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HETEROGENIZATION OF COMPLEXES WITH REDOX ACTIVE LIGANDS FOR
HYDROGEN EVOLUTION REACTION

By

Wuyu Zhang

B.A., Changzhou University, 2006

M.S., Beijing University of Chemical Technology, 2010

A Dissertation Submitted to the
Faculty of the College of Arts and Science of the
University of Louisville in Fulfillment
Of the Requirements for the Degree of

Doctor of Philosophy in Chemistry

Department of Chemistry

University of Louisville

Louisville, KY

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A Dissertation Approved on
September 22, 2017

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For Mom and 赵淑贞

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ABSTRACT

HETEROGENIZATION OF COMPLEXES WITH REDOX ACTIVE LIGANDS FOR
HYDROGEN EVOLUTION REACTION

Wuyu Zhang

September 22, 2017

Hydrogen fuel is a promising future energy carrier with many applications. Thermodynamically, 1.23 V is needed for the water electrolysis, which is a clean method to generate hydrogen gas. In practice excess potential is required, which is called overpotential, due to kinetic barriers. Catalysts to reduce the overpotential for the hydrogen evolution reaction (HER) include many homogeneous catalysts and heterogeneous catalysts. Heterogenization of homogeneous catalysts on electrode surfaces is an ideal way to study a catalyst by combining homogeneous and heterogeneous study together. In this dissertation, several characterization techniques have been employed, include cyclic voltammetry, linear sweep voltammetry, electrochemical impedance spectroscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy, chronopotentiometry, and density functional theory.

The heterogenization of the rhenium complex of the redox-active ligand 2-diphenylphosphinobenzenethiolate (ReL_3) on glassy carbon electrode surfaces generated a stable modified electrode work for HER electrocatalysis in aqueous acidic condition with a relatively large overpotential. The cation form of ReL_3 , $[\text{ReL}_3]^+$ has been drop casted on the GC surface to prepare GC- $[\text{ReL}_3]^+$ which showed improved overpotential. Addition of a carbon black layer to generate GC-CB- ReL_3 and GC-CB- $[\text{ReL}_3]^+$ decreased significantly the charge transfer resistance and overpotential for both catalysts. Tafel slope analysis for all electrodes indicates a Volmer rate determine step. The proposed mechanism is based on the homogeneous mechanism with support of DFT calculations.

The redox active bis-thiosemicarbazone ligands ATSM and ATSP and their Cu- and Zn- derivatives were fabricated on GC surface as heterogeneous HER catalysts. The overpotential for the ATSM and ATSP ligands are 1.12 V and 1.09 V, while the overpotential for CuATSM and CuATSP are 774 mV and 745 mV, respectively. The Zn derivatives de-metallation during the electrolysis as observed by UV-vis spectroscopy and XPS analysis.

Carbon paste electrodes (CPEs) have been used to improve the charge transfer resistance for the fabricated electrodes to achieve lower overpotential. The CPE- ReL_3 , CPE-ATSM and CPE-CuATSM electrodes were prepared and compared with GC electrodes. The CPE catalysts show significantly reduced overpotential compared to GC and the charge transfer resistance was decreased over 100 times relative to GC electrodes. Moreover, the CPEs exhibit excellent stability properties during the long-term electrolysis.

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CHAPTER I

INTRODUCTION

1.1 Hydrogen

Hydrogen is the simplest element as it contains only one proton and one electron. It is the most abundant element in the universe and is most commonly in the form of molecular hydrogen (H_2).¹⁻² Molecular hydrogen is an attractive energy carrier due to its high energy density.³ Global energy needs have traditionally been supplied by fossil fuels such as coal, oil, and natural gas.⁴⁻⁶ However, these resources are non-renewable and their conversion to usable forms by cracking and steam reformation along with their combustion releases significant quantities of CO_2 , which is greenhouse gas.¹ The international energy outlook in 2016 projects significant growth in worldwide energy demand over the 28-year period from 2012 to 2040.⁷ To meet these needs, additional energy resources are required. Several renewable energy sources have been used to generate energy. These include direct solar, biomass, wind, and geo-thermal. The capacity for renewable power is increases each year faster than increased capacity of traditional fuels. A prediction of needing for hydrogen fuel is shown in Figure 1, which indicates that the requirements for hydrogen energy will keep increasing in the near future all over the world.

Figure 1. The prediction of energy generation capacity additions

In the recent decades, hydrogen gas received a lot of attention because of its unique properties.⁸⁻⁹ It is the best energy carrier and an engine that burns pure hydrogen produces almost no pollution. NASA has used liquid hydrogen since 1970s to propel the space shuttle into orbit. Hydrogen fuel cells are one of the most important applications for the hydrogen energy.¹⁰⁻¹² Hydrogen and oxygen are combined to produce electricity, heat, and water as the final product. It converts the energy produced by a chemical reaction into usable electric power during this process.

Hydrogen is also an important reagent in industry. In the petroleum industry, hydrogen is reacted with hydrocarbons in several catalytic processes including hydrocracking and hydro processing.¹³ In the hydrocracking process, large hydrocarbons are fragmented into smaller molecules with higher C/H ratios.¹⁴⁻¹⁶ For hydro processing, hydrogen is used to hydrogenate nitrogen or sulfur compounds and form NH_3 or H_2S . Moreover, many petrochemicals, such as methanol, are produced using hydrogen as a

reagent. For example, methanol is produced by combining hydrogen with carbon monoxide at high temperature and pressure with the help of catalyst.¹⁷

There are several ways to produce hydrogen gas.¹⁸ The main method is a thermochemical process that uses heat to initiate chemical reactions that release hydrogen from organic materials. An alternate method is electrolysis of water or organic solvents.¹⁹⁻²⁰ Electrolysis of water involves the decomposition of water into hydrogen and oxygen gas due to an electric current being passed through the water. As shown in Figure 2, water is reduced to hydrogen at the cathode and oxidize to oxygen at the anode.²¹

Figure 2. Electrolysis of water into hydrogen and oxygen

The standard potential (ΔE^0) for water electrolysis can be calculated from the reduction potentials for the two half-reactions (Equation 1-2).

The overall reaction is a 4-electron process with a ΔE^0 of -1.23 V. The reaction is non-spontaneous and requires a potential difference of at least 1.23 V to drive the reaction.

The actual potential required will be larger due to the effects of overpotential. The overpotential represents a kinetic barrier that requires additional energy to overcome, which caused by activation energy, ion mobility, concentration, and resistance generated in system. Therefore, to increase the reaction rate and improve efficiency for the electrolysis, catalysts are used to minimize the overpotential.²²⁻²⁴

The catalysts in this dissertation will focus on the hydrogen evolution reaction (HER) that occurs at the cathode during the electrolysis of water. This reaction has been well studied with a large number of catalysts.²⁵⁻³⁴ The electrocatalysts for HER can be generally classified as homogeneous and heterogeneous depending on whether or not the catalyst and substrates are in the same phase. The homogeneous catalysts include soluble, small molecular complexes³⁵⁻³⁹ and the hydrogenase family of enzymes⁴⁰. Heterogeneous catalysts are insoluble species such as precious metals, non-precious metals and their alloys, and Transition metal chalcogenides.^{39, 41-47}

1.2 Fundamentals of HER

The E^0 value for HER of 0.0 V (equation X) applies to standard conditions where the activity of H^+ is 1 and the pressure of H_2 is 1 atmosphere. Under non-standard, Nernstian conditions, the potential for the HER, versus the normal hydrogen electrode (NHE), is described by equation below:

$$E_{HER} = E^0_{\left(\frac{H_2}{H^+}\right)} - \frac{RT}{F} \times \ln \left(\frac{a_{H^+}}{P_{H_2}^{\frac{1}{2}}} \right) = -0.059 \times (pH) vs. NHE = 0 V vs. RHE$$

The potential versus NHE shows a linear dependence on pH with more accessible potentials at lower pH values. For the purposes of determining overpotential, it is common to report values versus the reversible hydrogen electrode (RHE), which does not explicitly show a pH dependence. The potential versus RHE is related to that versus NHE as shown in equation described above.

The RHE potential represents the thermodynamic ideal for the reduction of H^+ to H_2 at a given pH. As noted above, there is an additional kinetic barrier that to be overcome to generate the hydrogen gas. This overpotential is largely the result of activation energy, ion mobility (diffusion) and concentration, wire resistance, surface hindrance including bubble formation (causes electrode area blockage), and entropy, but not only for the thermodynamics. The total applied potential (E_i) can be described as:

$$E_i = E_{HER} + iR + \eta$$

where E_{HER} is the standard potential needed for hydrogen evolution reaction, which is 0 V, iR is the ohmic potential drop caused by the flow of the current in ionic electrolytes, and η is the overpotential for drive the reaction.⁴¹ Overpotential is the most important parameter used to evaluate the electrochemical activity of a catalyst. Generally, the efficiency of a catalyst increases as the overpotential becomes smaller. For efficient HER electrocatalysts the value of the overpotential should be 100 mV or less.

1.3 Catalysts for Heterogeneous Hydrogen Evolution Reaction

There are many heterogeneous HER catalysts that have been synthesized and studied to date. These catalysts can be classified into three types: precious metals, non-

precious metals and their alloys, and transition metal chalcogenides. A short description of each class is provided below.

The first series of HER catalysts are precious metal (PGMs) based electrocatalysts. Catalysts in this group include Pt, Ru, Rh, Ir, and Pd. Of these, platinum is considered the ideal as it requires very small overpotentials to achieve high reaction rates in acidic conditions. Additionally, platinum is an excellent catalyst for the reverse reaction, hydrogen oxidation. Pt is always used to benchmark the activity of other HER electrocatalysts. In 1958, Parson firstly pointed out in that the maximum exchange current density is attained when the hydrogen adsorption free energy is close to 0 ($\Delta G_H \sim 0$).⁴⁸ Norskov and co-workers⁴⁹ calculated hydrogen adsorption free energy on different transition metals by using density functional theory, and the plot of experimentally measured HER exchange current density as a function of calculated free energy has been generated, with the peak position close to that of platinum. This plot is known as volcano plot, Figure 3. They also suggested that ΔG_H is a useful descriptor to determine the electroactivity for new HER catalysts. During the past few decades, PGM catalysts have been well studied and greatly improved by the development of material science and nanotechnology. However, the high cost of Pt and other precious metals limit their widespread applications.

Figure 3. Volcano plot of exchange current density (j_0) as a function of DFT-calculated Gibbs free energy (ΔG_{H^*}) of adsorbed atomic hydrogen on pure metals. Reprinted with permission from ref.X, copyright 2005, the Electrochemical Society.

