheme 3.1.2**).<sup>31</sup> The ligands were first deprotonated with two equivalents of KH and then combined with [Ni(CH<sub>3</sub>CN)<sub>6</sub>][BF<sub>4</sub>]<sub>2</sub> to generate the desired calixpyrrole complexes. The resulting orange or red solids could be isolated in moderate yields (54-65%).



**Scheme 3.1.2** General synthetic procedure for generating nickel-based calixpyrrole complexes 2a-c.

### 3.4. Electrochemical hydrogen evolution

The catalytic capacity of these three complexes towards HER was investigated using anilinium tetrafluoroborate ( $pK_a = 10.62$ ), a mild proton source. Their electrochemical activities were tested by cyclic voltammetry and were compared with anilinium tetrafluoroborate as a control in a glassy carbon electrode. In terms of onset potential (the potential at which the catalytic current begins to increase or shows catalysis) and the change in current amount (**Figure 3.2**), it was found that they are catalytically active for HER.



**Figure 3.2.** CVs of HER using **2a-c** (0.1 M TBAP, 0.25 mM catalyst, 0.25 M anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.0 1M Ag/AgNO<sub>3</sub> reference electrode, scan rate = 800 mV/s).



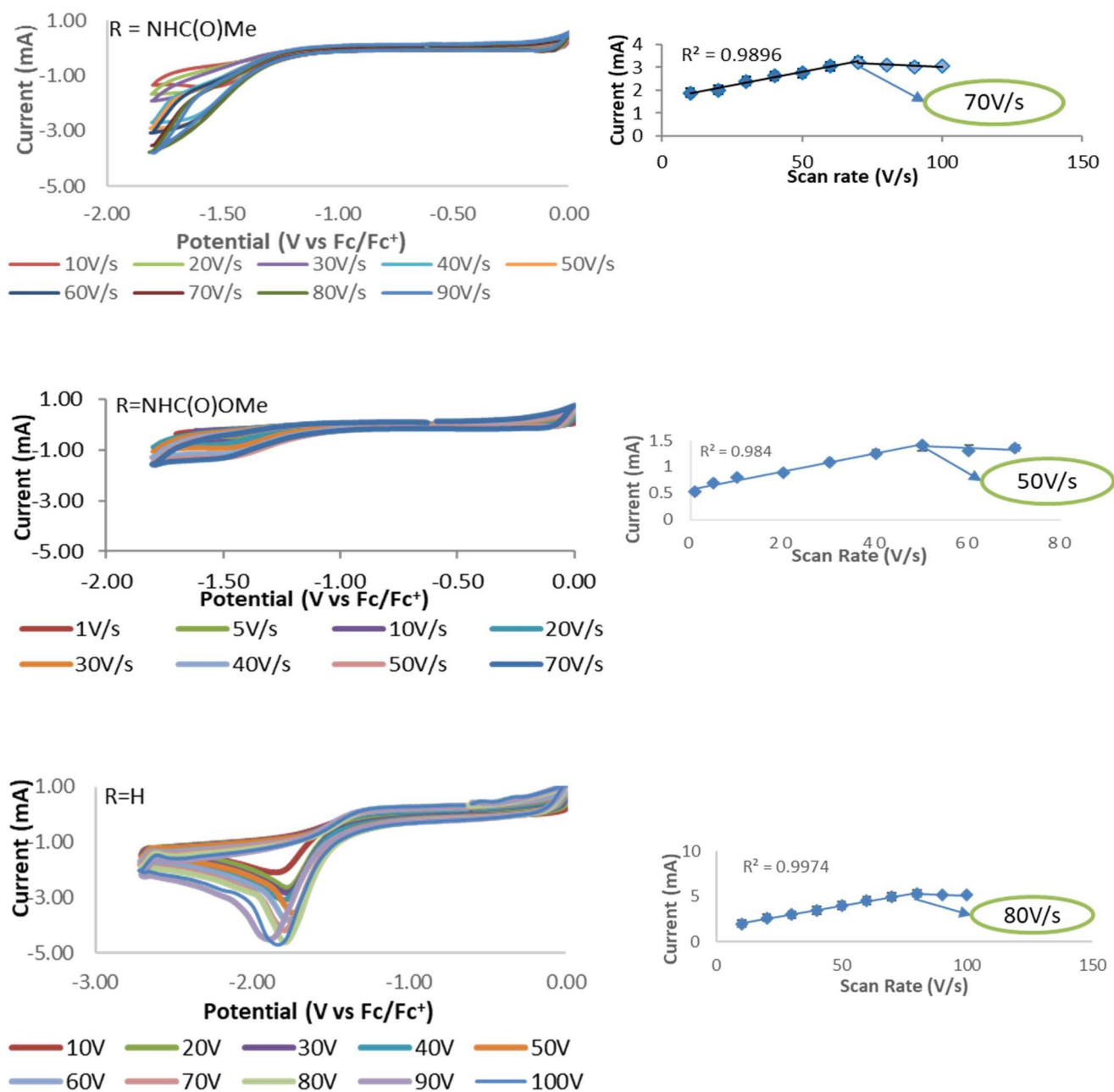
The onset of catalysis for the Ni complexes 2a-c showed a more positive potential than the glassy carbon control and an increasing current, meeting the requirement for HER electrocatalysts. An irreversible catalytic current ( $i_{cat}$ ) was apparent, indicative of electrocatalytic HER.

### **3.5. Kinetic evaluation**

#### **3.5.1. Scan Rate Dependence**

After checking the catalytic capacity of **2a-c**, kinetic evaluations were done.

To determine the nature of the catalysis, the scan rate dependence of HER with 2a-c was examined. From **Figure-3.3**, different scan rates have been used and the catalytic currents changed according to scan rate was analyzed. It was observed that the change in catalytic current was directly proportional to the scan rate. Therefore, this suggested that the catalysts were heterogeneous in nature,<sup>55</sup> which was similar to the results obtained with Ni complexes with pendant amine in anilinium tetrafluoroborate as the proton source.<sup>31</sup>

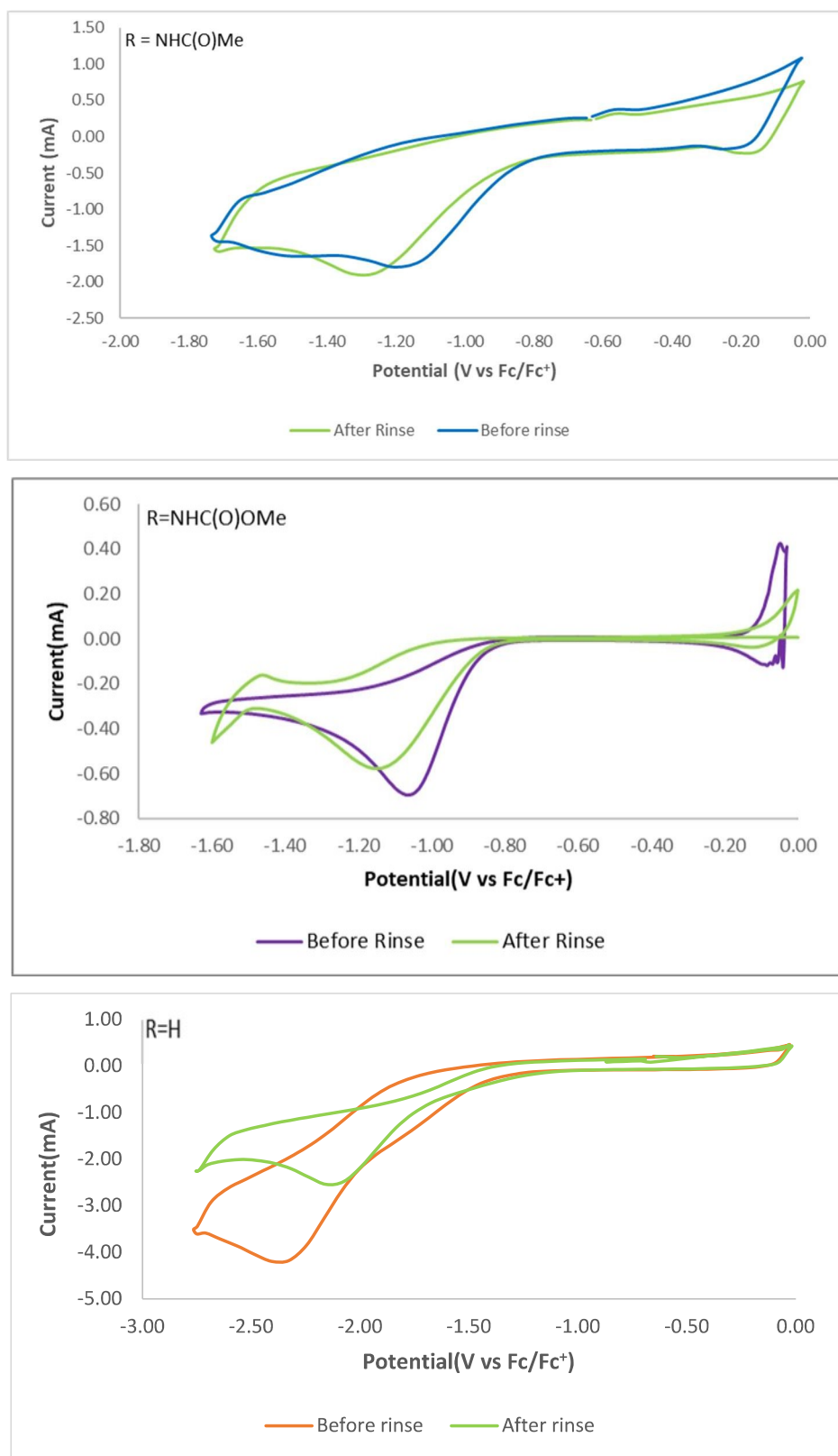


**Figure 3.3.** Catalytic CVs of HER in acetonitrile using different scan rates (0.1M TBAP, 0.25mM 2a-c, glassy carbon working electrode, platinum wire counter electrode, 0.01M AgNO<sub>3</sub> reference electrode) and General plot of catalytic current vs scan rate.

For these three systems, scan rate-dependent points were also observed. For the acyl-protected system, the scan rate independence point was 70V; for the Boc-protected system, 50V; and for the non-pendent system, 80V.

### 3.5.3. Rinse test

To confirm the heterogeneous nature of catalysis, rinse tests were performed for 2a-c. For a rinse test, if activity persists after catalysis and rinsing the working electrode, then catalysis is likely heterogeneous in nature <sup>62</sup>. For the experiments, first, a CV was performed with 0.25 mM of complex in acidic acetonitrile. Afterward, the working electrode was rinsed with TBAP solution in acetonitrile, and then another CV was performed with a fresh solution of acid in acetonitrile, without complex. From **Figure 3.4**, we can see that catalysis was present before and after rinsing, with high catalytic peak currents in both cases. This suggests that HER did work without complexes in solution, with catalysts deposited on the electrode surface, thus confirming their heterogeneous nature.

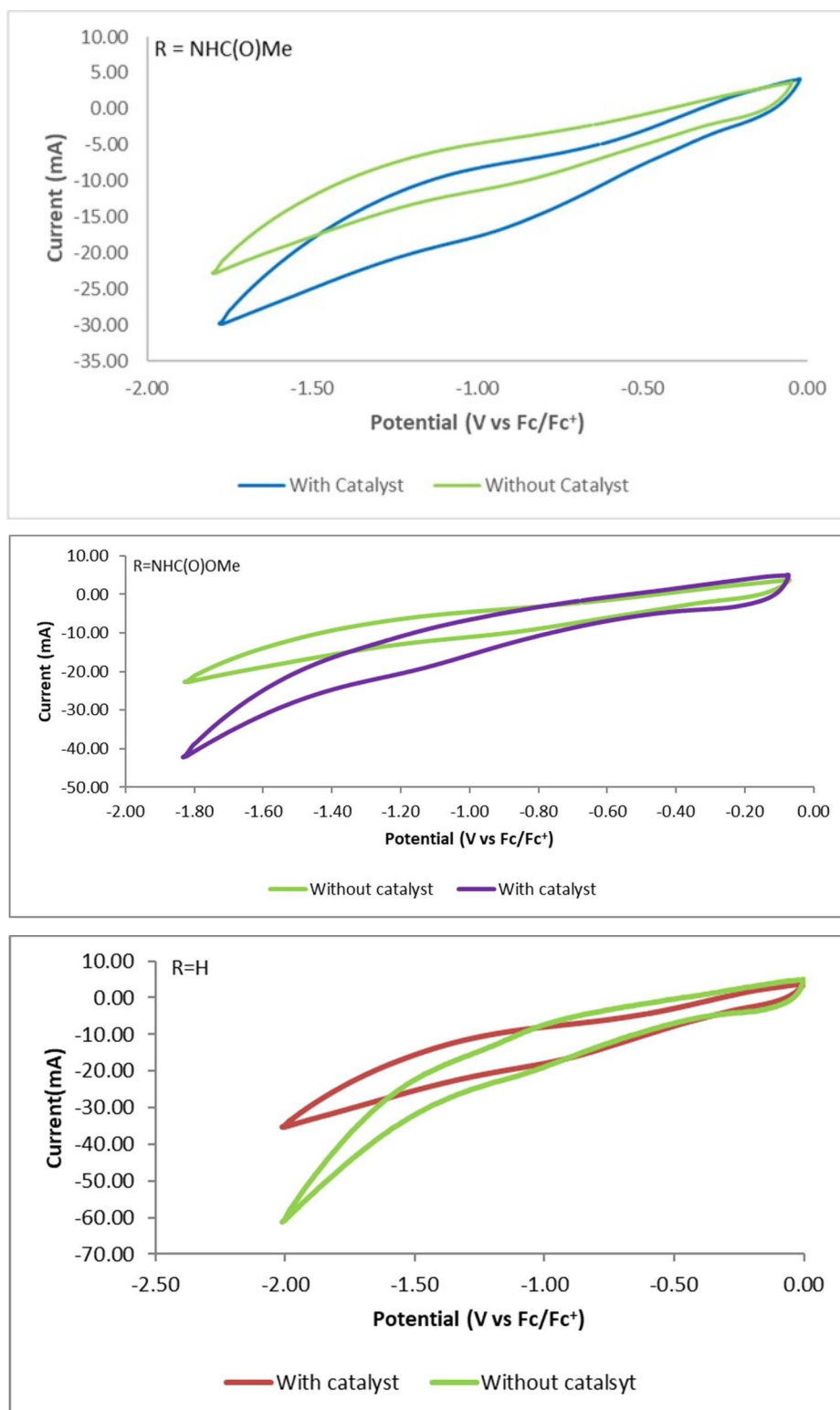


**Figure 3.4.** Rinse test results using acetonitrile as the rinsing<sup>3</sup>. media (0.1M TBAP in acetonitrile, 0 or 0.25mM of 2a-c, 0.25M anilinium tetrafluoroborate, glassy carbon working

electrode, platinum wire counter electrode, 0.01 M Ag/AgNO<sub>3</sub> reference electrode, scan rate= 800 mV/s)

### 3.5.3. Mercury Pool Test

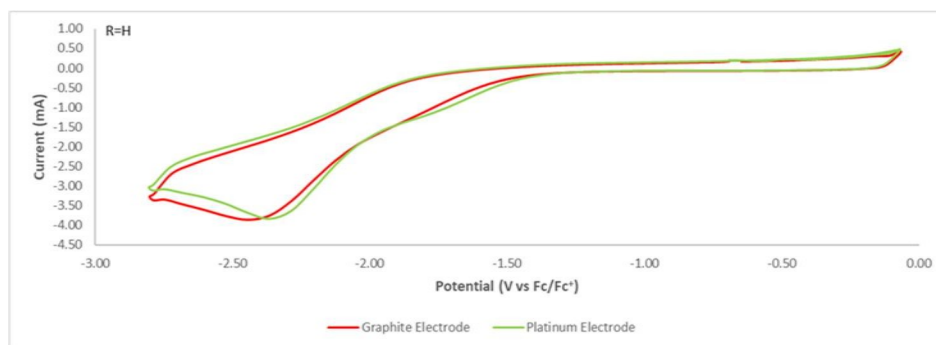
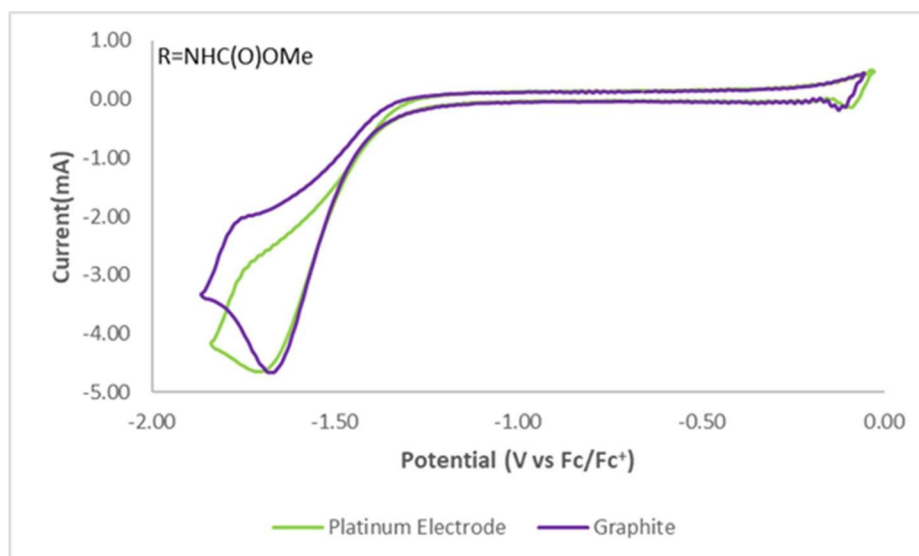
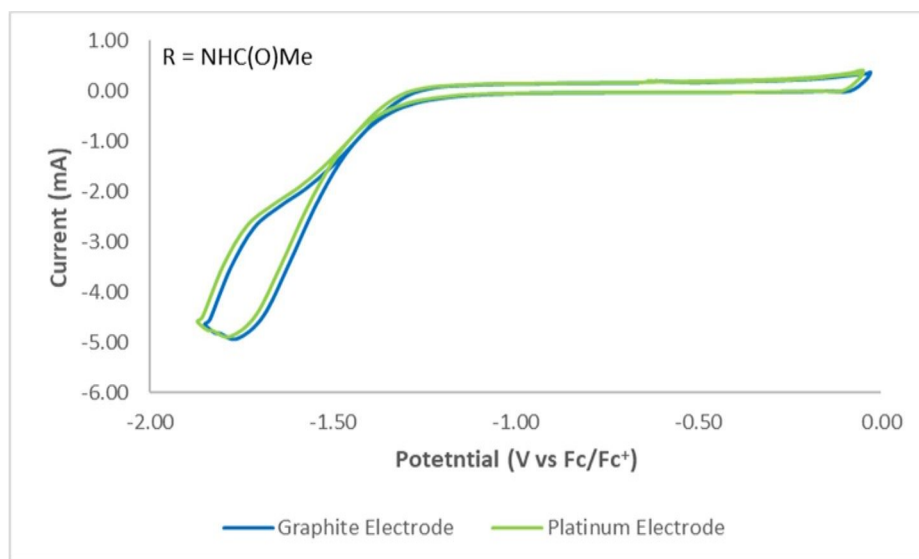
Mercury pool tests were also performed to assess whether soluble nanoparticles formed during HER. In a mercury pool test, the mercury pool serves as the working electrode. The idea is that if there were nanoparticles catalyzing HER, they would be deactivated by forming an amalgam with the mercury electrode or by adsorption onto the mercury electrode, thereby inhibiting catalysis.<sup>63,64</sup> From **Figure 3.5**, we can see that catalysis remained present and was not inhibited. These further supports that there was no nanoparticle formation.



**Figure-3.5** CVs of the mercury pool tests for HER using 2a-c (0.25mM or 0mM) in acetonitrile (0.1M TBAP, 0.25M anilinium tetrafluoroborate, mercury pool working electrode, platinum wire counter electrode, scan rate=scan rate independence point)

#### 3.5.4. Counter electrode impact

For all of the CVs discussed so far, platinum wire was used as the counter electrode. We know that platinum is considered as the benchmark catalyst for HER, so it is important to perform a control reaction to determine if there is an impact from the platinum counter electrode. Therefore, to check that, the counter electrode is not contributing to the catalytic current, a graphite electrode was also used as the counter electrode.<sup>61</sup> All the conditions were kept the same, such as 0.25mM of 2a-c in acetonitrile, 0.1M TBAP as the supporting electrolyte, glassy carbon was used as the working electrode, and Ag/AgNO<sub>3</sub> was used as the reference electrode. From **Figure-3.6**, CV plots both with and without a platinum wire counter electrode were similar. This means there was no impact from the platinum electrode; our catalysts 2a-c were actually performing as catalysts.

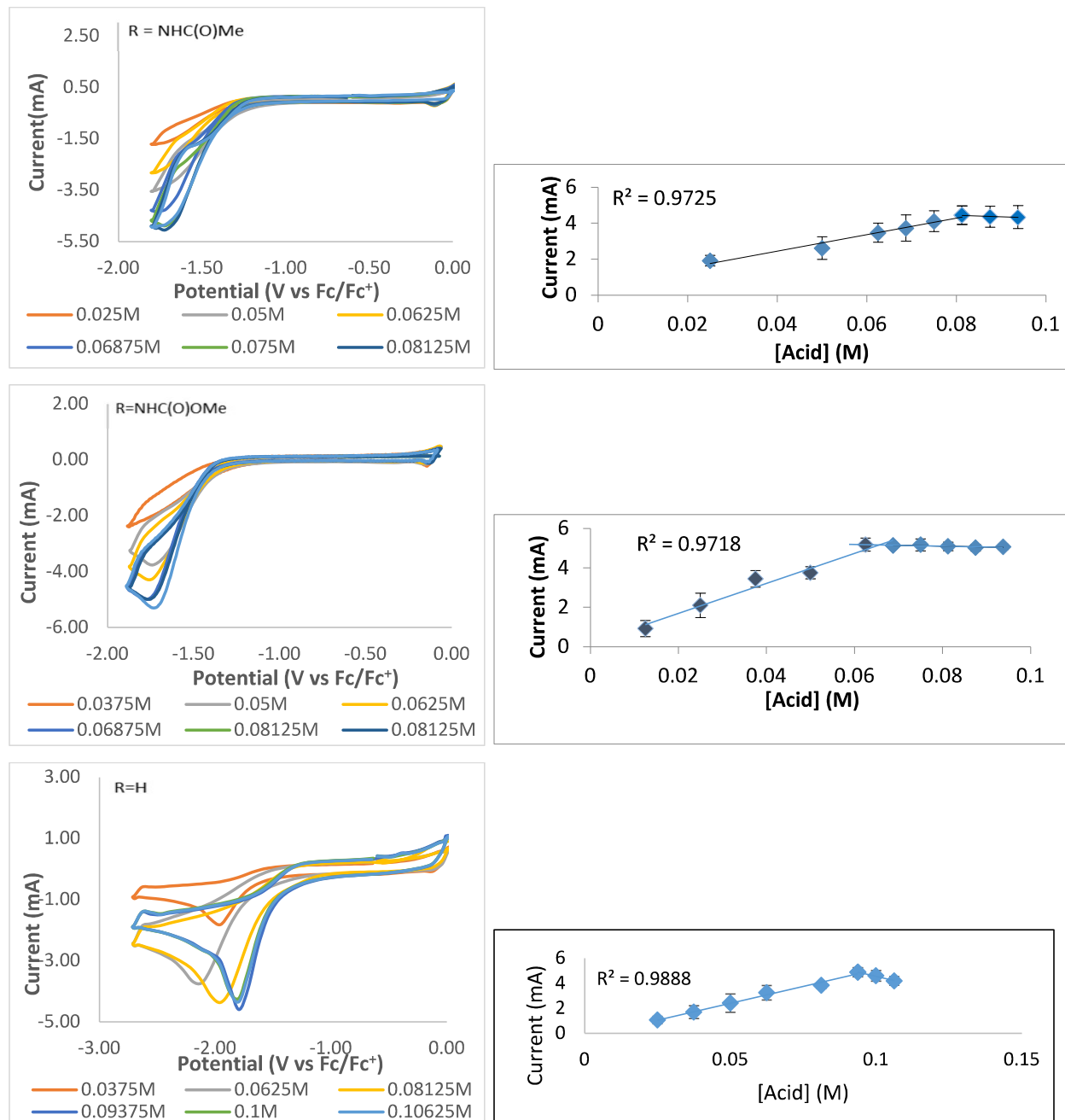




**Figure-3.6** CVs of 2a-c(0.25mM) in acetonitrile using platinum wire and graphite rod as the counter electrode (0.25M anilinium tetrafluoroborate, glassy carbon working electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=scan rate independence point)

### 3.5.5. Acid Dependence:

The acid dependence of HER using 2a-c was also examined, and different concentrations of anilinium tetrafluoroborate were used (**Figure 3.7**)