The second series of HER catalysts are non-precious metals and their alloys.⁵⁰⁻⁵² In addition to their low efficiency, the non-precious metals also have poor stability due to the corrosion and oxidation in acidic media limits their sustainable hydrogen production. Despite these drawbacks, Ni-based electrodes are commonly used in industry because of their low cost and relatively good pH corrosion resistance.⁵³ However, Ni electrode are subject to deactivation due to the reversible formation of nickel hydride species.⁵⁴⁻⁵⁵ Therefore, Ni-based alloys has been developed to improve the activity and durability.⁵⁶⁻⁵⁷ Vasu et al.⁵⁸ deposited Ni-Mo, N-Zn Ni-Co and Ni-Cr alloys on steel strips and studied their HER activities in alkaline solutions. They reported Ni-Mo as the best catalyst over the others with an overpotential at 0.18 V at 300 mA cm⁻², and it exhibited excellent durability over 1500 h in 6 M KOH solution. Following by this work, they reported a study on Ni-Mo-X ternary transition metal alloys showed excellent long term stability properties.

The third series is transition metal chalcogenides.⁵⁹⁻⁶⁴ The most promising candidate from this class is the molybdenum sulfide family of catalysts. The MoS₂ shows high activity for HER and on volcano plot, it appears close to $\Delta G_H = 0$, and the peak of the plot. Additionally, MoS₂ is highly stable in the presence of strong acids,⁶⁵⁻⁶⁹ which is beneficial for HER conditions. The active site of MoS₂ is proposed to be sulfur atoms on the molybdenum edges of the MoS₂ planes.⁷⁰ Bulk MoS₂ didn't give good results because the low exposure level of active site to the electrolyte. Numerous studies have been reported to address this issue. One approach was to synthesize clusters that contain a large number of sulfur edges. The Jaramillo group reported thiomolybdate [Mo₃S₁₃]²⁻ clusters as a HER catalyst with extremely high activity and excellent stability, which attributes to the exposure of high number of active sites was exposed because those [Mo₃S₁₃]²⁻ nanoclusters.⁷¹ Another approach to increase the HER performance of MoS₂ involves deposition of MoS₂ particles on a conducting, high surface area substrate. The Dai group used a selective solvothermal synthesis to grow MoS₂ nanoparticles on reduced graphene oxide (RGO) sheets in solution.⁷² The MoS₂/RGO catalyst exhibited superior electrocatalytic activity in the HER relative to other MoS₂ catalysts. Specifically, an onset potential near -0.110 V vs. RHE. These results demonstrate the ability of carbon materials to improve the electrocatalytic properties of HER catalysts.

1.4 Mechanism of H₂ Evolution for Heterogeneous systems

One of the biggest challenges in the study of heterogeneous HER catalysts is the ability to do detailed mechanistic investigations. Heterogeneous HER catalysts typically

follow one of two general mechanisms, which are referred to as Volmer-Tafel and Volmer-Heyrovsky (Figure X). In either mechanism, the first step is a Volmer step, which is a discharge reaction in which a proton and electron combine to form absorbed H atoms on the surface. In a Volmer-Tafel mechanism, the second (Tafel) step is Tafel step, which the hydrogen generates from two absorbed H atoms on the surface. In a Volmer-Heyrovsky mechanism, the second step is Heyrovsky step, which the hydrogen formed from one absorbed H atom and one external H atom, as shown in Figure 4.

Figure 4. Scheme of HER mechanism in heterogeneous conditions.

The Tafel slope can be used to analyze the electrocatalytic activity and determine the reaction mechanism of electrocatalysts. In this method, the sensitivity of the electric current response to the applied potential is analyzed to identify the rate determining step.⁷²⁻⁷⁴ The Tafel slope is defined according to the Butler-Volmer equation:

$$j = j_0 \left[-e^{-\frac{\alpha n F \eta}{RT}} + e^{\frac{(1-\alpha) n F \eta}{RT}} \right]$$

Here, j is the current density, j_0 is the exchange current density, α is the charge transfer coefficient, n is the number of the electrons transferred, F is the Faraday constant, R is the ideal gas constant and T is the temperature. When the overpotential is high ($\eta > 0.05\text{V}$), this equation could be simplified as;

$$\eta = a + b \log j = -\frac{2.3RT}{\alpha nF} \log j_0 + \frac{2.3RT}{\alpha nF} \log j$$

Based on this equation, the overpotential has linear relationship with $\log j$, with a slope of $b = \frac{2.3RT}{\alpha nF}$, which was defined as Tafel slope. In the literature, various Tafel slopes has been reported. Pt exhibits a Tafel slope of 30 mV/dec in 0.5 M H_2SO_4 , which is one of the most well studied catalysts,^{72, 75-76} 120 mV/dec under polymer electrolyte membrane fuel cell conditions⁷⁷ and 125 mV/dec in 0.5 M NaOH solution.⁷⁸ The difference of Tafel slope values could be caused by the difference in the pH value, and also, the potential region that has been chosen to obtain the Tafel slope could cause a large difference. For MoS_2 , the Tafel slope of 94 - 110 mV/dec was reported in 0.5 M H_2SO_4 ,^{72, 79} and 55 - 60 mV/dec in H_2SO_4 at pH 0.24.⁸⁰ Generally, a small Tafel slope indicates a steep rise of the electrocatalytic current density.

For HER heterogeneous catalysts, a Tafel slope of 30 mV per decade suggests that the mechanism proceeds through the Volmer–Tafel mechanism where the recombination step is the rate determining step. A Tafel slope of 40 mV per decade suggests hydrogen production via the Volmer–Heyrovsky mechanism with the electrochemical desorption step rate-limiting. Finally, a Tafel slope of 120 mV per decade may arise from various reaction pathways with a Volmer step as the rate determining step.^{72, 81}

However, Tafel slope analysis does not give the same degree of details about the reaction mechanisms as can be studied in homogeneous conditions. For homogeneous catalysts, despite the attractive properties in terms of activity and selectivity, they suffer from difficulties associated with separating the products from the catalysts, which is the biggest problem for their usage in industry. Also, the recycling of homogeneous catalysts causes problems on practical application.

One way to combine the benefits of homogeneous and heterogeneous catalysts is through the immobilization of known catalysts onto solid surfaces for letting them work in heterogeneous conditions.⁸²⁻⁸⁶ Abhishek et. al reported a Co-based electrocatalysts that can reduce H^+ from H_2O to form H_2 with an onset at -0.3 V vs NHE in aqueous sulfuric acid.⁸⁷ Schmittenmaer et. al reported a work of immobilization of a molecular catalyst ($[Ir(pyalc)(H_2O)_2(\mu-O)]_2^{2+}$) for water oxidation that binds to metal oxide surface, and this heterogenized molecular catalyst oxidized water with low overpotential, high turnover frequency and minimal degradation.⁸⁸ Nocera et. al⁸⁹ reported a work of immobilized an oxygen-evolving catalyst (contains Co^{2+} and phosphate) on Indium tin oxide (ITO) by electrodeposition, and exhibited catalytic activity in neutral water splitting.

The immobilization method is an important procedure which could change the electrochemical performance of the catalysts in the chemical and physical way. The interaction between catalysts and matrix surfaces could be physical adsorption or chemical interaction. Physical methods are characterized by weak interactions such as van der Waals force, affinity binding, ionic binding or hydrogen bonding.⁹⁰⁻⁹¹ In the chemical method, covalent bonds formed between catalyst and electrode surface, which

forms more stable surfaces than physical methods. However, chemical methods usually require further modification of the catalysts by adding more function groups which will cause the change of the catalytical activities of catalysts. Thus, the physical method has been chosen in our studies to run a quick investigation on catalysts that we already well studied in homogeneous.

In this dissertation, well-studied homogeneous catalysts developed in the Grapperhaus group are immobilized on electrodes for HER catalysis. In 2015, the Grapperhaus group reported a rhenium thiolate (ReL_3) complex as HER and HOR catalyst in homogeneous conditions. They reported the overpotential of 380 mV and a turnover frequency of $32 \pm 3 \text{ s}^{-1}$ for HER. This paper was the first paper that reported a ligand-centered mechanism, which means there was no metal hydride involved during the HER. Moreover, in the following year, they reported another work on non-transition-metal and metal-free ligand-centered electrocatalysts for HER and HOR. In that paper, they studied diacetyl-bis(N-4-methyl-3-thiosemicarbazone) and zinc diacetyl-bis(N-4-methyl-3-thiosemicarbazide) in methanol with acidic acid, and they displayed the highest reported TOFs of any homogeneous ligand-centered H_2 evolution catalyst, 1320 and 1170 s^{-1} , respectively. The reported catalysis proceeds via ligand-centered proton-transfer and electron-transfer while avoiding traditional metal hydride which is the same as in ReL_3 system. These studies identified a new direction for the design of electrocatalysts for HRE that does not involve metal hydrides.

1.5 Scope of dissertation

This dissertation present work focused on the heterogenization of homogeneous HER catalysts on different electrode surfaces. The catalysts studied in this study include the rhenium thiolate complex ($[\text{Re}(\text{DPPBT})_3]$ (DPPBT=2-diphenylphosphinobenzenethiolate)), diacetyl-bis(N-4-methyl-3-thiosemicarbazide) (ATSM), diphenylacetyl-bis(N-4-methyl-3-thiosemicarbazide) (ATSP) ligand and their Zn- and Cu- derivatives. These catalysts were modified on the electrode surfaces and used as working electrode to investigate their electrocatalytic properties in heterogeneous condition. Several parameters have been studied in this research: morphology studies, polarization curves, electrochemical impedance spectroscopy, Tafel slope calculation, long-term stability studies, and identification of active species. The current studies are performed in three-electrode cell with modified electrode as working electrode, Pt wire as counter electrode and Ag/AgCl as reference. The techniques including anaerobic synthesis, electrochemistry, gas chromatography mass spectroscopy (GC-MS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), X-ray photonelectron spectroscopy (XPS), UV-Vis, and density functional theory (DFT) studies. These techniques are critical for the characterization and identification of the complexes employed as catalysts. SEM and TEM provide detailed information about the morphology condition of the modified electrode surface, which directly determine the activity and stability of catalysts on the surface. XPS provides accurate information about the active species by showing the presence of elements on the surface with oxidation states and atom percentages of each elements.

Chapter II in this dissertation contains experimental details. This includes the preparation of modified electrodes and the general methods for electrochemical measurements. The chapter also includes an overview of electrochemical impedance spectroscopy and its interpretation. Additionally, a discussion of the DEFINE (XPS) including data analysis methods is presented.

In Chapter III, results of HER activity of modified glass carbon electrodes of ReL_3 and its oxidized derivative ReL_3^+ are discussed. Further, the impact of added carbon black on the overpotential and stability of modified electrodes is explored. All these electrodes demonstrated good long-term stability properties after an initial conditioning period. Although the relatively large overpotential for these modified electrodes limits the further application, however, the ligand centered HER mechanism opens the door to an alternative pathway and strategies for HER catalysts that does not involved metal hydride.