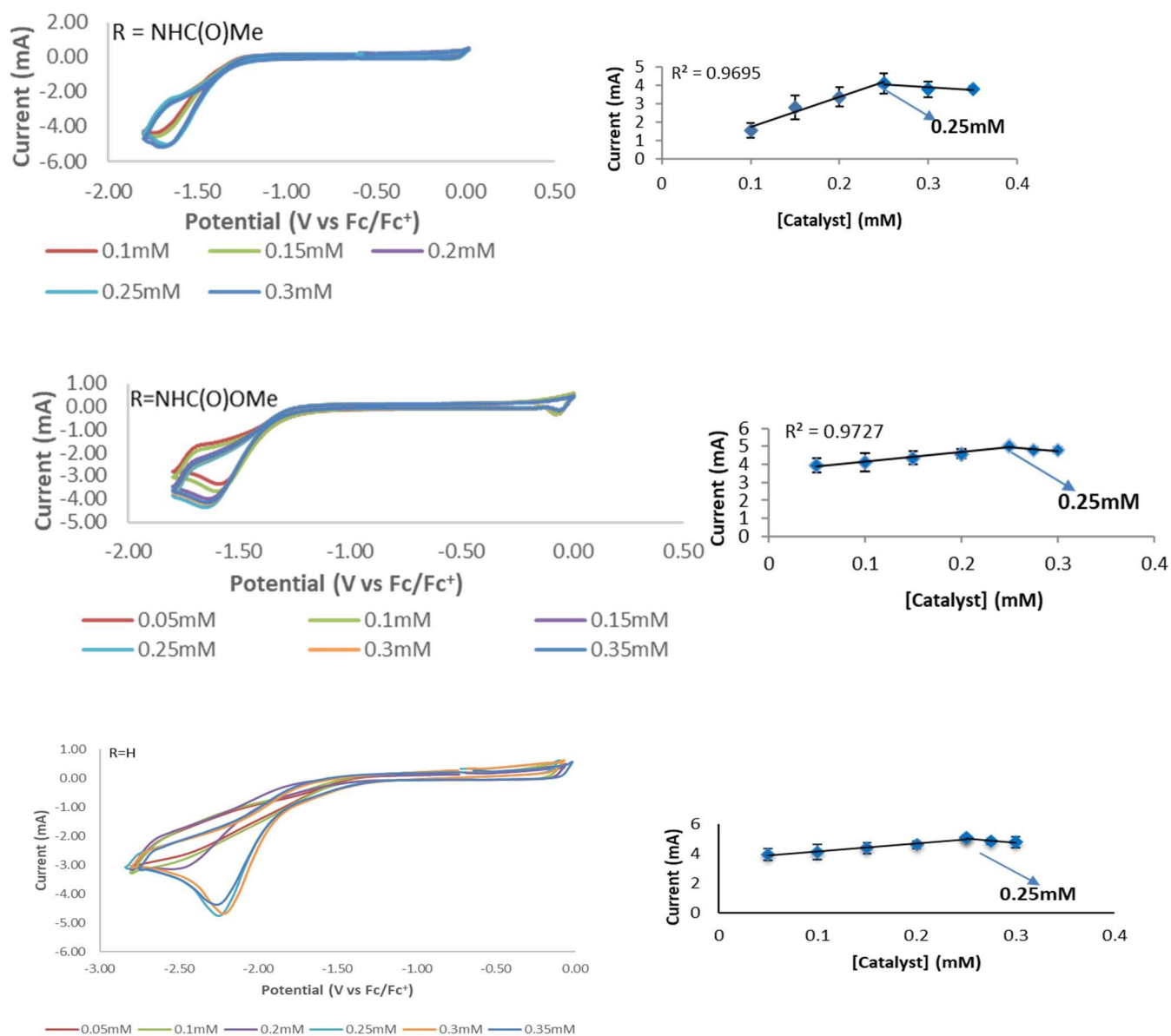


**Figure-3.7** (a) CVs with different acid concentrations (anilinium tetrafluoroborate) using 2a-c(0.25mM) in acetonitrile, (glassy carbon working electrode, platinum wire electrode, 0.01M AgNO<sub>3</sub> reference electrode, scan rate-scan rate dependence point)  
(b) General plot of catalytic current vs acid concentration.

The acid independence point for hydrogen evolution was found to be around 0.08125 M for the acyl group, 0.06875 M for the Boc group, and 0.09375 M for the non-pendant group. Catalytic current was found to increase linearly with acid concentration (**Error! Reference source not found.**). They showed first-order kinetics with respect to acid concentration. This gives idea that rate determining step can be Volmer or Heyrovesky step.<sup>65-67</sup>

### 3.5.6. Catalyst Dependence

The catalyst dependence for HER using 2a-c was also investigated at concentrations ranging from 0.05 mM to 0.35 mM. From **Figure 3.8**, it can be observed that the catalytic current was linearly dependent on catalyst concentration, which means that the reaction was first order in catalyst. Above 0.25 mM of catalyst, the current vs concentration graph plateaued, indicating that the electrode surface becomes saturated at that concentration.



**Figure-3.8** (a, graphs on the left) CVs with different concentrations of Pd complexes 2a-c (0.05mM to 0.35mM) in acetonitrile (0.25M anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=scan rate independence point), (b, graphs on the right) General plot of catalytic current vs concentration of catalyst

### 3.5.7. Catalytic evaluation parameters

For calculating TOF,<sup>69-70</sup> the surface area coverage of the adsorbed species was first required to know, and it was calculated using the following equation:

$$i_p = \frac{n^2 F^2}{4RT} \nu \Gamma^* \quad (1)$$

where  $i_p$ ,  $n$ ,  $F$ ,  $R$ ,  $T$ ,  $\nu$ , and  $\Gamma^*$  are the peak current of the adsorbed species in the absence of acid, the number of electrons transferred (estimated to be 1 for the observed redox couple), Faraday's constant, the ideal gas constant, the temperature, the scan rate, and surface area coverage of the electrode, respectively. With this value in hand, the TOF was calculated using the following equation:

$$TOF = \frac{j}{nF\Gamma^*} \quad (2)$$

where  $j$  and  $n$  are the catalytic current density and the number of electrons transferred (2 for hydrogen evolution). Using this formula,<sup>69-70</sup> the TOFs were found to be  $17,700.031 \pm 700 \text{ s}^{-1}$  for 2a acyl group,  $16794.021 \pm 569 \text{ s}^{-1}$  for 2b, Boc group and  $12031.68 \text{ s}^{-1}$  for 2c, non-pendent group. These higher reactions kinetics values compared to non-pendent group show the importance of having pendent groups in HER and these values for pendent groups are larger than literature known nickel diphosphacycloheptane catalysts.<sup>32-37</sup> Moreover, when these heterogeneous catalysts are compared with few examples from literature such as the fastest reported platinum nanoparticles (TOFs of  $1500$  to  $9000 \text{ s}^{-1}$ ),<sup>38</sup> these pendent systems showed better activities.

After achieving the acid independence point and standard conditions of HER, these heterogeneous catalysts showed catalysis at  $0.83\text{V} \pm 0.03\text{V}$  for acyl group,  $0.86\text{V} \pm 0.042\text{V}$  for boc group and  $0.95\text{V} \pm 0.053\text{V}$  for non-pendent group. These overpotentials again showed the significance of pendent groups but for pendent groups also, the overpotential were high which is similar to known nickel-based catalysts,<sup>12</sup> and for this systems, less acidic source was used compared to literature one.

$$\text{Overpotential} = [E_H^+ - \frac{E_{cat}}{2}] \quad (3)^{73}$$

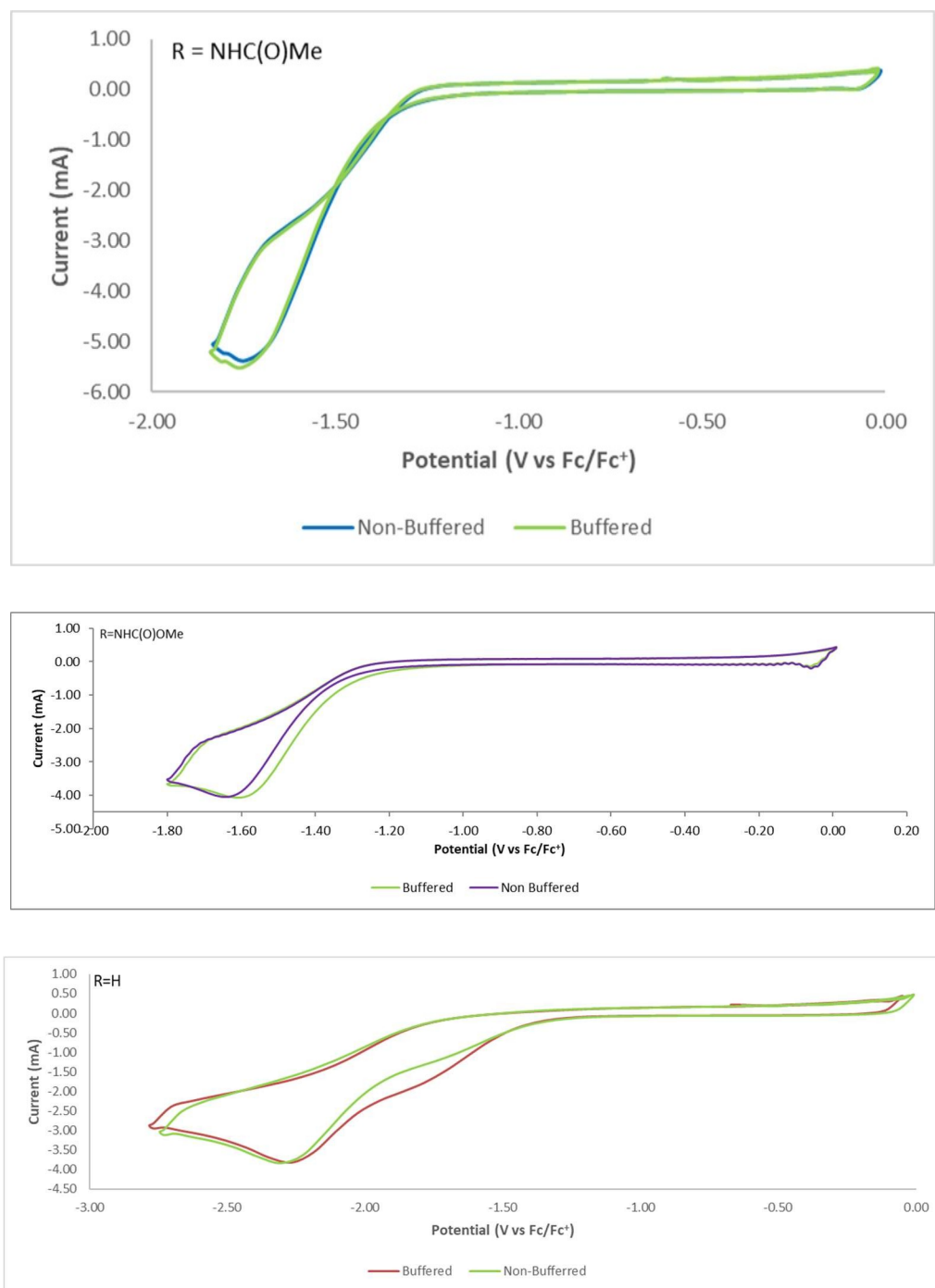
$$E_H^+ = E_H^{+0} - 0.05961V * pKa \quad [E_H^{+0} = -0.028V, pka = 10.62] \quad (4)^{71,72}$$

Controlled potential electrolysis (CPE) studies were also carried out using the Ni calixpyrrole complexes. The catalyst with pendant groups in the secondary coordination sphere once again

demonstrated the most desirable properties and displayed the highest faradaic efficiency (FE) of  $95.9\pm0.02\%$  for 2a, acyl group and  $95.6\pm0.05\%$  for 2b, boc group compared to non-pendent group,  $91.08\pm0.01\%$ . The pendent groups ensured maximum stability to maintain HER and that helps to get high reaction kinetics as they are not decomposed. They were not undergoing large structural changes during the catalytic cycle.