Chapter IV introduces another sets of homogeneous HER catalysts (ATSM, ATSP and their Zn- and Cu- derivatives) that are immobilized on glassy carbon. By employing the similar methods as in Chapter III, the HER activity for each complex has been studied under heterogeneous conditions. The results indicate that the pure ligands and their Cu complexes are active for catalysis, while the Zn complexes suffered demetallation during extended studies. Although these complexes exhibited relatively large overpotential compared to traditional heterogeneous catalysts, this study proved that the pure ligand itself showed some HER electroactivity, which strongly indicated that the CuATSM and CuATSP go through the ligand-centered mechanism.

In chapter V, the carbon paste electrode has been employed to replace the GC electrode. The catalysts were mixed with graphite powder to prepare the carbon paste. The reason for choosing the carbon paste electrode is its low cost and high sensitivity. The results of CPE-ReL₃, CPE-ATSM and CPE-CuATSM have been shown in this chapter and compare to GC systems. The overpotential for CPE system improved dramatically than GC systems, and the EIS studies revealed the correlations between charge transfer resistance on catalyst film and overpotential, which directly influence the catalytic activity of catalyst on the surface.

The last chapter, chapter VI, summarizes the conclusions of the dissertation and provides future directions. The drop casting method has been used in this dissertation, which is the simplest method to give a quick investigation on our catalysts, however, drop casting method generally result non-uniform and unstable films. Thus, different immobilization methods will be tried for our catalysts, such as electrodeposition, or chemical methods, which form chemical bond between catalysts and substrates without changing the electroactivity of complexes.

CHAPTER II

EXPERIMENTAL DETAILS

2.1 Materials and Physical Methods

All chemicals were purchased from commercial sources (Aldrich, VWR Chemicals) and used without further purification unless noted. The ligand 2-diphenylphosphinobenzenethiolate (HL) and its metal derivatives ReL_3 and $[\text{ReL}_3][\text{PF}_6]$ were synthesized by the reported literature methods as described in literatures.⁹² AgPF_6 for oxidation reactions was obtained from Aldrich and stored in an argon filled dry glove box. Carbon black was purchased from Columbian Chemicals Company (Marietta, GA). The ATSM (diacetyl-bis(N-4-methyl-3-thiosemicarbazide)) and ATSP ligand (diphenylacetyl-bis(N-4-methyl-3-thiosemicarbazone)) and its Zn and Cu derivatives were prepared according to the published literature methods as described below.⁹³⁻⁹⁴ All solvents were purified using an MBraun solvent purification system.⁹⁵ All reactions were performed under anaerobic conditions by using standard Schlenk line techniques unless noted.

Voltammetry and coulometry measurements were performed using a Gamry Interface 1000 potentiostat with a three-electrode cell. The working electrode was a glassy carbon electrode, a modified glass carbon electrode, or a carbon paste electrode

as described below. In all cases a platinum wire was used as the counter electrode with a Ag/AgCl saturated in 3.5 M KCl reference electrode. For all the measurements, the sample was purged for 15 min with N₂ and then kept under an N₂ atmosphere. Electrochemical impedance spectra (EIS) were collected on a CHI 660 electrochemical work station using the same three electrode cells as above. Reported potentials are scaled versus the reversible hydrogen electrode (RHE) according to equation 3 using a value of +0.205 V for E°_{Ag/AgCl}.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{Ag/AgCl}} \quad (\text{Eq. 3})$$

Scanning electron microscopy (SEM) images were obtained using a LEO 1550 field emission SEM. Transmission electron microscopy (TEM) images were generated using a FEI Tecnai F20 electron microscope operating at 200 kV. UV–vis absorbance spectra were recorded on a UV-3600 Shimadzu UV–vis–near infrared (NIR) spectrophotometer. A Gow-Mac series 400 GC-TCD with a molecular sieve column was used to identify the hydrogen gas that was generated after electrolysis. The column was heated to 130 °C under N₂ gas flow, and 250 µL samples were drawn from the headspace of the electrolysis cell and then injected into the column using a gastight syringe.

X-ray photoelectron spectroscopy data were collected at the Indiana University by Dr. Yaroslav Losovsky at Molecular Structure Center. X-ray photoelectron spectroscopy (XPS) analyses were performed on PHI VersaProbe II Scanning X-ray Microprobe system. All the samples were coated on carbon tape. The high-resolution scans were taken with 187 eV pass energy, 0.1 eV energy step and with 3 repeats to reduce instrument noise.

Peak fits and atomic surface concentration analyses were performed using CasaXPS software.

2.2. Electrode Modifications

A series of modified electrodes containing immobilized HER catalysts were prepared and evaluated. The HER activity of the catalysts on the modified electrodes not only requires effective electron transfer on the surface, it also requires proton transport to the active site for H₂ generation. Thus, by forming a catalyst film on the electrode surfaces, the film itself introduces resistance that causes an increase of the overpotential. This behavior has been observed previously with MoS₂ systems.⁹⁶ The poor charge/ion transportation limits electrocatalytic activity of MoS₂ resulting in an increased Tafel slope that does not reveal the true HER mechanism.⁹⁷ The incorporation of a highly conductive material, such as carbon black or graphene, into the electrocatalyst can help to improve conductivity. For example, Dai group integrated MoS₂ with reduced graphene oxide sheets and achieved an onset potential near -0.110 vs. RHE, and Kim group used carbon nanotubes as the substrate to achieve HER onset potential of -0.07 V vs RHE.^{72, 98} In this dissertation, two methods were investigated to improve the conductivity of HER modified electrodes. In Chapter 3, ReL₃ based catalysts with and without carbon black are investigated. In Chapter 5, ReL₃ and ATSM/ASTP based catalysts are dispersed in carbon paste electrodes.

2.2.1. GC-ReL₃ Electrodes

GC electrodes of model number MF-2012 with a 3.0 mm diameter were purchased from Bioanalytical Systems Inc. (West Lafayette, IN). Electrodes were polished with alumina slurry (0.5 μm) before use and then sonicated in acetone, isopropanol, and deionized water for 15 min, separately. Solutions of ReL₃ were typically prepared by dissolving 3.0 mg (2.5×10^{-3} mmol) of ReL₃ in 1.00 mL of dichloromethane (DCM). Aliquots of the catalyst solution were then carefully drop-cast onto the clean glassy carbon electrodes (area = 0.071 cm²) using a micropipette, ensuring that all of the solutions remained on the electrode until evaporation. Loading amounts ranged from 10 to 160 nmol of catalyst. Optimal loading conditions were determined by voltammetric methods. The GC-ReL₃ electrodes were stored open to air prior to use.

2.2.2. GC-[ReL₃]⁺ Electrodes

The GC-[ReL₃]⁺ electrodes were prepared using methods similar to GC-ReL₃ in an argon filled glovebox from a freshly prepared stock solution of 2.5 mM [ReL₃]PF₆ in dry, degassed DCM. The drop-casting method, catalyst loadings, and optimization procedure were the same as that described for GC-ReL₃. The GC-[ReL₃]⁺ electrodes were stored open to air.

2.2.3. GC-CB-[ReL₃] and GC-CB-[ReL₃]⁺ Electrodes

The CB modified electrodes GC-CB-[ReL₃] and GC-CB-[ReL₃]⁺ were prepared using methods similar to GC-ReL₃ as follows. A 1.0 mg portion of CB was added to 1.0 mL of dimethylformamide (DMF), and the mixture was sonicated for 30 min. Then, 12 μL of the CB solution was transferred to the surface of a clean GC electrode and heated under an

infrared heating lamp for ~15 min to evaporate the solvent. The resulting CB film evenly covered the electrode surface. Next, 60 nmol of either ReL_3 or $[\text{ReL}_3][\text{PF}_6]$ was carefully deposited on top of the CB layer by drop-casting of DCM solutions as noted above. After evaporation of the solvent, a 5.0 μL portion of a 5.0% w/w Nafion solution was added via micropipette. The electrode was dried under an infrared heating lamp. Electrodes were stored in air prior to use.

2.2.4. GC-ATSM and GC-ATSP Electrodes

GC-ATSM modified electrodes were prepared using electrodes of model number AFE2M050GCPK with 5.0 mm disk OD, 12.0 mm OD PEEK shroud that were purchased from PINE. Electrodes were polished with alumina slurry (0.5 μm) before use and then sonicated in acetone, isopropanol, and deionized water for 15 min, separately. For preparing GC-ATSM electrodes, 3.0 mg of ATSM was dissolved in 1.00 mL of dichloromethane (DCM) to form a homogeneous solution. Aliquots of the catalyst solution were then carefully drop-cast onto the clean glassy carbon electrodes (area = 0.196 cm^2) using a micropipette, ensuring that all of the solution remained on the electrode until evaporation. Loading amounts ranged from 20 nmol to 200 nmol of catalyst. Optimal loading conditions were determined by voltammetric methods. The GC-ATSM electrodes were stored open to air prior to use.

2.2.5. GC-CuATSM, GC-ZnATSM Electrodes

Modified electrodes containing the metal complexes CuASTM and ZnATSM were prepared using method similar to GC-ATSM. The catalysts solutions were prepared by dissolving 3.0 mg of CuATSM or ZnATSM in 1.00 mL DCM. The drop-casting method,

catalyst loadings and optimization procedure were the same as that described for GC-ATSM. The GC-CuATSM and GC-ZnATSM were stored open in the air.

2.2.6. GC-CuATSP and GC-ZnATSP Electrodes

Modified electrodes containing the metal complexes CuASTP and ZnATSP were prepared using methods similar to GC-ATSM. The catalysts solutions were prepared by dissolving 3.0 mg of ATSP, CuATSP and ZnATSP in 1.00 mL DCM. The drop-casting method, catalyst loadings and optimization procedure were the same as that described for GC-ATSM. The GC-CuATSM and GC-ZnATSM were stored open in the air.

2.2.7. Carbon Paste (CP) Electrode: CPE-ReL₃ and CPE-CuATSM

CPE-ReL₃ and CPE-CuATSM electrodes were prepared according to general methods previously described for the incorporation of metal complexes into carbon paste.⁹⁹⁻¹⁰¹ in this dissertation, 3 mg of graphite powder was used with 0.6 g of paraffin oil to prepare the carbon paste. The general procedure to prepare the carbon paste electrode was as follows. Different amounts of ReL₃/CuATSM along with appropriate amount of graphite powder, and paraffin oil were thoroughly mixed. The resulting mixture was transferred into a plastic syringe. Electrode bodies were made from 1 mL NORM-JECT syringes (5 mm diameter), the tip of which had been cut off with a cutter. After the well mixed, the paste was packed carefully into the tube tip and pressed tightly and Nafion film was covered on the CPE surface by drop-casting Nafion liquid on the top. A copper wire was inserted into the opposite end of the paste to establish electrical contact. The external electrode surface was smoothed with weighting paper. A new surface was produced by scraping out the old surface and replacing the carbon paste.

Optimal proportion of catalyst to graphite powder were determined by voltammetric methods.