### 3.6. Mechanistic Studies:

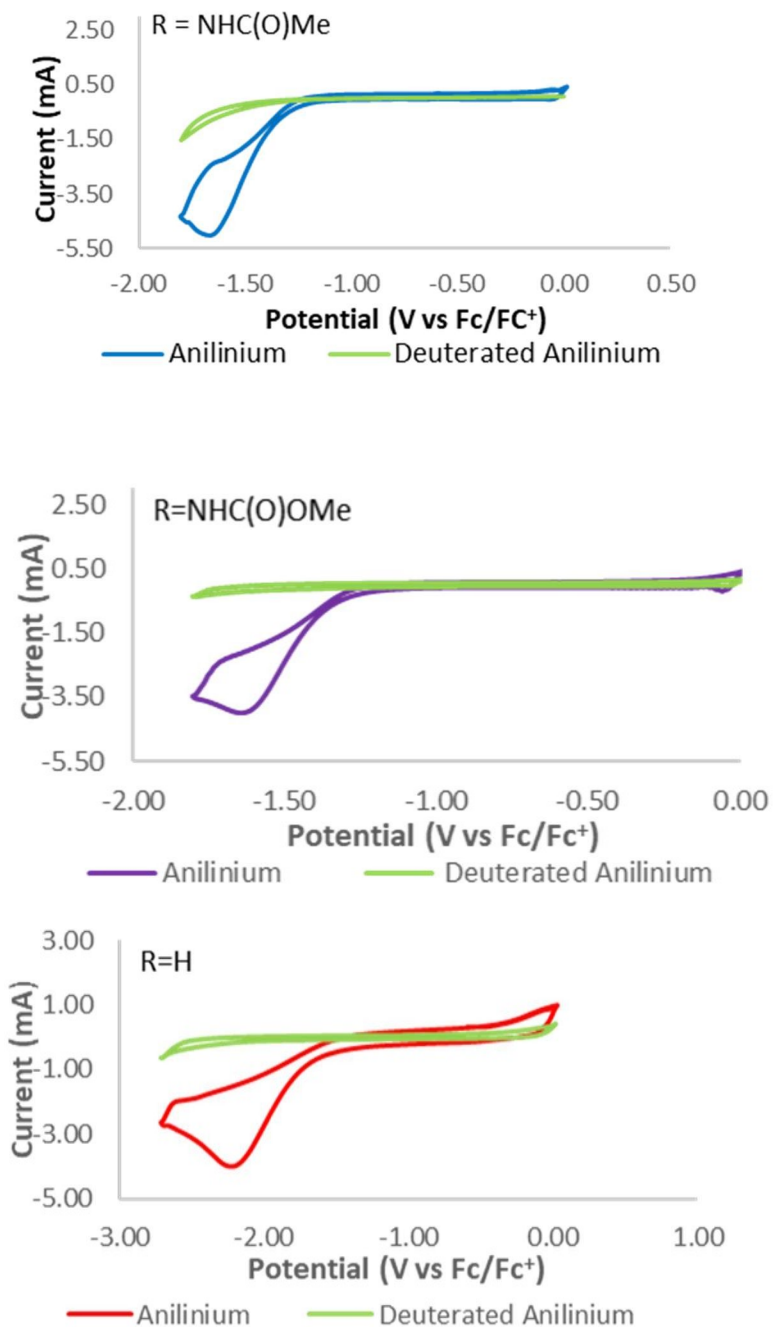
Whenever conducting HER in non-aqueous solvents, it is best practice to perform a control experiment using a 1:1 buffer solution of the acid being utilized and its conjugate base in order to rule out homoconjugation or pairing effects, which increase the apparent acidity of the proton source in low dielectric constant solvents. Homoconjugation or pairing effects of the proton source have also been investigated. As such, homoconjugation would be expected to lead to higher-than-expected catalytic rates and enhanced HER activity<sup>68</sup>. To test homoconjugation, a buffer solution containing a 1:1 ratio of aniline to anilinium tetrafluoroborate was used. (**Figure 3.9**) For buffered solutions and non-buffered solutions, all three catalysts showed similar catalytic behavior, which means proton entrapment between aniline-anilinium conjugation will not happen.



**Figure-3.9** CVs of HER in buffered solution as well as without buffer solution ( 0.1M TBAP, 0.25mM of Ni complexes 2a-c, 1:1 of anilinium tetrafluoroborate as non-buffered solution, anilinium tetrafluoroborate and aniline as buffered solution, glassy carbon working electrode, platinum wire electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=scan rate independence point)

### 3.7. Mechanistic studies

To further probe the catalytic mechanism and the rate-determining step for the Ni calixpyrrole catalysts, kinetic isotope effect (KIE) studies were performed using anilinium- $d_3$  tetrafluoroborate as the deuterium source (**Figure 3.10**).



**Figure-3.10.** CVs of H/D (KIE) studies in acetonitrile (0.25 mM **2a-c**, 0.25M anilinium or deuterated anilinium tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode, scan rate=Scan rate independence point)

For **2a**, **2b**, and **2c**, H/D KIE values of  $5.6 \pm 0.09$ ,  $5.31 \pm 0.065$ , and  $4.90 \pm 0.08$  were obtained, respectively. These results provided strong evidence that proton/deuteron transfer is involved in the rate-determining step for these catalysts. Furthermore, such large values may indicate PCET processes. A very similar KIE of 5.7 was seen for the nickel analog of **2a**, which was thought to proceed through a rate-limiting PCET nickel-hydride formation step. The rate law for the nickel species was found to be first order in acid concentration. So, PCET nickel hydride formation will be the rate-limiting step.

### 3.7. Mechanistic implications

A careful observation of the nickel based calixpyrrole systems signifies the pendent groups in secondary coordination sphere in controlling electrocatalytic HER behavior. In this work, Ni compounds with pendent amide and carbamate groups were compared with analogous systems without pendent groups, showing visible trends in catalytic behavior.

The inclusion of pendent groups enhances catalytic activity across various parameters. Pendent groups containing Ni complexes showed lower overpotentials and higher turnover frequency in comparison to non-pendent counterparts. This revealed that pendant groups facilitate efficient proton delivery or stabilization of intermediates during HER. It also means that pendant groups can control the local environment around the metal center via hydrogen-bonding interactions with the proton source. By positioning the acid close to the active site, these interactions facilitate more efficient proton transfer, thereby increasing overall catalytic capacity.

The most important observation is the higher faradaic efficiencies observed for the pendant groups. The higher FE indicates greater selectivity for HER and suggests enhanced catalytic stability under standard HER conditions. On the contrary, non-pendant groups suffer from side reactions, catalyst decomposition, or deactivation pathways, which reduce catalytic efficiency.



Compared with previously reported Ni systems with pendant amine groups, the amide and carbamate groups still provide substantial benefits, even though they are less basic and do not participate in proton shuttling. Though the pendant amine system showed higher TOF due to proton shuttling than amide and carbamate, it still showed comparatively higher reaction kinetics than known Nickel diphosphacycloheptane catalysts. This shows that strong proton-relay behavior is not strictly required for high catalytic activity. Intermolecular proton transfer can also enhance catalytic efficiency. So, hydrogen bonding and proper positioning of the proton source play a dominant role.

An important difference of the Ni system is its nature with a mild proton source, anilinium tetrafluoroborate, compared to Pd calixpyrrole systems, where the Ni system shows heterogeneity in contrast to Pd calixpyrroles' homogenous nature. This shows a practical standpoint, as heterogeneity is more convenient for industrial applications due to its ease of separation, recyclability, and long-term operational stability.

Additionally, using Nickel instead of Pd further increases the practicality of the system. Ni is a more abundant and cost-effective metal than Pd, making it lucrative for large-scale applications. Together, the heterogeneous nature and the incorporation of cheap metals make the Ni calixpyrrole system an important pathway for scalability in HER.

Overall, these findings revealed that the inclusion of pendant groups in the secondary coordination sphere is an important strategy for enhancing HER catalysis in nickel systems. By lowering overpotential, increasing TOF, and enhancing FE, these groups improve both the catalyst's activity and stability. Most importantly, this result suggests that carefully designed hydrogen-bonding interactions can be effective as a traditional proton shuttle, providing important insights for the future design of efficient and robust HER electrocatalysts.

### **3.8. Conclusions**

In summary, a series of nickel-based calixpyrrole systems was electrochemically evaluated for HER, with a focus on the importance of pendant groups in the secondary coordination sphere. Complexes with pendant amide and carbamate showed enhanced activities in catalytic behavior

compared to non-pendent groups, including lower overpotential, higher TOF, and increased Faradaic efficiencies.

The higher FE observed for the pendant groups indicated greater selectivity for HER and reduced contributions from competing side reactions or catalyst degradation. In contrast, the lower efficiency of the non-pendant group indicated reduced stability due to less controlled catalytic secondary coordination sphere and increased susceptibility to catalyst deactivation.

Mechanistic investigations showed that all three systems go through heterogeneous catalytic pathways in the presence of anilinium tetrafluoroborate. Kinetic studies indicated first-order dependence on acid and catalyst concentration, with large kinetic isotope effects supporting the idea of proton transfer in the rate-determining step, consistent with PCET pathways.

Another important point is that pendant groups enhance HER catalysis via hydrogen-bonding interactions, efficiently positioning the proton source near the active center. These results suggest that strong proton shuttle is not prerequisite for high HER efficiency. Instead, strategic design of the secondary coordination sphere to enable intermolecular hydrogen-bonding interactions can yield comparable catalytic activity. In addition, the heterogeneous nature of the Ni system under the HER conditions offers practical benefits for catalyst stability and scalability.

From the collective results, the use of Ni, a cheap and earth-abundant metal, further increased the system's relevance for industrial applications. The combination of improved catalytic behavior, operational stability, and economically feasible position makes these Ni compounds valuable platforms for sustainable, green HER. Overall, this research highlights secondary coordination-sphere modifications and valuable catalyst-design implications for the improvement of future HER electrocatalysts.

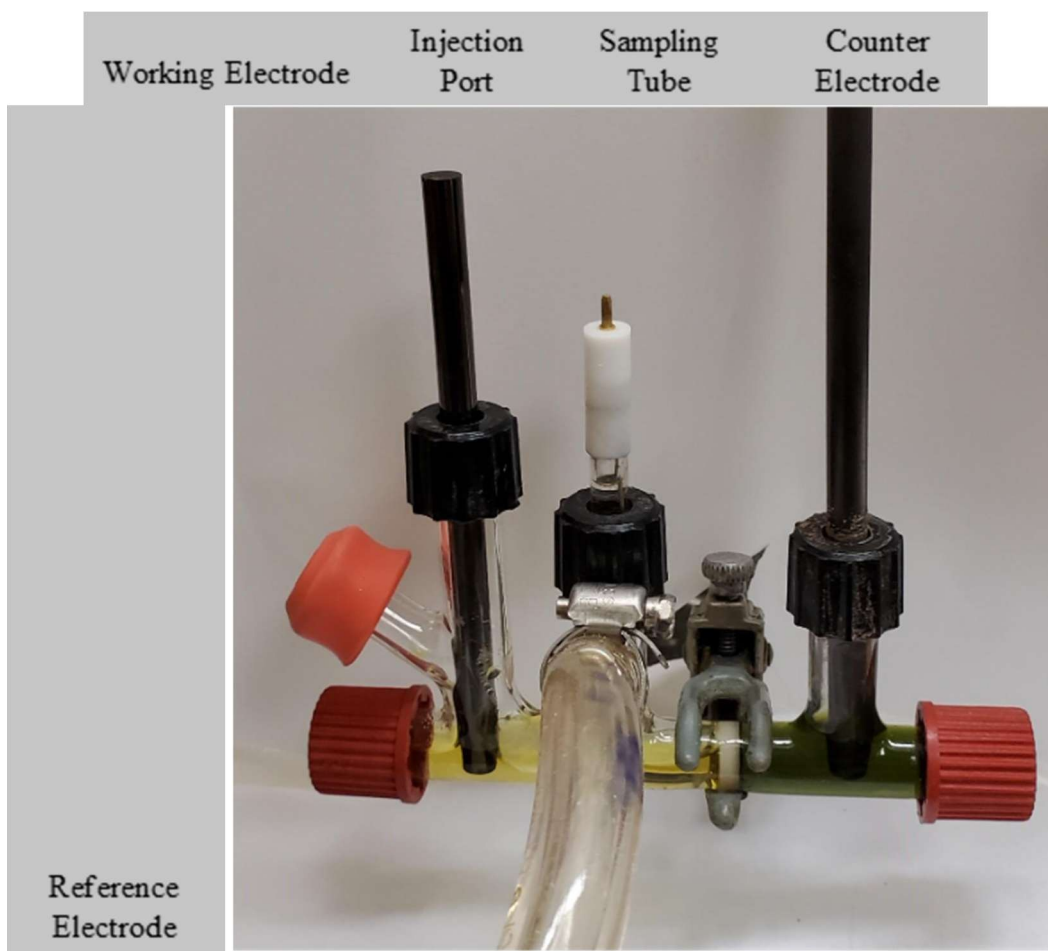
### 3.8. Experimental

**General Considerations.** All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using a LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under a nitrogen atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. **1a**, **1b** and  $[\text{Ni}(\text{MeCN})_6][\text{BF}_4]_2$  were synthesized according to literature procedures.<sup>61,74</sup> All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. Cyclic voltametric measurements were recorded using a Bio-Logic model SP-50 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer (-30 °C). The working electrode was a glassy carbon electrode; the reference electrode was a Ag/AgNO<sub>3</sub> non-aqueous electrode (0.01 M in CH<sub>3</sub>CN with 0.1 M TBAP); and a platinum wire was used as the counter electrode. The glassy carbon electrode was polished with 0.05 μm alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature under an argon or nitrogen atmosphere and processed using EC-Lab V11.21. Ohmic drop was accounted for using the current interrupt method available in EC-Lab V11.21. Reported half-wave potentials were referenced to the Fc/Fc<sup>+</sup> redox couple by adding high purity ferrocene to the sample solution.

**Electrocatalytic H<sub>2</sub> evolution.** The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte in acetonitrile, 0.05 mM to 0.25 mM of **2a**, **2b**, or **2c**, 1 to 400 equivalents of anilinium tetrafluoroborate (0.05M to 0.10625 M), and scan rates between 800 mV/s to 90 V/s. The three-electrode setup consisted of a glassy carbon working electrode or mercury pool electrode, a platinum wire or graphite rod counter electrode, and a 0.01 M Ag/AgNO<sub>3</sub> reference electrode. All CVs were referenced versus the Fc/Fc<sup>+</sup> redox couple. All CVs were recorded under a nitrogen atmosphere in dry acetonitrile. For the “rinse” test results, the working electrode was removed from the cell following catalysis, rinsed with either acetonitrile or acetone solvent,

and then placed in a fresh electrolyte solution without **2a**, **2b**, or **2c** present (0.1 M TBAP, 0.25 M anilinium tetrafluoroborate). To determine the kinetic isotope effect (KIE), anilinium tetrafluoroborate- $d_3$  (0.25 mM) in acetonitrile- $d_3$  was utilized (0.1 M TBAP, 0.25 mM **2a**, **2b**, or **2c**). For buffered solutions, a 1:1 mixture of anilinium tetrafluoroborate and aniline were used (0.1 M TBAP, 0.25 mM **2a**, **2b**, or **2c**).

**Controlled potential electrolysis.** The glassy carbon working electrode was placed into a sealed bulk electrolysis cell filled with a solution of 0.1 M TBAP in acetonitrile, 0.25 mM **2a**, **2b**, or **2c**, and anilinium tetrafluoroborate, along with a 0.01 M Ag/AgNO<sub>3</sub> reference electrode reference electrode (**Figure 3.11**). The graphite counter electrode, separated by a porous frit, was submerged in a solution of 0.1M TBAP in acetonitrile and ferrocene.



**Figure 3.11.** Image of the electrolysis cell utilized for controlled potential electrolysis after 1 C of charge had been passed.

### 3.9. Sample Calculations

Overpotential Calculations<sup>71-73</sup>

$$\text{Overpotential} = [E_H^+ - \frac{E_{cat}}{2}]^{73}$$

$$E_H^+ = -0.028V - 0.05961V * 10.62 \quad [E_H^{+0} = -0.028V, pka = 10.62]^{71,72}$$

$$= -0.6568V$$

$$\text{Overpotential} = -0.6568 - (-1.48061)$$

$$= 0.854V$$

Sample Turnover Frequency Calculation<sup>69-70</sup>

$$i_p = \frac{n^2 F^2}{4R} v \Gamma^* \quad (1)$$

$$TOF = \frac{j}{nF^*} \quad (2)$$

$$\Gamma^* = i_p * 4 * R * T / (n * n * F * F * V * A)$$

$$\Gamma^* = 0.1324 * 4 * 8.314 * 298 / (1 * 1 * 96485 * 96485 * 80 * 0.070686)$$

$$= 2.285 * 10^{-11}$$

$$TOF = 3.98 / (2 * 96485 * 0.070686 * 2.285 * 10^{-11})$$

$$= 12769 s^{-1}$$

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## **Chapter 4. Electrode-Associated Nickel Calixpyrrole Catalysts for Hydrogen Evolution: Influence of Proton Source Acidity**

### **4.1. Abstract**

The development of green, efficient electrocatalysts for the hydrogen evolution reaction (HER) poses a critical challenge in the pursuit of clean energy. In this context, a nickel-based calixpyrrole complex with pendant amine has been analyzed as a molecular electrocatalyst with heterogeneous characteristics. The catalyst was deposited on a glassy carbon electrode in the presence of anilinium tetrafluoroborate, generating a surface-associated electrocatalyst. The main goal was to assess the influence of proton-donor strength; the resulting surface-associated catalyst was analyzed using triethylammonium tetrafluoroborate as the proton source.

To probe the influence of proton-donor strength, the surface-bound catalyst was evaluated using triethylammonium tetrafluoroborate as external proton source. Electrochemical studies with this acid reveal that the catalytic current increases with increasing acid concentration and reaches a plateau beyond 0.075 M, indicating the onset of an acid-independent regime. Scan rate-dependent studies show a linear relationship between peak current and scan rate, consistent with a surface-confined catalytic process and supporting the formation of a heterogeneous, electrode-bound species.

Controlled-potential electrolysis confirms efficient hydrogen production, with a Faradaic efficiency of 95.3%, demonstrating high selectivity for hydrogen evolution. The catalyst operates with an overpotential of  $0.896 \pm 0.014$  V and achieves a turnover frequency (TOF) of approximately  $1775\text{ s}^{-1}$  under the studied conditions. The pendant amine functionalities are proposed to act as proton relays, facilitating proton-coupled electron transfer (PCET) and promoting efficient H–H bond formation at the nickel center.

In line with prior reports on surface-immobilized molecular catalysts, these findings suggest that interfacial confinement can influence catalytic pathways while retaining key molecular design features. This study highlights the effect of proton-donating strength on a surface-associated catalyst and provides insight into the interplay among proton availability, catalyst structure, and interfacial reactivity in HER electrocatalysis.

## 4.2. Introduction

The growing search for green, carbon-free energy sources has intensified research into hydrogen as a sustainable, clean fuel. Molecular hydrogen attracts attention in the energy carrier field for its high energy density and environmentally clean combustion, which generates only water as a byproduct<sup>1-3</sup>. However, hydrogen production on an efficient, industrial scale still faces significant challenges, especially due to dependence on noble-metal catalysts such as platinum.<sup>4</sup>

Inspired by the hydrogenase enzyme, significant research has focused on developing catalysts based on earth-abundant metals<sup>5-7</sup>. A key feature of these systems is the presence of pendant amines in the secondary coordination sphere, which facilitates proton delivery to the metal-active center via a proton-coupled electron transfer (PCET) mechanism.<sup>8-11</sup>

One significant example of earth-abundant metal-based synthetic hydrogen evolution electrocatalysts is Nickel diphosphacycloheptane, in which the inclusion of proton relays in the secondary coordination sphere showed that the pendant amine played a significant role in achieving high turnover frequencies (TOFs) exceeding 100,000 s<sup>-1</sup><sup>19-11</sup>

Beyond homogeneous systems, there has been rapid growth in research on translating molecular catalyst frameworks into electrode-based heterogeneous systems, as heterogeneous systems give well-defined active sites for catalysis and recyclability. Different strategies have been employed, such as covalent bonding, polymerization, and non-covalent adsorption.<sup>12-15</sup> From the work of Vincent Artero and coworkers, it has been found that nickel-based catalysts can be integrated into

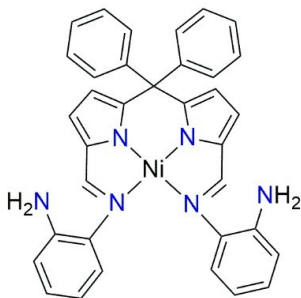
carbon-based materials to provide efficient hydrogen evolution systems.<sup>16-17</sup> Another notable work by Surendranath and co-workers demonstrated that molecular catalysts deposited on the electrode surface can exhibit different behavior, shifting from outer-sphere electron transfer to metal-surface reactivity, depending on the nature of electronic coupling between the electrode and the catalyst.<sup>18-</sup>

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After catalyst immobilization, another important topic in HER catalysis is the role of the proton source. A range of pKa values based on strength plays an important role in determining catalytic onset, rates, and mechanistic ideas<sup>20</sup>. Several studies have shown that acid strength influences the catalyst in solution, indicating that stronger acids activate catalysis at more anodic potentials, while weaker acids favor reduced intermediates.<sup>21</sup> Literature work by Artero and co-workers on cobalt and nickel has found that changing the proton donor can change catalytic pathways, including shifts between metal-centered and ligand-centered activity.<sup>22</sup>

Few studies have investigated how a catalyst associated with the electrode surface behaves in a proton source under otherwise identical conditions. These analyses can help determine whether the catalyst acts through intrinsic molecular properties or through interfacial effects at the electrode.

In this work, nickel-based calixpyrrole complexes bearing pendant amine groups have been selected as electrocatalysts (**Figure 4.1**). A previous literature study by Trowridge et al. found that Ni-calixpyrrole with a pendant amine, in the presence of anilinium tetrafluoroborate, behaves as a heterogeneous species deposited on a glassy carbon electrode.<sup>23-24</sup>



**Figure 4.1.** Structure of the nickel-based Schiff-based calixpyrrole HER electrocatalyst with pendant amine groups.

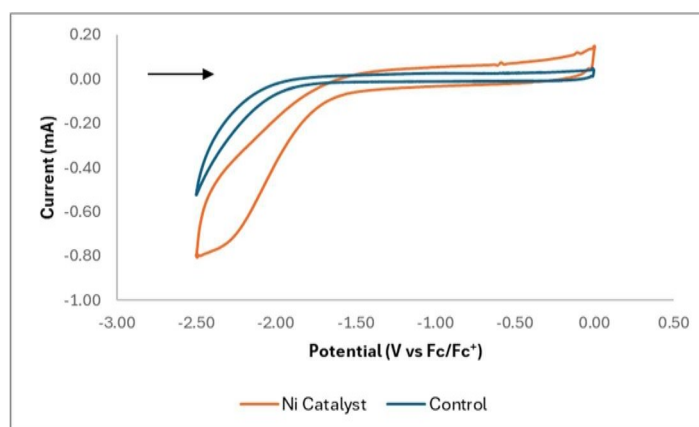


This catalyst showed efficient catalytic activity with faster reaction kinetics at 25,900 s<sup>-1</sup> TOF and high stability, and through proton relay, it undergoes proton-coupled electron transfer.<sup>24</sup> Based on this system, the catalytic behavior of this Nickel calixpyrrole deposited on the electrode in the presence of anilinium tetrafluoroborate was further investigated using a different proton source, triethylammonium tetrafluoroborate, to check the influence of acid strength on the surface-associated catalyst. the surface-associated catalyst.

This research enables comparison of catalytic behavior under different proton donor conditions while maintaining a consistent, efficient catalyst framework at the electrode. Such studies provide insight into the interplay among the catalyst framework, proton availability, and reaction kinetics, and deepen understanding of how molecular design modulation translates into an electrocatalytic system at the interface.

#### 4.2.1. Catalyst deposition and Electrochemical behavior

The Ni calixpyrrole catalyst was deposited on the glassy carbon electrode in the presence of 81.25mM of anilinium tetrafluoroborate at a 40V/s scan rate, and a surface-bound catalytic film was formed. Then, in the presence of triethylammonium tetrafluoroborate, the cyclic voltammetric response of the modified electrode showed a catalytic wave at negative potential, due to hydrogen evolution. The appearance of this catalytic current indicates that the immobilized nickel complex is electrochemically active for proton reduction at the electrode surface.<sup>25</sup> (**Figure 4.2**)