2.3. Electrochemical Methods

Cyclic Voltammetry (CV) was used to evaluate the HER activity the ReL_3 based catalysts on GC described in Chapter 3. The current density for HER was calculated using the maximum observed current of the reduction event and the area of the electrode (0.071 cm^2). The potential was referenced to RHE according to equation 1. Blank and control experiments were performed for non-modified glassy carbon electrode under the same condition of those modified electrodes. All experiments were repeated at least 5 times.

Polarization curve measurements were used to establish the HER overpotential for each system. A polarization curve is a plot of current density (j) versus electrode potential (E) for a specific electrode-electrolyte combination. The polarization curve represents the basic kinetic law for any electrochemical reaction. The measurements with all systems were conducted using the 3 electrode cells described above with a volume of $\sim 10 \text{ mL}$ of $0.5 \text{ M H}_2\text{SO}_4$ solution. The cell was washed and dried in an oven overnight before use. Before measurement, the solution was purged with N_2 for 15 min. Polarization curves were generated from linear sweep experiments conducted using a three-neck cell which described before. The applied potential on working electrode was ranged from 0.72 V to -1.48 V vs. RHE, at scan rate of 50 mV/s . All the overpotentials are reported at a current density of 10 mA/cm^2 . Blank and control experiments were performed for non-

modified glassy carbon electrode under the same condition of those modified electrodes. All experiments were repeated at least 5 times.

The polar curves were analyzed to determine the Tafel slope to study the electron transfer between modified electrode and the solution. A Tafel plot is merely a plot of the logarithm of the current density as a function of the applied potential or overpotential. Tafel slopes for numerous multistep electrochemical reactions have been derived from first principles. The value of Tafel slope can be used to determine the electrochemical mechanism and identify the rate-determine step. Based on reported literature values, if the Volmer step is the rate-determine step, a slope of ~120 mV/dec should be observed, while a rate determining Heyrovsky or Tafel step should produce slopes between 30 and 40 mV/dec (ref). Additionally, a Tafel slope of 120 mV/dec was observed in the higher coverage region ($\theta_H > 0.6$) for the Heyrovsky rate determining step. Therefore, a high Tafel slope of 120 mV/dec could be from either the Volmer rate determining step or the Heyrovsky rate determining step with high adsorbed hydrogen atom coverage (ref). Conventionally, the Tafel analysis results to two parameters: Tafel slope and the exchange current density. Empirically, the following Tafel relation has been well confirmed:

$$\eta = a + b \log(j)$$

where η defines the overpotential, which is the difference between the electrode and standard potentials ($\eta = E - E_0$), j denotes the current density, and b is the Tafel slope. Thus, by plotting $\log(j)$ as function of η , Tafel slope value (b) can be calculated.

Bulk electrolysis (BE) was conducted to calculate the Faradic efficiency of HER and to study the stability of the catalyst on the surface before and after electrolysis. The potential for BE experiments was set equal to the potential of maximum HER current density for each catalyst. The potential was applied for 3 minutes. For calculations of Faradaic efficiency, BE experiments were conducted in an H-cell to quantify and collect gaseous products. The left side of the reactor was the working electrode (modified glassy carbon electrode) and reference electrode (Ag/AgCl), while the right side of the reactor was the counter electrode (Pt). The bridge between the two parts and both sides were filled with 0.5 M H_2SO_4 solution. When applying potential on the working electrode, on the working electrode surface, gas was generated and collected on the top of the left column. The bulk electrolysis only ran for 3 min, which is short enough to ignore the dissolution of gas into the solution. The collected gas volume can be measured by the change of the height of solution in left side. The product also was injected into a gas chromatography to do identification. A Gow-Mac series 400 GC-TCD with molecular sieve column was used for product detection. The column was heated to 130 °C under N_2 gas flow with 250 μL injection samples injected onto the column. The H_2 peak has been confirmed by running standard H_2 gas which has retention time at 3.1 min.

Stability studies have been performed to evaluate the short-term and long-term stability of the modified electrodes. For short-term stability studies, a series of 500 continuous cycles in 0.5 M H_2SO_4 at 200 mV/s were performed by CV using the modified electrode. The HER overpotential before and after the CV cycles were measured. For long-term stability study, a chronopotentiometry experiment was conducted. The

overpotential required to maintain a catalytic current density of 10 mA/cm² was recorded over 24 hours.

2.4 Impedance Study and Simulations

Electrochemical Impedance Spectroscopy (EIS) also is called AC, and which consists in measuring the response of an electrode to a potential modulation at a range of frequency. There are number of books that introduce the theory, terminology and definitions, and experimental setup for EIS measurements.¹⁰²⁻¹⁰⁴ Generally, the potential-current dependencies of electrochemical systems are non-linear, and it is possible to extract a small fraction of this dependence, where mentioned dependence can be approximated as liner, for instance, in the range of 5-10 mV, and that's why the amplitude 5-10 mV were applied during the testing. The electrochemical impedance of electrode reaction(Z) is defined analogous to Ohm's law as equation 4:

$$Z(\omega) = \frac{E(t)}{I(t)} = \frac{|E_0| \sin(\omega t)}{|I_0| \sin(\omega t - \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t - \phi)} \quad \text{Equation 4}$$

here: E_0 and I_0 is amplitude of potential and current, respectively, $\omega = 2\pi f$ is the radial frequency in rad/s (f is a frequency expressed in Hz). With the mathematical identity, these functions can be described as:

$$\exp(jx) = \cos x + j \sin x$$

it is obtained

$$E(t) = |E_0| \exp(j\omega t)$$

$$I(t) = |I_0| \exp(j\omega t - j\phi)$$

here j is a complex unit $j = \sqrt{-1}$.

Therefore, the original equation can be written to define the impedance as a sum of real (Z_{Re}) and imaginary parts (Z_{Im}) at certain ω :

$$\begin{aligned} Z(\omega) &= |Z_0| \exp(j\phi) \\ &= |Z_0|(\cos \phi + j \sin \phi) = |Z_0| \cos \phi + j|Z_0| \sin \phi = Z_{Re} + j Z_{Im} \end{aligned}$$

Z_{Re} and Z_{Im} are marked as Z' and Z'' in Nyquist plot, respectively.

The Nyquist plot makes it easy to see the effects of the ohmic resistance, which can be read directly from the plot. The shape of the curve (usually semicircles) does not change when the ohmic resistance changes. Moreover, the Nyquist plot emphasizes circuit components that are in series. By knowing the frequency, ohmic resistance and polarization (charge transfer) resistance can be calculated. EIS data can be analyzed by fitting it to an equivalent circuit model consisting of different elements such as resistor, capacitor and CPE. To be useful, the elements in the circuit should have physical meaning for the system, for example, R_s can be explained as contact resistance in heterogeneous system between electrode surfaces and solution.

The explanation of EIS data is based on the circuit model that are used to do the fitting. Regardless the variety of electrode processes, such as deposition and oxide film formation, they contain similar steps such as the presence of contact resistance and charge transfer resistance, sometimes include diffusion resistance, therefore, for different systems, same equivalent circuits can be applied but with different explanations.

Zview has been used to process the EIS fitting and calculate the electrochemical impedance as a function of frequency.

The model should be built based on the consequence of the reaction by elements or circuits connected in series or parallel. Most used equivalent models are provided in Figure X. In real systems, more complicated models have been used to give better physical interpretations. One of the most important element is constant-phase element (CPE), which is caused by the distribution of microscopic material properties. For example, the surfaces of modified electrodes are not smooth and uniform on the microscopic level.

The electron impedance spectroscopy (EIS) measurements were conducted under the same conditions as CV, linear sweep, and bulk electrolysis experiments described above. The data was collected over a frequency of 10^{-2} to 10^5 at an applied overpotential at 1.3 V.

EIS data were fit using Zview with different models. An overview of commonly applied models for different shaped Nyquist plots has been reported by H. Cesiulis et. al.¹⁰⁵ For ReL_3 , R_s (solution resistance), R_{ct} (charge transfer resistance) and CPE parameters has been used to build the circuit. For GC-ATSM, GC-ATSP, GC-CuATSM and GC-CuATSP electrodes, the same model has been used as GC- ReL_3 . For carbon paste electrodes, the Nyquist plot of CPE- ReL_3 was fitted by a model included R_s (solution resistance), R_D (diffusion resistance) and R_{ct} (charge transfer resistance). A Warburg diffusion element (W) was added for CPE-ATSM and CPE-CuATSM.

2.5. ReL₃: Sample Faradaic Efficiency (FE) Calculations

Theoretical Moles of Hydrogen Made via Total Charge:

$$(Q_{\text{net}}) \times (1 \text{ mol e}^- / 96485 \text{ C}) \times (1 \text{ mol H}_2 / 2 \text{ mol e}^-) = \text{Theoretical moles H}_2.$$

$$\text{FE} = \text{Real generated H}_2 / \text{theoretical generated H}_2$$

The volume of real generated H₂ was calculated by the method described before. The radius of tube is 1.12 cm, and the change of the height can be measured.

$$\text{Thus, the } V_{\text{real}} (\text{cm}^3) = 3.14 \times 1.12^2 (\text{cm}^2) \times \text{height} (\text{cm})$$

For ReL₃:

The Chronopotentiometry has been conducted at overpotential of -1.48 V for 180 s in the three-neck cell which has been used for CV measurements. The volume of gas dissolution into the solution is ignored because of the short time. The reaction takes place at 298 K with assumption of ideal gas behavior.

Calculation Procedure:

1. Calculate the theoretical moles of H₂ based on the total charge at 100% Faradaic efficiency.
2. Measure and calculate the volume of H₂ that generated from the reaction, and the method has been described before. (ref)
3. Calculate the moles of H₂ based on the 2nd step volume.
4. Divided the moles of step 3 by step 1.

Experimental Calculation:

1st Trial:

$$96500c/(1\text{ mol})=19.55c/(2x\text{ mol})$$

$$X=1.35\times 10^{-4}\text{ mol}$$

$$\text{Real generated H}_2: V=3.14\times 1.12^2\times 0.75\text{ (cm}^3\text{)}=2.95\times 10^{-3}$$

$$(1\text{ mol})/(22.4\text{ L})=(x\text{ mol})/(2.95\times 10^{-3})$$

$$X=1.32\times 10^{-4}$$

$$\text{FE}=1.32\times 10^{-4} / 1.35\times 10^{-4} =97.78\%$$

2nd Trial:

$$96500c/(1\text{ mol})=25.63c/(2x\text{ mol})$$

$$X=1.33\times 10^{-4}\text{ mol}$$

$$\text{Real generated H}_2: V=3.14\times 1.12^2\times 0.74\text{ (cm}^3\text{)}=2.91\times 10^{-3}$$

$$(1\text{ mol})/(22.4\text{ L})=(x\text{ mol})/(3.03\times 10^{-3})$$

$$X=1.30\times 10^{-4}$$

$$\text{FE}=1.30\times 10^{-4} / 1.33\times 10^{-4} =97.74\%$$

3rd Trial:

$$96500c/(1\text{ mol})=22.03c/(2x\text{ mol})$$

$$X=1.15\times 10^{-4}\text{ mol}$$

$$\text{Real generated H}_2: V=3.14\times 1.12^2\times 0.65\text{ (cm}^3\text{)}=2.56\times 10^{-3}$$

$$(1\text{ mol})/(22.4\text{ L})=(x\text{ mol})/(2.56\times 10^{-3})$$

$$X=1.14\times 10^{-4}$$

$$\text{FE}=1.14\times 10^{-4} / 1.15\times 10^{-4} =99.13\%$$

2.6. XPS Fitting with CasaXPS

CasaXPS is a popular computer aided surface analysis software for X-ray photoelectron spectroscopy. It offers a powerful data processing environment to process XPS data and also very powerful in fitting.