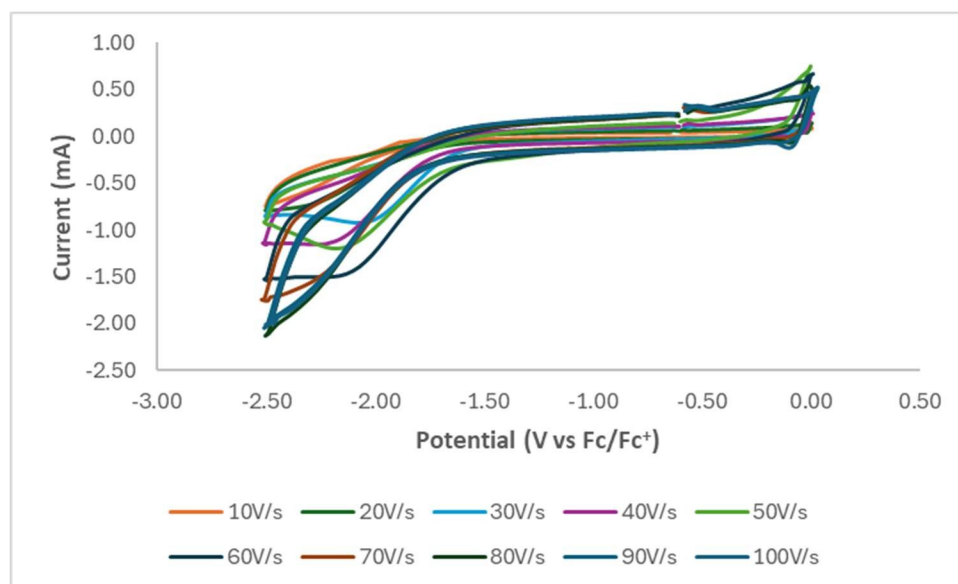


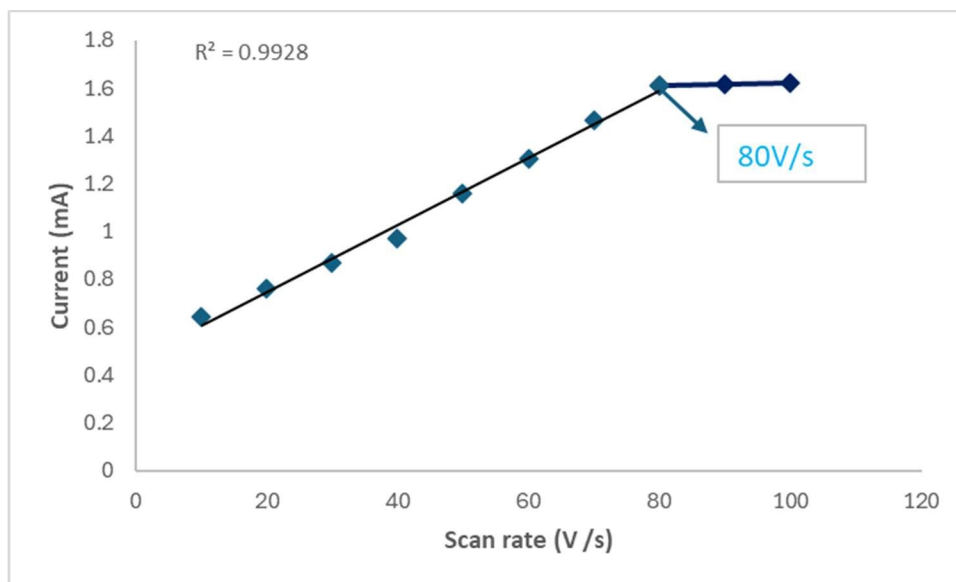
**Figure 4.2.** CVs of HER using Ni catalyst (0.1 M TBAP, 0.25 mM catalyst deposited on electrode by 81.25mM of anilinium tetrafluoroborate, 25mM triethylammonium

tetrafluoroborate, glassy carbon working electrode, platinum wire counter electrode, 0.0 1M Ag/AgNO<sub>3</sub> reference electrode, scan rate = 10V/s).

Compared with the control of triethylammonium tetrafluoroborate, the Ni-calixpyrrole-modified electrode showed an earlier onset potential and increased catalytic current, indicating catalytic activity for hydrogen evolution under the given conditions.<sup>25</sup>

To investigate the nature of the catalytic process, a scan rate dependence test has been performed. The catalytic current increased with increasing scan rate from 10 V/s to 100 V/s, and at 80 V/s, the current exhibited a region of scan-rate independence (**Figure-4.3**). This nature determines the fastest catalytic kinetics and indicates that the system is not limited to slow electron-transfer processes. The linearity between the catalytic current and the scan rate is consistent with a surface-confined catalyst that operates efficiently under these conditions.<sup>26</sup>

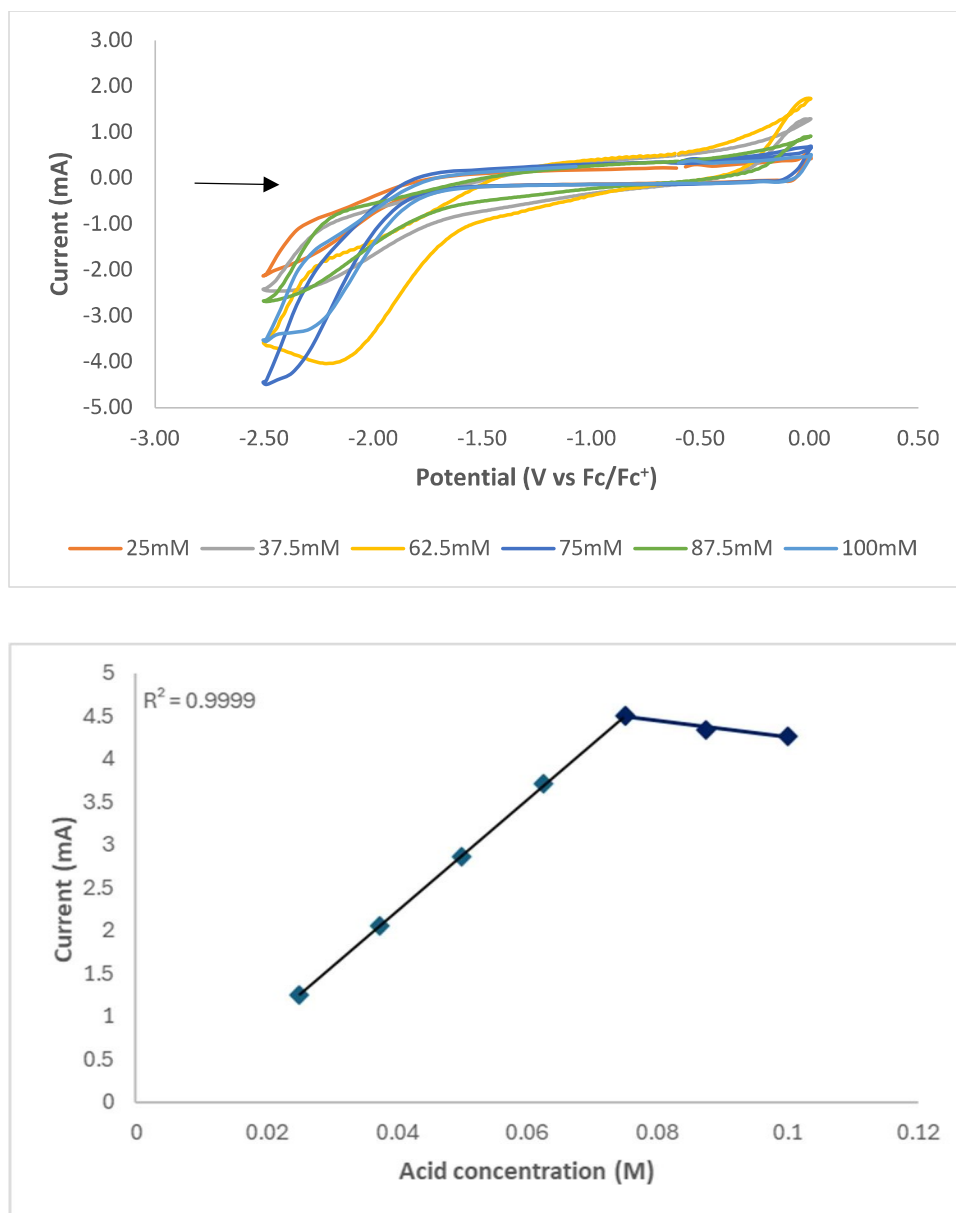




**Figure 4.3.** (a) Catalytic CVs of HER in acetonitrile using different scan rates starting from 10V/s to 100V/s (0.1M TBAP, 0.25mM catalyst deposited on glass carbon electrode in presence of 81.25mM anilinium tetrafluoroborate, platinum wire counter electrode, 0.01M AgNO<sub>3</sub> reference electrode, 25mM triethylammonium tetrafluoroborate), (b) General plot of catalytic current vs scan rate.

#### 4.2.3 Acid dependence and role of proton source

The influence of proton donors on catalytic efficiency was investigated by using triethylammonium tetrafluoroborate as an external proton source (**Figure 4.4**).



**Figure 4.4** CVs with different acid concentrations (starting from 0.025M to 0.1M triethylammonium tetrafluoroborate) using 0.25mM Ni catalyst deposited in glassy carbon electrode in the presence of 81.25mM anilinium tetrafluoroborate in acetonitrile, platinum wire electrode, 0.01M AgNO<sub>3</sub> reference electrode, scan rate=80V/s  
(b) General plot of catalytic current vs acid concentration.

The catalytic current increased with increasing concentration, indicating that proton availability plays a role in HER. The acid independence point was found at an acid concentration of 0.075 M and showed first-order dependence on acid concentration. This first-order rate dependency on acid

concentration provides insight into the mechanism of the rate-determining step in the Volmer or Heyrovsky step.<sup>27</sup>

The finding is important because the catalytic process depends not only on external acid but also on anilinium tetrafluoroborate, a localized proton reservoir in the catalyst film. In addition, the pendant amine group in the calixpyrrole framework serves as an internal proton shuttle, enhancing proton transfer to the active center.

That's why hydrogen evolution by this catalyst in the presence of a weaker acid, like triethylammonium, is still found, and this behavior signifies the important role of the secondary coordination sphere in maintaining proton transfer and catalytic activity.<sup>28</sup>

#### 4.2.4. Overpotential and catalytic efficiency

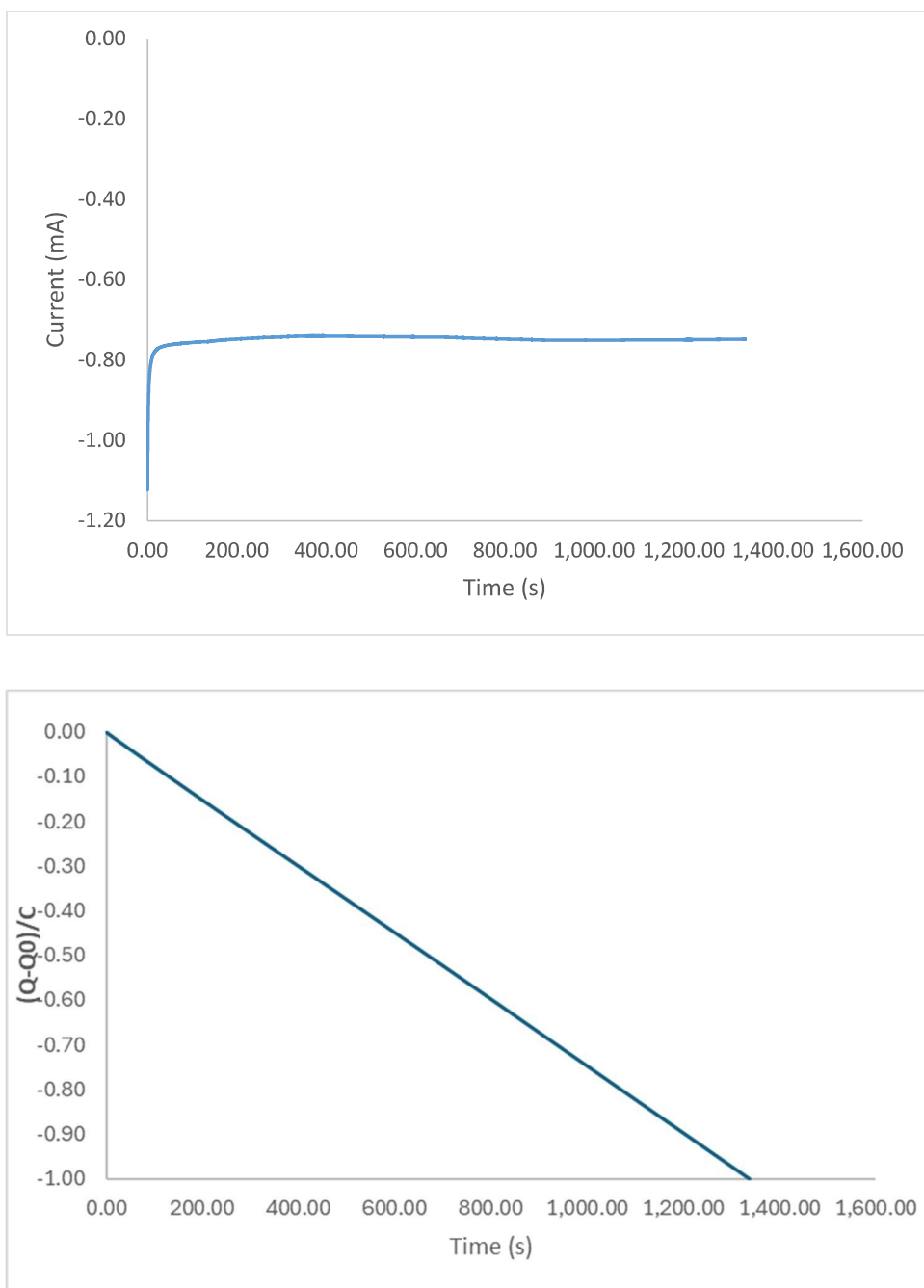
The overpotential was calculated at the 0.075 M acid-insensitive point for triethylammonium tetrafluoroborate at a scan rate of 80 V/S. The calculated value for overpotential was found to be around  $0.90\text{V} \pm 0.034$ .

$$\text{Overpotential} = [E_H^+ - E_{\frac{cat}{2}}] \quad (1)^{29}$$

$$E_H^+ = E_H^{+0} - 0.05961\text{V} * pKa \quad [E_H^{+0} = -0.028\text{V}, pKa = 18.8] \quad (2)^{29,30}$$

This value is within the typical range for nickel-based molecular electrocatalysts operating in non-aqueous media. Although the overpotential is relatively high, the system operates with weaker proton donors.