The procedure of using CasaXPS:

1. load the experiment file
2. select a spectrum for processing
3. identify peaks
4. annotate peaks using element markers
5. create quantification regions
6. adjust region start and end points
7. results output

The identification of peaks can be done using Library, which contains binding energy database for every element. The Element Library is maintained by CasaXPS system and provide the information that describes the X-ray induced transitions, such as peak position, peak widths and relative sensitivity factors.

Quantification of peaks is processed by using Main Toolbar. The first step is defining one or more energy regions. The regions determine the starting and ending point of peaks. Each region requires the following information: 1. Name: the name is important as quantification object and needs to have reasonable physical meanings. 2. Relative sensitivity Factor (R.S.F.): RSF are used to scale the measured peaks areas so that

variations the peaks areas are representative of the amount of materials in the surface of sample. The element library contains RFSs for XPS transitions. Common RSF value can be found on www.xpsfitting.com. 3. Start: start point for the integration interval. 4. End: end point for the integration interval. 5. Background setting: the back ground setting has four types, include Tougaard, Shirley, Linear and None. The Tougaard background is a methodology for integrating the intensity of the background at a given binding energy from the spectral intensities to higher kinetic energies.¹⁰⁶ The problem of using Tougaard background is even it is the most accuracy method but it's too complicated for real applications. Linear background is the simplest method which will give a straight line or linear background. However, the linear background suffers from large peak area changes depending on the chosen of the range, thus, the accuracy is very poor. Shirley background provides background intensity proportional to the intensity of the total peak area above the background in the lower binding energy peak range. The accuracy of Shirley background is between Tougaard and Linear. Thus, Shirley background has been use in the fitting. 6. Average Width: Number of channels used to fix end points for the backgrounds. For example, the parameters in Region for ZnATSM is shown in Figure 5.

Figure 5. Parameters for XPS fitting of ZnATSM

After set up for regions, in components, different numbers of component can be created to fit the peak. Generally, the peak fitting should be based on the actual physical structure of sample. For ZnATSM, the structure is shown in Figure 6, it has four types of carbons with different electronic environments. The two hydrocarbons should be very close and the lowest binding energy is at 284.8 eV, while the other one should have a very close value. The C (C₃) that bonds two N (with one single bond and one double bond) and one S should be the one in the middle BE, and the C (C₄) that bond to one carbons and double bond with N should at the highest binding energy. The ration of these C 1s is 1:1:1:1. The fitting in CasaXPS has been shown in Figure 7, with information of name, position (binding energy) and areas. The binding energy for each C is: C1 +C2 at 284.8 eV, C 2 at 285.60 eV, C 3 at 287.39 eV and C 4 at 287.39 eV which represents the C-O contamination.

Figure 6. Structure of CuATSM

Figure 7. C 1s fitting for CuATSM

The finally step is save the data to the clipboard and use Excel or Igor to plot the data. C 1s fitting is very important for the whole fitting. The C-C component should be always set to a binding energy at 284.8 eV, which needs to be used as standard to do the calibration for other elements. Binding energy of common chemical states for C 1s are shown in Table 1.

Table 1. Binding energy of common chemical states for C 1s.

Chemical States	Binding Energy Mg1s/eV
C-C	284.8
C-O	~286
C=O	~289
CF ₂	~292
CF ₃	~294

For S 2p, the primary XPS binding energy of common chemical states are shown in Table 2.

Table 2. Binding energy of common chemical states for S 2p.

Chemical States	Binding Energy Mg1s/eV
Metal sulfide	~161.5
Thiol bound to gold, Au-S	162.5
Thiol, R-SH	~164
Na ₂ (SO ₃) ₂	166.5
Metal sulfate	~169

* These number referenced to calibrated C 1s peak at 284.8 eV.

For N 1s, the typical region is from 397-405 eV, and the binding energy of common chemical states are shown in Table 3.

Table 3. Binding energy of common chemical states for N 1s.

Chemical States	Binding Energy Mg1s/eV
Metal nitrides	~397
NSi ₃ (Si ₃ N ₄)	398.0
NSi ₂ O	399.9
NSiO ₂	402.5
C-NH ₂	~400
Nitrate	>405

Region Parameters for ATSM ligand, and the structure of ATSM is shown in Figure 8:

Figure 8. Structure of ATSM Ligand

Table 4. Region parameters of ATSM fitting

Region	C 1s	N 1s	S 2p
R.S.F	1	1.8	1.91
Start	288.992	405.877	168.179
End	283.636	400.343	162.699
BG Type	Shirley	Shirley	Shirley
Av. Width	1	1	1

Based on the ATSM structure, four types Cs has been used to fit the C 1s signal and one C at high BE was contamination. One type of S has been used to fit the S 2p signal, and the doublet of S2p peaks has been fixed with energy difference of $\Delta=1.16\text{eV}$, and intensity ratio=0.511. Three Ns have been used to run the fitting, because there are three types of N in the system and the ratio is 1:1:1. A small bump was observed at high BE, which is caused by contamination.

For ZnATSM and CuATSM:

The ZnATSM and CuATSM are the derivatives of ATSM ligand, thus, the C 1s, N1s and S 2p fitting parameters are the same as ATSM. For Zn and Cu peak fittings, the parameters are shown in Table 5.

Table 5. Parameters for XPS fitting of ZnATSM and CuATSM.

Region	Zn 2p 3/2	Zn 2p 1/2	Cu 2p 3/2	Cu 2p 1/2
R.S.F	31.592	31.592	27.8782	27.8782
Start	1024.6	1047.5	937.066	955.937
End	1018.66	1041.77	929.702	947.997
BG Type	Shirley	Shirley	Shirley	Shirley
Av. Width	1	1	1	1

For Zn, single peaks were used to fit Zn 2p 3/2 and Zn 2p 1/2, and in CuATSM, two oxidation states of Cu(I) and Cu(II) was observed and satellites was showed in the range of 937-948 eV. For ATSP Ligand systems, the fitting parameters are the same as in ATSM systems.

CHAPTER III

LIGAND-CENTERED HYDROGEN EVOLUTION REACTION (HER) ACTIVITY AND MECHANISM OF A RHENIUM-THIOLATE ON ELECTRODE SURFACE

3.1. Background

The use of hydrogen as an energy carrier offers a potential carbon-free alternative to fossil fuels.¹⁰⁷ Estimates suggest a hydrogen-based economy would require as much as 150 million tons of H₂ annually,¹⁰⁸ fueling the need for efficient electrolytic and/or photochemical catalysts.¹⁰⁹ The development of heterogeneous and homogeneous catalysts for the hydrogen evolution reaction (HER), $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$, and the hydrogen oxidation reaction (HOR), its reverse, has received significant attention.¹¹⁰⁻¹²¹ The ideal catalyst is Pt; however, its application in large-scale hydrogen production is limited by the its cost and scarcity.¹²² This has prompted the development of new earth-abundant electrocatalysts, including transition-metal phosphides,^{75, 123} selenides,¹²⁴ and sulfides. Molybdenum sulfides have shown great promise as an economical alternative to Pt.^{80, 125-126} The high activity of MoS₂ arises in large part from the location and number of cis-sulfur edge sites.⁸⁰

Recently, the Grapperhaus Group reported the homogeneous electrocatalytic HER/HOR activity of ReL₃ (L = diphenylphosphinobenzenethiolate).¹¹² The ReL₃ complex

contains three thiolate donors with cis-thiolates similar to the S edges of MoS₂. The HER mechanism of ReL₃ is proposed to follow a unique ligand-centered mechanism that avoids metal hydrides.¹¹² This reactivity deviates from most homogeneous systems which operate via crucial metal-hydride intermediates, with several displaying low overpotentials, high turnover frequencies, and faradaic efficiencies >90%.^{111, 117} The ReL₃ system is one of only a few examples of ligand-centered HER/HOR reactions reported to date^{112, 127-131} as well as one of the only ligand-centered homogeneous systems employing a cis-sulfur active site, affording a unique opportunity to correlate ligand-centered homogeneous catalytic and mechanistic studies with heterogeneous studies.

This Chapter describes the fabrication of surface modified electrodes through simple physisorption, which avoids modification of the molecular ReL₃ catalyst while retaining solution HER activity of ReL₃. To this end, we translated the homogeneous HER activity of ReL₃ in nonaqueous solution to a series of four modified glassy carbon (GC) electrodes (Scheme 1) for heterogeneous application in an acidic aqueous environment. To benchmark the catalytic activity, a recent protocol reported by Jaramillo and co-workers was followed to establish the efficiency and long-term stability of HER electrocatalysts.¹²⁸ A portion of the contents of this Chapter have been reported as part of a publication in the *American Chemical Society journal Inorganic Chemistry*.¹³²

The immobilization of homogeneous HER catalysts on electrode surfaces by physisorption has previously been reported.¹³³⁻¹³⁸ Notable examples include Fontecave and co-worker's multiwalled carbon nanotube [Ni(P^{Ph}₂N^{Ph}₂)₂] modified electrodes, which display high catalytic activity for both HER and HOR in acetonitrile.¹³⁴ Pantani and co-

workers observed HER activity with Co $-(\text{dmgBF}_2)_2(\text{CH}_3\text{CN})_2$ /carbon black (CB)/Nafion coated GC electrodes,¹³⁵ while Peters and co-workers modified GC electrodes with cobaloximes as HER catalysts with low overpotentials in aqueous solutions ($\text{pH} < 4.5$).^{133,}
¹³⁵ Other electrode surfaces modified with cobalt porphyrin,¹³⁹ metal-phthalocyanine,¹⁴⁰⁻
¹⁴³ and an organometallic Rh complex incorporated in a Nafion film¹⁴⁴ have also been reported as HER electrocatalysts but at higher overpotentials.

Scheme 1. Schematic of ReL_3 modified electrodes.

3.2. Results and Discussion

3.2.1. Electrode Modification

A series of four modified GC electrodes were prepared based on the homogeneous HER catalysts ReL_3 (Scheme 1). The ReL_3 complex and its oxidized derivative $[\text{ReL}_3][\text{PF}_6]$ are readily soluble in dichloromethane (DCM) but insoluble under aqueous conditions, attributable to the large number of phenyl rings in the structure. As such, evaporation of DCM solutions of ReL_3 or $[\text{ReL}_3][\text{PF}_6]$ on GC surfaces yield water-stable films due to adhesive dispersion forces and/or ion-induced dipole interactions. Once prepared, all modified electrodes were stable under ambient conditions and upon

submersion in aqueous solution over a pH range of 0.25–13 as determined by voltammetry over a period of several days.