Faradaic efficiency through controlled potential experiment further showed catalytic stability and high-performance efficiency of the system. The amount of hydrogen generated under bulk electrolysis almost matched the theoretical value based on 1C charged passed, demonstrating 95% Faradaic efficiency (**Figure 4.5**).



**Figure 4.5.** Controlled potential electrolysis results in acetonitrile (0.1M TBAP, 0.25 mM of Ni catalyst deposited on glassy carbon electrode in presence of 81.25mM of anilinium tetrafluoroborate in acetonitrile), 0.075M Triethylammonium tetrafluoroborate, 6mm glassy carbon rod working electrode, 0.01M Ag/AgNO<sub>3</sub> reference electrode and 0.1MTBAP, 0.25M ferrocene, 6mm graphite counter electrode, 1C of charge passed) (1) current vs time (2) charge passed vs time

This high value indicated a stable, consistent catalyst framework over time, with minimal contribution from side reactions.<sup>31</sup>

#### 4.2.5. Turnover frequency and catalytic activity

The catalytic kinetics of the system were quantified using the turnover frequency (TOF), which indicates the rate of hydrogen production per catalytically active site. Using the current density and surface coverage of the catalyst, TOF was found to be the order of  $10^3 \text{ s}^{-1}$ .

$$i_p = \frac{n^2 F^2}{4RT} \nu \Gamma^* \quad (3)$$

where  $i_p$ ,  $n$ ,  $F$ ,  $R$ ,  $T$ ,  $\nu$ , and  $\Gamma^*$  are the peak current of the adsorbed species in the absence of acid, the number of electrons transferred (estimated to be 1 for the observed redox couple), Faraday's constant, the ideal gas constant, the temperature, the scan rate, and surface area coverage of the electrode, respectively. With this value in hand, the TOF was found at  $1775 \text{ s}^{-1}$  using the following equation.<sup>26-27</sup>

$$TOF = \frac{j}{nF \Gamma^*} \quad (4)$$

Where  $j$  and  $n$  are the catalytic current density and the number of electrons transferred (2 for hydrogen evolution).

Although the value is somewhat lower than the highest reported values in literature, it remains important for surface-associated molecular catalysts under mild acid conditions of triethylammonium tetrafluoroborate.<sup>30</sup>

#### 4.3. Mechanistic insights

The experimental results indicate hydrogen evolution can happen via proton-coupled electron transfer (PCET) pathways. Either simultaneously or in a closely coupled sequence, electron transfer from the electrode and proton transfer from the surrounding proton environment occur.<sup>32</sup>

A key structural characteristic, the presence of pendant amine groups as proton relays, facilitates proton transfer from the bulk proton solution to the active center.<sup>28</sup>

The inclusion of anilinium tetrafluoroborate during catalyst deposition helps maintain the structural integrity and stability of the catalysts on the electrode surface. This stabilization protects the catalytic framework during operation under HER conditions and ensures PCET throughout the cycle, even when proton sources are used.<sup>28,32</sup>

The relatively weak dependence on external acid strength supports the idea of proton transfer via an internal proton transfer, maintaining catalyst efficiency.<sup>27,32</sup>

#### 4.4. Conclusion

In this research, nickel calixpyrrole with pendant amine groups was deposited on a glassy carbon electrode in the presence of anilinium tetrafluoroborate and investigated in the presence of triethylammonium tetrafluoroborate, a weak acid for HER. This system showed high catalytic efficiency, with faradaic efficiency of 95% and TOF on the order of  $10^3 \text{ s}^{-1}$ .

The experimental investigations also indicated that the catalyst could proceed via a PCET mechanism, in which the secondary coordination sphere plays a critical role with pendant amine. The structure enhances the coupling between electron and proton transfer, enabling sustained TOF.<sup>27</sup>

Though the motivation was to explore a range of proton sources, the results using triethylammonium give valuable insight into the mechanism. The catalytic structural integrity and stability indicate that, with a weaker acid, internal proton transfer dominates the reaction mechanism. The analysis showed modest dependence on acid strength and indicates catalyst operation via internal proton transfer.<sup>28</sup>

Overall, this work underscores the importance of secondary coordination spheres in controlling the tuning efficiency of electrocatalysts and how molecular frameworks can retain high efficiency when deposited on electrode surfaces. By incorporating pendant amine and maintaining a local environment at the electrode surface, high catalytic efficiency can be achieved under mild acidic conditions. These results provide a broader understanding of molecular electrocatalysts and offer



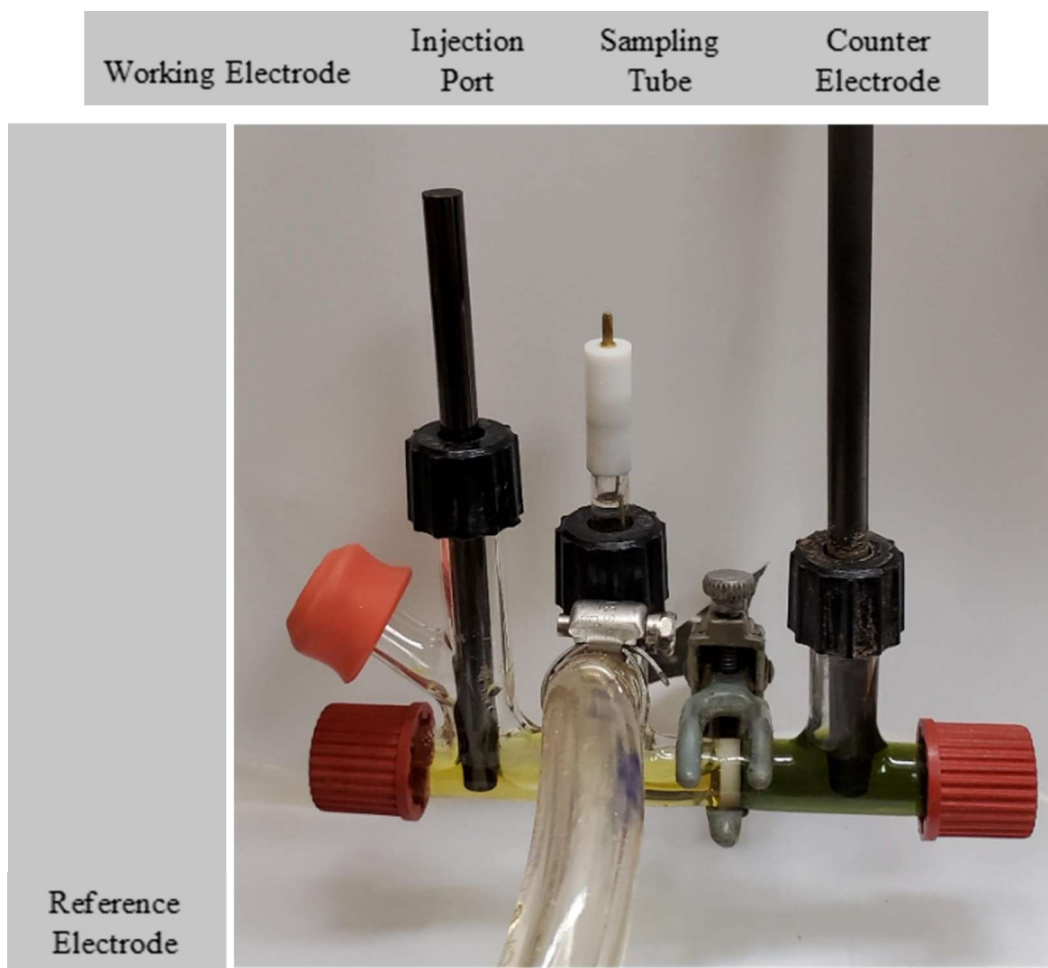
a path to advance next-generation HER catalysts by integrating the catalyst framework, proton-transfer pathways, and electrochemical characteristics.<sup>28,32</sup>

#### 4.5. Experimental

**General Considerations.** All procedures and manipulations were performed under an argon or nitrogen atmosphere using standard Schlenk-line and glove box techniques unless stated otherwise. Solvents were dried and deoxygenated under argon using a LC Technology Solutions Inc. SP-1 stand-alone solvent purification system. All alcohols were dried and distilled over activated magnesium (magnesium turnings and a crystal of iodine) under a nitrogen atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Sigma Aldrich, Acros Organics, or Alfa Aesar, degassed, and dried over activated molecular sieves prior to use. Nickel calixpyrrole with pendent amine was synthesized according to literature procedures.<sup>24</sup> All other reagents were purchased from commercial sources and utilized without further purification unless stated otherwise. Cyclic voltametric measurements were recorded using a Bio-Logic model SP-50 potentiostat. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte and was recrystallized prior to use by slow addition of pentane into a THF solution followed by cooling in a freezer (-30 °C). The working electrode was a glassy carbon electrode; the reference electrode was a Ag/AgNO<sub>3</sub> non-aqueous electrode (0.01 M in CH<sub>3</sub>CN with 0.1 M TBAP); and a platinum wire was used as the counter electrode. The glassy carbon electrode was polished with 0.05 µm alumina and washed with distilled water prior to each measurement. Electrochemical measurements were conducted at room temperature under an argon or nitrogen atmosphere and processed using EC-Lab V11.21. Ohmic drop was accounted for using the current interrupt method available in EC-Lab V11.21. Reported half-wave potentials were referenced to the Fc/Fc<sup>+</sup> redox couple by adding high purity ferrocene to the sample solution.

**Electrocatalytic H<sub>2</sub> evolution.** The electrochemical conditions of the catalytic trials included 0.1 M TBAP electrolyte in acetonitrile, 0.25mM of Ni catalyst deposited on the glassy carbon electrode under 81.25mM of anilinium tetrafluoroborate, scan rates between 10 to 100 V/s and triethylammonium tetrafluoroborate concentrations from 25mM to 100mM. The three-electrode setup consisted of Nickel catalyst deposited on glassy carbon working electrode, a platinum wire or graphite rod counter electrode, and a 0.01 M Ag/AgNO<sub>3</sub> reference electrode. All CVs were referenced versus the Fc/Fc<sup>+</sup> redox couple. All CVs were recorded under a nitrogen atmosphere in dry acetonitrile.

**Controlled potential electrolysis.** The glassy carbon working electrode was placed into a sealed bulk electrolysis cell filled with a solution of 0.1 M TBAP in acetonitrile, 0.25 mM of **nickel catalyst deposited under 81.25mM** and anilinium tetrafluoroborate, along with a 0.01 M Ag/AgNO<sub>3</sub> reference electrode reference electrode (**Figure 4.6**). The graphite counter electrode, separated by a porous frit, was submerged in a solution of 0.1M TBAP in acetonitrile and ferrocene.



**Figure 4.6.** Image of the electrolysis cell utilized for controlled potential electrolysis after 1 C of charge had been passed.

#### 4.6. Sample Calculations

Overpotential Calculations<sup>29-30</sup>

$$\text{Overpotential} = [E_H^+ - E_{cat}]^{29-30}$$

$$E_H^+ = -0.028V - 0.05961V * 18.8 [E_H^{+0} = -0.028V, pka = 18.8^{29-30}]$$

$$= -1.14V$$

$$\text{Overpotential} = -1.14 - (-2.037)$$

$$= 0.8971V$$

Sample Turnover Frequency Calculation<sup>26-27</sup>

$$i_p = \frac{n^2 F^2}{4RT} \nu \Gamma^* \quad (1)$$

$$TOF = \frac{j}{nF^*} \quad (2)$$

$$\Gamma^* = i_p * 4 * R * T / (n * n * F * F * V * A)$$

$$\Gamma^* = 0.982 * 4 * 8.314 * 298 / (1 * 1 * 96485 * 96485 * 80 * 0.070686)$$

$$TOF = 4.45 / (2 * 96485 * 0.070686 * 9.69 * 10^{-9})$$

$$= 1775 s^{-1}$$

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## Chapter 5 - Conclusions and Future Directions

### 5.1. Conclusions

Hydrogen has emerged as a continuous, reliable energy source and a green, renewable energy system. Though it has potential, advancing efficient hydrogen generation remains a challenge, underscoring the need for innovation in catalyst design. Overall, the efficacy of the hydrogen evolution reaction depends primarily on the intrinsic properties, activity, and stability of the electrocatalyst. This work demonstrates the tuning of the secondary coordination sphere of Pd- and Ni-based calixpyrrole electrocatalysts with pendant groups to enable efficient hydrogen production.