The simplest electrode, GC-ReL₃, consists of a GC surface coated with an electroactive film of ReL₃. The film was fabricated by drop-casting a controlled volume of a 2.5 M DCM solution of ReL₃, which leaves a known molar quantity of catalyst on the electrode upon solvent evaporation. Similar methodology was employed to prepare GC-[ReL₃]⁺, which has a film of formal Re(II) catalyst precursor [ReL₃][PF₆]. A key difference between GC-ReL₃ and GC-[ReL₃]⁺ is that the former has a charge neutral catalyst film, while the latter has an ionic catalyst film. Diffuse reflectance spectra confirm the presence of ReL₃ (544 nm) and [ReL₃]⁺ (580 nm) on the surface of GC-ReL₃ and GC-[ReL₃]⁺, respectively (see Appendix Figure AX).⁵¹

Multilayer modified electrodes GC-CB-ReL₃ and GC-CB-[ReL₃]⁺ were prepared to enhance conductivity and promote substrate binding. These electrodes consist of a GC surface with an initial CB layer, followed by a catalyst film of ReL₃ or [ReL₃][PF₆] and topped with a layer of Nafion. The CB, added to improve conductivity between the GC surface and the catalyst,⁷⁰ was drop-cast as a DMF slurry followed by drying upon an infrared heat lamp. After incorporation of the catalyst film, addition of the ionic polymer Nafion to promote film stability and proton binding was done by drop-casting an aqueous Nafion solution with further drying under the heating lamp.

Microscopy studies reveal distinct differences in the morphology of the charge neutral film of GC-ReL₃ and the ionic film of GC-[ReL₃]⁺. The SEM image of GC-ReL₃ (Figure

9a) shows a porous multilayer structure distributed with uneven surface coverage. This is consistent with a preference for cohesive interactions between ReL_3 molecules over adhesive interactions between ReL_3 and the GC surface. The TEM image (Figure 9b) reveals that the ReL_3 film is comprised of randomly arranged plate-shaped nanoparticles approximately 10 nm in diameter. In contrast, the SEM image of $\text{GC-}[\text{ReL}_3]^+$ (Figure 9c) displays more highly uniform film coverage, although substantial cracking is evident. The uniformity is attributed to stronger adhesive interactions between the complex ions and the GC surface. The TEM image of the $[\text{ReL}_3]^+$ film (Figure 9d) finds larger dendritic shaped nanoparticles aligned in two dimensions.

Figure 9. Film topography prior to HER. SEM (a) and TEM (b) images of GC-ReL_3 and SEM (c) and TEM (d) images of $\text{GC-ReL}_3\text{GC-}[\text{ReL}_3]^+$.

3.2.2. Electrocatalytic Hydrogen Evolution Reaction

As previously reported, ReL_3 is an effective homogeneous HER electrocatalyst in DCM with a maximum turnover frequency of $32 \pm 3 \text{ s}^{-1}$.¹¹² To determine the optimal loading of immobilized ReL_3 and $[\text{ReL}_3]^+$ on GC for heterogeneous activity, a series of electrodes were prepared and evaluated. A $2.5 \times 10^{-3} \text{ mmol}$ ReL_3 stock solution has been prepared by dissolving 3.0 mg of ReL_3 in 1.00 mL DCM, and different amount of solution has been drop casted on the GC surface by micropipette. The CV of modified electrodes (GC-ReL_3 and GC-ReL_3^+) with different loadings from 10×10^{-3} to $120 \times 10^{-3} \text{ mmol}$ were measured in 0.5 M H_2SO_4 at 200 mVs^{-1} , and the current densities were calculated and displayed in Figure 10. For GC-ReL_3 , catalytic current steadily increases upon addition of catalyst up to 60 nmol as the porous structure of small nanoplates provides a pathway for substrate/electrolyte transfer deeper into the film. In contrast, the uniform dendritic film of $\text{GC-}[\text{ReL}_3]^+$ displays optimal HER activity at lower loading (10 nmol). Decreased activity at higher loading suggests an increased charge transfer resistance through thicker layers as confirmed by electron impedance spectroscopy (Table 6). For GC-ReL_3 and $\text{GC-}[\text{ReL}_3]^+$, SEM images (Appendix A Figure A3 and A4) collected after H_2 evolution reveal film degradation.

Figure 10. Optimum Loading Amount of GC-ReL₃ and GC-[ReL₃]⁺

Table 6. Simulated Nyquist plot parameters for ReL3 modified electrodes from the impedance spectra.

Electrode/Load (nmol)	R _s (Ω)	R _{ct} (MΩ)	CPE-T (sP/mΩ)	CPE-P (sP/Ω)
GC-ReL ₃ /10	43.3	1.38	0.6	0.83
GC-ReL ₃ /60	41.1	0.72	2.0	0.88
GC-ReL ₃ /120	39.5	0.88	1.5	0.84
GC-[ReL] ₃ ⁺ /10	19.5	0.09	0.2	0.84
GC-[ReL] ₃ ⁺ /60	18.6	0.25	9.0	0.90
GC-[ReL] ₃ ⁺ /120	19.5	0.87	2.0	0.80
GC-CB-[ReL] ₃ /60	31.3	0.06	170	0.79
GC-CB-[ReL] ₃ ⁺ /60	50.0	0.04	240	0.70

To evaluate the HER activity of ReL_3 under heterogeneous aqueous conditions, polarization curves were recorded for the modified electrodes in 0.5 M H_2SO_4 under ambient conditions (Figure 11). Results are summarized in Table 612, which compares the overpotential required to obtain a current density of 10 mA/cm^2 for the 4 electrodes at 60 nmol catalyst loading. The charge neutral film of GC- ReL_3 exhibits the largest overpotential of 0.919 V, whereas incorporation of the ionic, oxidized catalyst precursor $[\text{ReL}_3]^+$ lowers the overpotential of GC- $[\text{ReL}_3]^+$ by as much as 0.192 V. Notably, the optimized loading of GC- $[\text{ReL}_3]^+$ (10 nmol catalyst) is substantially lower than that of GC- ReL_3 (60 nmol catalyst). Overpotential decreases by an additional 0.43–0.47 V in the multilayered electrodes. Thus, overpotentials as low as 0.357 V are observed for GC-CB- $[\text{ReL}_3]^+$, which is 0.290 V lower than cobaloxime modified GC electrodes.¹³³ As detailed below, the overpotential of ReL_3 modified electrodes correlates with film morphology and resistance.

To evaluate the Faradaic efficiency, controlled potential coulometry at -1.48 V versus RHE was applied for a fixed time. Electrolysis was performed in a two-compartment cell with the evolved H_2 collected in the headspace above the cathode. To calculate the Faradaic efficiency, the molar quantity of H_2 as determined from the volume of the collected gas and compared to the quantity of charge passed. Faradaic efficiencies of GC- $[\text{ReL}_3]$ and GC- $[\text{ReL}_3]^+$ were calculated as 97 and 98%, respectively, over 160 s. For the CB modified electrodes, Faradaic efficiencies of 87 and 90% were measured for GC-CB- $[\text{ReL}_3]$ and GC-CB- $[\text{ReL}_3]^+$, respectively, over 100 s.

Figure 11. Polarization curves of GC-[ReL₃]ⁿ⁺ and GC-CB-[ReL₃]ⁿ⁺ (n = 0 and 1) recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference electrode.

Table 7. HER Overpotentials (η) and Tafel Slopes of the ReL₃ Modified Electrodes.

Electrode	Loading (nmol)	η [a] vs. RHE (mV)	Tafel Slope (mV/dec.)
GC-ReL ₃	60	919	154
GC-[ReL ₃] ⁺	60	835	175
GC-[ReL ₃] ⁺	10	727	190
GC-CB-ReL ₃	60	487	199
GC-CB-[ReL ₃] ⁺	60	357	155

[a] Converted to RHE from values measured versus Ag/AgCl using $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.205 \text{ V}$.

3.2.3. Stability Study and Microscopy Studies of Modified Electrodes

Initial assessments of the electrode stabilities of GC-[ReL₃] and GC-[ReL₃]⁺ were conducted by cyclic voltammetry (CV). Continuous scanning over 500 cycles ranging from +0.32 to −1.48 V versus RHE at a scan rate of 200 mV/s resulted in an increase of overpotential by 300 and 350 mV for GC-[ReL₃] and GC-[ReL₃]⁺, respectively (Figure 12). The results indicated that the modified GC surfaces were not stable during the short term

continuous scanning measurement, and the increasing of the overpotential probably caused by the conditioning of the surface at the beginning.

The long-term stability of GC-[ReL₃]ⁿ⁺ (n = 0 or 1) was benchmarked through chronopotentiometry at a fixed catalytic current density of 10 mA/cm² over 24 h. For GC-[ReL₃]. The overpotential increases by 510 mV over the first 3 h but then remains constant over the remainder of the experiment, consistent with initial conditioning of the electrode. For GC-[ReL₃]⁺, the increase in overpotential is slightly less, 430 mV, over the first 2 h with a good stability for the remainder of the experiment (Figure 13). The initial increase in overpotential can be attributed to a decrease in the number of active sites on the surface, which would increase the potential required to maintain the same current density. For both GC-[ReL₃] and GC-[ReL₃]⁺, no further change in overpotential was observed upon placing the conditioned electrode in a fresh 0.5 M H₂SO₄ solution and applying a potential.

Figure 12. Initial stability study of GC--ReL₃ (a), GC-[ReL₃]ⁿ⁺ (b), GC-CB-ReL₃ (c) and GC-CB-[ReL₃]ⁿ⁺ (d).

Figure 13. Extend stability study of (a) GC-ReL₃ and GC-[ReL₃]ⁿ⁺ and (b) GC-CB-ReL₃ and GC-CB-[ReL₃]ⁿ⁺.

The stability of CB modified electrodes was similarly evaluated. The initial CV studies revealed an increase in overpotential of 340 and 400 mV for GC-CB-[ReL₃] and GC-CB-[ReL₃]⁺, respectively, after 500 cycles. Chronopotentiometry measurements of GC-CB-[ReL₃] required an increase in overpotential of 1.0 V during the first 1.5 h to maintain a current density of 10 mA/cm². Notably, the final overpotential of 1.53 V is statistically equivalent to the value observed for GC-[ReL₃], indicating that the benefits of CB do not persist over prolonged electrolysis. The GC-CB-[ReL₃]⁺ electrodes behave similarly with an increase in overpotential of 1.0 V to a final value consistent with GC-[ReL₃]⁺.

3.2.4. Impedance Studies

Electrochemical impedance spectroscopy confirms a correlation between film resistance and HER overpotential. Data were collected over a frequency range of 10⁻² to 10⁵ Hz at an applied overpotential of 1.3 V. Nyquist plots of the EIS data (see Figure 14

and Figure 15) were simulated using the model in Figure 16. Simulation parameters are provided in Table 2. The similarity among the responses of all fabricated GC electrodes suggests a similar mechanism for hydrogen evolution, and the lack of Warburg impedance indicates that mass transport is rapid enough so that the reaction is kinetically controlled.¹²⁵ The R_{ct} term, which represents charge transfer resistance within the catalyst film, has the largest impact on overpotential (Table 8). The multilayered modified electrodes require the least overpotential and also display the lowest R_{ct} with values of 0.004 and 0.006 M Ω for GC-CB-[ReL₃]⁺ and GC-CB-ReL₃, respectively. The R_{ct} for the ionic film of GC-[ReL₃]⁺ is 0.09 M Ω under optimal loading conditions, which is 24 times larger than that for GC-CB-[ReL₃]⁺. Additional catalyst loading increases the R_{ct} of GC-[ReL₃]⁺ consistent with slower electron transfer through the thicker film. The charge neutral catalyst film of GC-ReL₃ displays the largest R_{ct} of 0.72 M Ω under optimal loading conditions and also requires the largest overpotential.

Figure 14. Nyquist plots of GC-ReL₃ (left) and GC-[ReL₃]ⁿ⁺ (right) at 10, 60, and 120 nmol catalyst loadings at $\eta=1.3$ V in 0.5 M H₂SO₄.

Figure 15. Nyquist plots of GC-ReL₃ (orange) and GC-CB-ReL₃ (blue) (left) and GC-[ReL₃]ⁿ⁺ (blue) and GC-CB-[ReL₃]ⁿ⁺ (right) at $\eta=1.3$ V in 0.5 M H₂SO₄

Figure 16. Model of EIS Simulation where R_{ct} represents charge transfer resistance in the film.

Table 8. Simulated Nyquist plot parameters for ReL₃ modified electrodes from the impedance spectra.

Electrode/Load (nmol)	R_s (Ω)	R_{ct} ($M\Omega$)	CPE-T (sP/m Ω)	CPE-P (sP/ Ω)
GC-ReL ₃ /10	43.3	1.38	0.6	0.83
GC-ReL ₃ /60	41.1	0.72	2.0	0.88
GC-ReL ₃ /120	39.5	0.88	1.5	0.84
GC-[ReL ₃] ⁺ /10	19.5	0.09	0.2	0.84
GC-[ReL ₃] ⁺ /60	18.6	0.25	9.0	0.90
GC-[ReL ₃] ⁺ /120	19.5	0.87	2.0	0.80
GC-CB-[ReL ₃]/60	31.3	0.006	170	0.79
GC-CB-[ReL ₃] ⁺ /60	50.0	0.004	240	0.70

3.2.5. Evaluation of Active Species

To investigate the identity of the active species on the electrode surface, a series of UV-visible studies was performed. First, to verify the presence of intact complex on the electrode surface, diffuse reflectance measurements of catalysts deposited on

optically transparent indium tin oxide (ITO) electrodes were collected after initial deposition and following catalysis. The spectra (Figures 17a and 17b) confirm the presence of ReL_3 (544 nm) and $[\text{ReL}_3]^+$ (580 nm) on the surface of freshly prepared ITO- ReL_3 and ITO- $[\text{ReL}_3]^+$, respectively.⁵¹ Following HER, both films display a peak at 544 nm, indicating that all surface exposed complex has been converted to the ReL_3 catalyst resting state. To evaluate if the bulk material has also been converted to ReL_3 , the $[\text{ReL}_3]^{n+}$ film was removed from the GC electrode surface by washing with DCM, and UV-visible analysis of the resulting solution was performed. The spectra of DCM washings collected after HER at an applied potential of -1.48 V in 0.5 M H_2SO_4 for 3 min are identical to those collected prior to catalysis (Figures 17c and 17d). The results indicate the complexes are stable during catalysis with no formation of additional DCM soluble species. Further, the DCM rinsed electrodes are inactive for HER upon reimmersion into the H_2SO_4 solution, precluding the presence of a metal sulfide cluster or similar species on the GC surface or dispersion in the aqueous solution as the HER catalyst. The combined spectroscopic results convincingly establish intact $[\text{ReL}_3]^{n+}$ complexes on the modified GC electrodes. Because $[\text{ReL}_3]^{n+}$ is active for homogeneous HER, we attribute the heterogeneous HER activity to these surface confined $[\text{ReL}_3]^{n+}$ species but cannot exclude the possibility that activity could also result from an unobserved degradation product.

Figure 17. Diffuse reflectance spectra before and after HER catalysis of (a) ITO-[ReL₃] and (b) ITO-[ReL₃]ⁿ⁺. Solution electronic spectra of DCM washings before and after HER catalysis of (c) GC-[ReL₃] and (d) GC-[ReL₃]ⁿ⁺.

3.2.6. Tafel Slope Analysis and Mechanism Discussion

The Tafel plot for an HER displays the relationship between the applied overpotential and catalytic current density. The slope of the Tafel plot is dependent on the rate limiting step, and its value is commonly used to evaluate the mechanism of HER on metal surfaces under acidic conditions. The two dominant mechanisms for HER on metal surfaces are Volmer–olmerfel pleqs 2 and 3) and Volmer–Tafel (eqs 2 and 4).⁵³

Volmer (discharge reaction):

Heyrovsky (ion atom reaction):

Tafel (combination reaction):

Both mechanisms begin with a Volmer step, which is a discharge reaction that combines H^+ and an electron to yield a metal hydride (cat-H). In the Volmer–Heyrovsky mechanism, the second step is a Heyrovsky “ion + atom” reaction that releases H_2 following the addition of a second proton and electron to cat-H. Alternately, in a Volmer–Tafel mechanism, the second step is a Tafel combination reaction with H_2 release upon combination of two equivalents of cat-H. If the Volmer step is rate limiting, the theoretical Tafel slope is 116 mV/decade regardless of the identity of the subsequent step. However, if the Volmer step is fast, the Tafel slope is dependent on the second step. For a Volmer–Heyrovsky mechanism with a slow Heyrovsky step, a Tafel slope of 38 mV/dec is predicted, whereas a slope of 29 mV/decade is expected for a Volmer–Tafel mechanism with a slow Tafel step. Ideal Tafel slopes serve as benchmarks to assign the rate limiting HER step on metal surfaces, although actual values may deviate.^{20,53,54}

Although Tafel slope interpretations were developed for HER at metal surfaces, they have been applied to evaluate the mechanism of other heterogeneous catalysts such as molybdenum sulfides^{20,21} that are deposited on electrode surfaces. Tafel analyses of the HER polarization curves of the $[\text{ReL}_3]^{n+}$ modified electrodes (Figure 18) reveal slopes from 139 to 193 mV/decade (Table 1). The slopes did not significantly change for data collected using a rotating disk electrode at variable rotation speeds (see Figure 19). The

slopes are considerably greater than the 31 mV/dec observed for Pt but consistent with the proposed HER mechanism for ReL_3 complexes in homogeneous solution (Scheme 2).

Figure 18. Tafel slope plots for $\text{GC-}[\text{ReL}_3]^{n+}$ and $\text{GC-CB-}[\text{ReL}_3]^{n+}$ ($n = 0$ or 1).

Figure 19. Tafel slope plots for GC-ReL_3 for data recorded on rotating disk GC electrodes at a scan rate of 5 mV/s and various rotation rates. Data were recorded in 0.5 M $\text{H}_2\text{SO}_4(\text{aq})$ with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

The proposed homogeneous HER mechanism for ReL_3 (Scheme 2) correlates with the proposed heterogeneous HER mechanism of the ReL_3 modified electrodes (Scheme 3). The “like” term signifies that the steps on the modified surface resemble those on traditional heterogeneous metal surfaces with the notable exception that all bond-making and bond-breaking occurs at the sulfur ligands of a single metal site. That is, immobilization of ReL_3 on GC translates both the HER activity and the HER mechanism from homogeneous to heterogeneous conditions.

Scheme 2. Proposed Volmer–Heyrovsky–Tafel-like Mechanism for Heterogeneous HER ReL_3 Modified Electrodes^a

^aFor simplicity, only the $\text{Re}-(\text{SR})_2$ portion of the catalyst is shown.

Scheme 3. Proposed Homogeneous HER Mechanism for ReL_3 Highlighting Re-Dithiol vs Re-Hydride Isomers as the Key Intermediates.

The large Tafel slopes for the ReL_3 modified electrodes suggest a rate limiting Volmer-like step, which corresponds with initial thiolate protonation and complex reduction. The second step is described as a Heyrovsky-like step, as it involves the reaction of the second proton and electron at the initial active site to yield the formal Re^{I} -dithiol $\text{Re}(\text{LH})_2\text{L}$. This is distinct from a second Volmer step, which would involve proton/electron addition at a second reactive site (see Scheme 3). The final H_2 evolution step involves hemolytic S–H bond cleavage of the cis-thiols similar to the coupling of metal hydrides in a Tafel step. The similarity of the homogeneous and heterogeneous mechanisms derives from the fact ReL_3 serves as the active catalyst under both conditions. For the ReL_3 modified electrodes, the electrode surface provides reducing equivalents without significantly altering ReL_3 reactivity. The proposed mechanisms are supported by density functional theory computations.

The proposed HER mechanism on ReL_3 modified surfaces invokes elements of both the Volmer-Heyrovsky and Volmer-Tafel mechanism. As in the Volmer-Heyrovsky

mechanism, the reaction occurs at a single active site and includes the addition of an exogenous proton. However, unlike a true Volmer-Heyrovsky mechanism, this does not result in H_2 evolution. The H_2 generating step is more Tafel-like as it involves the coupling of two bound hydrogens. It is not a true Tafel step, as the hydrogens are bound at the same active site, as opposed to adjacent metal sites. The combination of steps are best described as Volmer-Heyrovsky-Tafel as they include an initial Volmer discharge step, followed by a Heyrovsky addition of an exogenous proton, with H_2 release through a Tafel coupling of catalyst bound hydrogens. This mechanism would not be accessible on a pure metal surface, as each active site only binds one H. However, for molecular catalysts on a surface that include multiple H-binding sites such a mechanism is plausible.

3.3. Conclusion

In summary, we fabricated a series of modified electrodes to translate the nonaqueous, homogeneous HER activity of ReL_3 to a solid support for heterogeneous application in an acidic aqueous environment. The GC- $[\text{ReL}_3]$ and GC- $[\text{ReL}_3]^+$ electrodes demonstrate good, long-term stability in overpotential following an initial conditioning period. The overpotential can be significantly decreased in freshly prepared electrodes by incorporation of CB, but after conditioning for 1.5 h, the improvement in overpotential is diminished.