In chapter 2, Palladium complexes (1-3) bearing a calixpyrrole framework<sup>1</sup> with pendant groups were electrochemically analyzed, and their HER electrochemical activities were explored. In the presence of anilinium tetrafluoroborate (pK<sub>a</sub>-10.62) as a proton source, these complexes were found to be homogeneous in nature, and they displayed a second-order dependence on acid concentration and a first-order dependence on the catalyst. They showed remarkably high TOFs up to  $4.65 \times 10^6 \text{ s}^{-1}$  for 2a, up to  $4.19 \times 10^6 \text{ s}^{-1}$  for 2b, and up to  $3.09 \times 10^6 \text{ s}^{-1}$  for 2c, approaching the diffusion rate limit. In addition, based on the H/D KIE values of 5.2, 4.2, and 5.4 for 2a, 2b, and 2c, respectively, it is hypothesized that the release of H<sub>2</sub> was the rate-limiting step for these catalysts. Moreover, CPE experiments showed good stability under the conditions explored and high FEs: 97.7% for 2a, 95.7% for 2b, and 95.3% for 2c. These results revealed that proton shuttles are not the only functionalities capable of producing extremely active HER catalysts, and that, under these conditions, correctly positioned hydrogen bond donors can perform nearly as well. By incorporating calixpyrrole frameworks with rigid backbones that link the directing groups in the secondary coordination sphere to the active metal centers, catalytic systems displaying ultrafast reaction kinetics were developed. The overpotentials still needed to perform such reaction rates were high. Modifications in the secondary coordination sphere can tune the reduction potential. Overall, these Pd complexes demonstrated the importance of calixpyrrole frameworks for achieving enzyme-like reaction kinetics in HER.

In Chapter 3, two calixpyrrole ligands with pendent protected amine moieties (acyl- and Boc-protected, respectively) and another calixpyrrole ligand with no functionalities in the secondary coordination sphere were electrochemically investigated for HER. This work replaced Pd with Ni

to make the catalysts more economical. Anilinium tetrafluoroborate, used as a proton source, showed that these complexes were heterogeneous and active for HER, with first-order dependence on catalyst concentration and second-order dependence on acid concentration. These nickel complexes did not go through direct protonation. The electrocatalytic hydrogen evolution of the Ni complexes is significantly influenced by the pendant functional groups. The amide and the carbamate derivatives functionalized complexes showed the higher activities with high TOFs of  $17701.35\text{ s}^{-1}$ , an overpotential of 0.85 V, F.E of 96.8% ( for amide), and TOF of  $14039.21\text{ s}^{-1}$  with an overpotential of 0.84 V, F.E of 95.6% ( for carbamate) compared to the unsubstituted system with a lower TOF of  $12031.68\text{ s}^{-1}$  and a higher overpotential of 0.95V, F.E of 91.08%. Analysis of Tafel slope and KIE revealed that the rate-limiting step includes proton discharge onto the electrode surface or a Volmer-like step. The incorporation of pendant amide and carbamate groups showed enhanced kinetics and lower overpotentials, and, most importantly, higher stability of the complexes. That enhancement is due to proton delivery via hydrogen bonding. These pendant groups indicated higher selectivity towards HER with minimal side reactions. The high stability demonstrated that the pendant groups position the proton at the active center, preventing catalytic decomposition and maintaining the overall efficiency of HER. These results highlight the importance of the secondary coordination sphere in increasing catalytic characteristics and stability, opening a clear path for the development of efficient HER electrocatalysts.

In chapter 4, a nickel calixpyrrole complex bearing a pendant amine group can be transformed into a surface-associated electrocatalyst for the hydrogen evolution reaction while retaining the key molecular design. Deposition of this molecular catalyst into a glassy carbon electrode in the presence of anilinium tetrafluoroborate yields a stable, heterogeneous system capable of catalyzing the hydrogen evolution reaction. This catalyst deposited on the electrode was then electrochemically investigated using triethylammonium tetrafluoroborate as a weak proton source, allowing evaluation of proton donor strength on HER activity. Electrochemical evaluation using triethylammonium tetrafluoroborate showed high Faradaic efficiency with excellent stability, with turnover frequencies on the order of  $10^3\text{ s}^{-1}$ . The catalytic current increases with increasing triethylammonium tetrafluoroborate concentrations and reaches a plateau at higher concentrations, indicating a transition to an acid-independent regime. Mechanistic investigations indicate there can be possibilities of a proton-coupled electron transfer (PCET) pathway in which the secondary coordination sphere plays an important role. The pendant amine groups work through internal

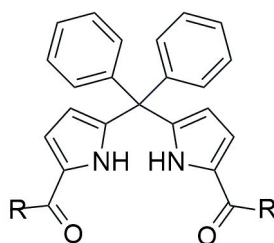
proton transfer, facilitating proton transfer from triethylammonium tetrafluoroborate to the active site and enabling the efficient formation of catalytically relevant nickel hydride intermediates.

Furthermore, electrode deposition enhances catalyst stability and integrity without compromising activity, ensuring sustained hydrogen evolution under mild conditions. The system's ability to maintain high efficiency in the presence of a weak acid underscores the robustness of proton transfer by the pendant amine groups. Overall, this research signifies the combination of the secondary coordination sphere with interfacial catalyst design. By showing efficient HER catalysis in the presence of a weak acid, triethylammonium tetrafluoroborate, this research indicates the dominating behavior of internal proton shuttling by pendant amine over direct proton delivery from solution.

## 5.2 Future Directions

### 5.2.1. Push-pull method of tuning of calixpyrrole:

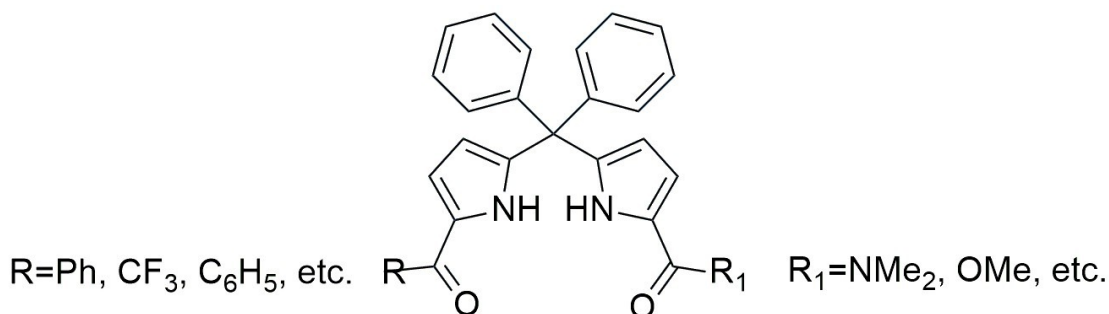
Among the Calixpyrrole-based ligand architectures with pendant groups, we have found that they exhibit high overpotentials in HER. It may be related to the need for highly cathodic potentials to generate catalytically active species.<sup>2</sup> These high cathodic potentials increase the cost and generate undesired side reactions like reduction of ligand-centered functionalities (imine moieties) in the presence of a proton source<sup>3,4</sup>. To overcome the overpotential and side-reaction problems, electronic tuning of the ligand provides a feasible approach to balance redox properties and enhance catalytic behavior. Incorporating a push-pull ligand framework with electron-withdrawing and electron-donating groups can balance redox properties and reduce overpotential. Electron-withdrawing groups (EWGs; -CF<sub>3</sub>, perfluoroaryl, etc.) can shift the reduction potential toward the anodic region, reducing the applied potential required to achieve catalytically relevant redox states.<sup>5</sup> The framework of these complexes can be tuned through the synthesis of various keto-substituted dipyrromethanes (**Figure 5.1**), which can easily form an imine.



R=Ph, CF<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, etc.

**Figure 5.1.** Structure of proposed diketodipyrromethane with EWGs

But excessive electron withdrawal can decrease electron density at the metal active center, hindering the formation and stability of important reduced intermediates. In this situation, the inclusion of electron-donating groups (**Figure 5.2**), EDGs (-NR<sub>2</sub>, -OR, etc.), in proximal positions The metal-binding site can balance redox activity. These groups balance the electron density with EWGs, facilitating the formation of a metal hydride (an important intermediate) necessary for HER. Also, the spatial separation of EDG and EWG creates an internal electronic gradient that helps charge delocalization and stabilizes transition states during HER catalysis.<sup>6,7</sup> This method enables control over thermodynamic and kinetic parameters, decreasing overpotential and enhancing catalytic activities.



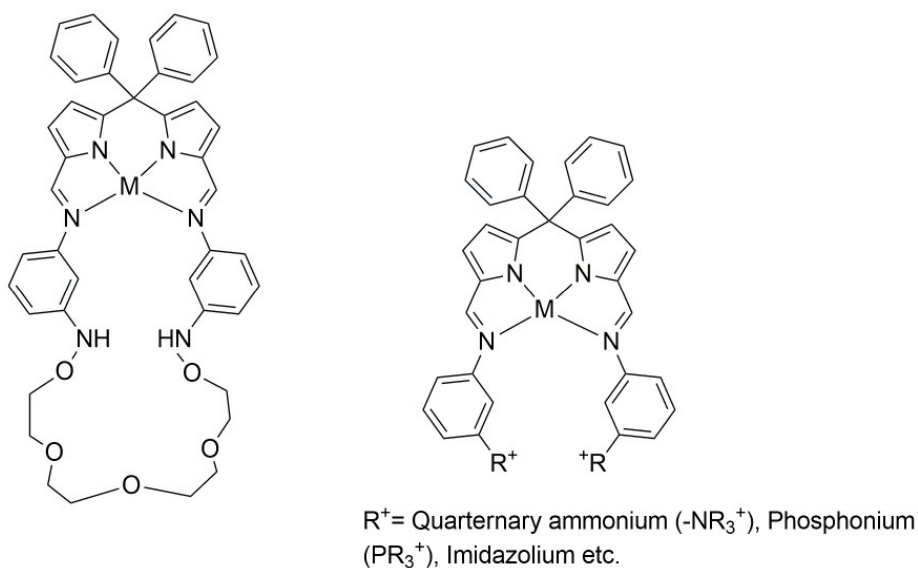
**Figure 5.2.** Proposed substituted diketodipyrromethanes

### 5.2.2. Cation's incorporation

Another method for tuning the reduction potential is to incorporate cationic functionalities into the ligand structure. This can be achieved through either the encapsulation of metal cations using crown ether moieties<sup>8</sup> or the introduction of permanently charged groups such as phosphonium, imidazolium, and quaternary ammonium (**Figure 5.3**),<sup>9,10</sup>. These positively charged groups, when incorporated into the secondary coordination sphere, create local electrostatic interactions that enhance the electronic environment of the active metal center. This positively charged group makes the catalytic system more positive, which draws the electron for reduction at a lower potential, thereby reducing overpotential.

The literature indicates that the presence of such cationic functionalities can stabilize reduced intermediates and enhance electron transfer, thereby shifting the reduction potential anodically. Both encapsulated and covalently attached charged groups can generate an internal electric field

that lowers the activation barriers for catalytic species. Moreover, it can enhance catalytic activity by facilitating proton-coupled electron transfer through electrostatic stabilization, and, in a few cases, direct protonation can occur.<sup>10-13</sup> So, the inclusion of cationic species provides a strategy for controlling redox properties and reducing overpotential in HER by making the entire catalytic system positively charged, thereby attracting electrons more readily for reduction.



**Figure 5.3** Structures of modified calixpyrrole with cationic species

### 5.2.3. pKa of the proton source

By carefully matching the proton source acidity with the basicity of the calixpyrrole catalytic system, proton-coupled electron transfer (PCET) can be achieved. Depending on the strength of the proton source, the protonation system of the ligand or the catalyst varies. If the proton source is too strong, non-selective protonation of the catalyst can occur, leading to decomposition and energy loss. If the weak acid acts as a proton source, slow proton transfer can occur, requiring a higher overpotential for HER. A properly tuned proton source ensures simultaneous proton and electron transfer, facilitating active formation of metal hydride intermediates, and that's how it decreases overpotential. This idea has been observed in molecular electrolysis, where the HER rate and overpotential were related to acid strength.<sup>14-17</sup>

#### 5.2.4. Reaction mechanism

The electrochemical characterization of the Pd/Ni calixpyrrole complexes was performed by Cyclic voltammetry, which provides insights into redox properties and catalytic performance. To gain deep insight into the reaction mechanism, computational studies and stoichiometric reaction studies can be employed. Density Functional Theory (DFT) is primarily used for computational studies to investigate catalytic mechanisms, identify intermediates, and determine the Gibbs free energy of catalysts, thereby rationalizing cyclic voltammetry and providing molecular-level insights.<sup>18,19</sup> In addition to computational studies, Stoichiometric reaction studies with chemical reductants and proton donors provide an important method for probing mechanistic details under reaction conditions. This method gives a way to generate and characterize catalytic intermediates outside the electrochemical conditions. By relating intermediates observed in stoichiometric studies to cyclic voltammetry data, detailed pictures of the catalytic cycle can be obtained.<sup>20,21,2</sup>



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