Although the relatively large overpotential of these electrodes limits their practical application, the ligand-centered HER by ReL_3 opens the door to novel scaffolds and strategies for catalytic HER development. Furthermore, these electrodes represent a

rare example of a well-characterized homogeneous catalyst translated to a heterogeneous surface by simple physisorption. We propose that these catalysts remain intact on the surface as the active HER species but cannot rule out the presence of an undetected quantity of catalytically active degradation products. The remarkable features of this system include long-term stability without inclusion of covalent linkers to the surface, and the proposed translation of both activity and mechanism across homo- and heterogeneous environments.

The metal-thiolate modified electrodes serve as a proxy for a traditional heterogeneous metal surface. All bond-making and bond-breaking is proposed to occur at the sulfur-ligands with the electrode surface providing reducing equivalents without impacting reactivity. The localization of reactivity on the cissulfur sites is analogous to the proposed sulfur-edge active site of MoS₂. The strategy of substituting ligand-centered events for reactions on metal surfaces may be also applicable to other molecular catalysts. In this regard, we very recently reported ligand-centered catalytic HER with zinc- and metal-free complexes involving the coupling of N–H bonds.⁵⁵ Preparation and evaluation of modified electrodes based on these and related systems is ongoing.

CHAPTER IV

ATSM, CuATSM, ATSP and CuATSM FABRICATED GLASSY CARBON ELECTRODE FOR HER UNDER HETEROGENEOUS CONDITION

4.1 Background

Results for the study of GC-ReL₃ in Chapter 3 open the door to the development of novel scaffolds and strategies for generating new catalysts for HER development. The proposed ligand-centered mechanism for ReL₃ has been evaluated by electrochemical and spectroscopic studies as well as DFT calculation.

Haddad et al.¹⁴⁵ also reported that bis-dithiosemicarbazone (BTS), such as diacetyl-bis(N-4-methyl-3-thiosemicarbazone) and its Zn- and Cu- complexes function as HER catalysts under homogeneous conditions. The BTS ligands display the highest reported TOFs of any homogeneous ligand-centered H₂ evolution catalysts, 1320 s⁻¹, while the Zn complex displays a TOF of 1170 s⁻¹. The proposed mechanism was reported to process through ligand centered proton transfer and electron-transfer events, while avoiding traditional metal-hydride intermediates. Therefore, this system seemed idea to explore the feasibility of translating the activity of a well studied homogeneous catalyst to a solid surface. Chemically modified glassy carbon electrodes were fabricated and used as electrocatalysts for HER in this chapter.

4.2 Results and Discussion

4.2.1. Microscopy Studies

The morphology of modified GC surfaces has been studied by SEM in Chapter 2. The SEM images before and after electrolysis has been collected and compared. The bulk electrolysis was conducted in 0.5 M H₂SO₄ at -1.48 V vs. RHE for 180 s in a three-electrodes cell as described before.

GC-ATSM

The SEM images for GC-ATSM are shown in Figure 20. In low resolution SEM images of GC-ATSM before electrolysis, the ATSM fabricated GC surface appears to be rough and non-uniform, ATSM appears to aggregated solids on the GC surface. Figure 21 (right) is the high resolution image of ATSM on the electrode surface, and shows a more detailed image of the surface. After electrolysis, the morphology of surface was analyzed and found to be slightly altered based on the SEM images at both low and high-resolution.

Figure 20. SEM images of GC-ATSM before electrolysis: low resolution (left) and high resolution (right).

Figure 21. SEM images of GC-ATSM after electrolysis: low resolution (left) and high resolution (right).

GC-ZnATSM

The SEM images of GC-ZnATSM before and after electrolysis are shown in Figure 22. The fabricated GC-ZnATSM surface didn't display a uniform film by drop casting but rather showed formation of needle-shaped crystals on the GC surface. Distribution of crystals is not uniformly on the surface. After electrolysis (Figure 23), the lower resolution images indicated loss of catalyst noticed on from the surface, and the higher resolution images showed that the surface confined of crystals were now very fragmented giving rise to a rougher appearance of the electrode surface.

Figure 22. SEM images of GC-ZnATSM before electrolysis: low resolution (left) and High resolution (right).

Figure 23. SEM images of GC-ZnATSM after electrolysis: low resolution (left) and high resolution (right).

GC-CuATSM

The drop casted CuATSM generated a uniform film on the surface based on the SEM image in Figure 24 (left). As with ZnATSM, the high-resolution image of the CuATSM shows stick-shaped solids rods on the surface. After electrolysis, the electrode appears to contain a highly porous network material on the surface. The high-resolution image (Figure 25 (right)) of the electrode revealed very high surface coverage of the catalyst.

Figure 24. SEM images of GC-CuATSM before electrolysis: low resolution (left) and high resolution (right).

Figure 25. SEM images of GC-CuATSM after electrolysis: low resolution (left) and high resolution (right)

GC-ATSP

The surface image of GC-ATSP showed a uniform film was formed by drop casting deposition of ATSP on the GC surface with some volcano like structures. Low and high resolution images were collected on the GC-ATSP film after electrolysis, which show the loss of uniformity after electrolysis with holes in the film, which are likely due to the generating of H_2 gas during electrolysis. High-resolution images show detailed structure

of the holes. Also, formation of holes in the film resulted the loss of catalyst material from the surface.

Figure 26. SEM images of GC-ATSP before electrolysis.

Figure 27. SEM images of GC-ATSP after electrolysis: low resolution (left) and high resolution (right).

GC-ZnATSP

The SEM image of the GC-ZnATSM surface after drop casting before electrolysis showed needle shaped crystals were deposited on the GC surface. The high-resolution image indicates the surface of the crystals surfaces are smooth. After electrolysis, the

crystals retained their shape but the surfaces were cracked. Also, the surface coverage of CuATSP appeared similar to pre-electrolysis conditions.

Figure 28. SEM images of GC-ZnATSP before electrolysis: low resolution (left) and high resolution (right).

Figure 29. SEM images of GC-ZnATSP after electrolysis: low resolution (left) and high resolution (right).

GC-CuATSP

The surface of drop casted CuATSP GC electrode is uniform and smooth based on the SEM image in Figure 30. However, after electrolysis, the catalyst appears to aggregate on the surface and the film loses its uniform appearance. The roughness and porosity of

the film increased the surface area of the coating resulting in greater permeability of the film to the solution.

Figure 30. SEM images of GC-CuATSP before electrolysis: low resolution (left) and High resolution (right).

Figure 31. SEM images of GC-CuATSP after electrolysis: low resolution (left) and high resolution (right).

4.2.2. Identification of Active Species by XPS

XPS is used to evaluate the composition of the active species deposited on the modified GC surface. Prior to electrolysis, fresh powder of the catalysts was directly coated on carbon tape and analyzed. The solution electronic spectra were collected

before and after electrolysis for all samples. Varying concentration of catalysts were drop-casted on the GC surface from DCM solution, and the UV-Vis spectra were collected. A parallel study was conducted to prepare modified GC surfaces that were used to evaluate HER activity at an applied overpotential of -1.48 V in 0.5 M H₂SO₄ for 180 s. After catalysis, the catalysts were removed from the GC surface with DCM and UV-Vis spectra were recorded.

4.2.2.1 ATSM on GC-ATSM before and after electrolysis

The survey of ATSM on the GCE surface before electrolysis showed peaks associated with C, S and N, consistent with the expected formula: C₈ H₁₄ N₆ S₂ (Figure 33). A small peak for O is also observed. The XPS survey after electrolysis (after) still contains peaks associated with C, S, and N. However, the peak assigned to O is significantly increased.

Figure 32. Survey of ATSM before and after electrolysis.

The atomic percentages calculated from two spots for ATSM (before) is consistent with the theoretical atomic percentages for the compound, Table 8. The atomic percentages for ATSM also calculated after electrolysis on two spots are listed in Table 9. The data indicates the presence of ATSM on the GCE surface. The O signal could indicate the presences of some contamination on the surface (eg. C-O or S-O). An intense C signal was observed in ATSM sample after electrolysis. The calculated C atomic percentage is 78.33%, which is much higher than the original sample (48.7%). This is attributed to the small sample size after electrolysis resulting in signals from the carbon tape used during the XPS sample preparation. Moreover, the large intense of C signal caused the decreased of the atomic percentage of N and S, which is observed for all the samples after electrolysis.

Table 9. Atomic Percentage of ATSM Before Electrolysis

Elements: Theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 50%	48.7	47.53	50.12
N 1s: 37.5%	35.3	37.94	35.29
S 2p: 12.5%	11.5	13.15	11.85
O 1s: 0%	4.5	1.38	2.75

Table 10. Atomic Percentage of ZnATSM After Electrolysis

Elements: theoretical At%	Spot 1	Spot 2
C 1s: 50%	78.33	75.32
N 1s: 37.5%	6.38	6.4
S 2p: 12.5%	6.54	6.54
O 1s: 0%	11.75	11.75

XPS-HR Analysis

The XPS-HR data for ATSM (before) were collected on three spots. For each spot, data were fit for C, S, N and O using the following parameters: based on the electronic structure of ATSM ligand, there are three types of C 1s with different electronic environments with the ratio of 2:1:1 (Figure 34 (top left)). The C1 (sp^3 carbon) should appear at 284.8 eV, which was used as a standard to do the calibration. The C2 peak appeared at 285.6 eV while the C3 was at 287.39 eV. The peak at highest BE was assigned to C-O contamination because of the explosion of samples in the air. The complex contains two equivalent sulfur atoms producing the S 2p signal in Figure 34 (top right). The two peaks were fit with an area ratio of 1:0.51 and a peak position difference of 1.16 eV. The peaks are centered at 161.70 eV and 162.86 eV. The N 1s signal was fit with three peaks of equal area at N1: 399.64 eV, N2: 400.06 eV and N 3: 400.30 eV.

Figure 33. Three types of C atoms in the ATSM ligand.

Figure 34. XPS-HR of ATSM before electrolysis: C 1s (top left), S 2p (top right) and N 1s (bottom).

The same approach was used to fit the XPR-HR spectra for ATSM samples on GCE surfaces after electrolysis on GCE surface and shown in Figure 35. As above, data were collected on two spots, and C, S and N signals were fit with the following parameters as with ATSM before electrolysis. The C 1s data of ATSM after electrolysis were also modeled using four peaks: C1 appeared at 284.8 eV, C2 at 285.64 eV and C3 at 286.12 eV. The peak at the highest BE is assigned to C-O contamination, and this signal is more intense after

electrolysis. The complex contains one type of sulfur, which was modeled with two peaks with an area ratio of 1:0.51 and peak position difference of 1.16 eV. The peaks were observed at 161.91 eV and 163.11 eV, respectively. Three peaks were used to model the N 1s signal at 399.79 eV, 400.18 eV and 400.48 eV.

Figure 35. XPS-HR data of ATSM after electrolysis: C 1s (top left), S 2p (Top right) and N 1s (bottom).

Based on the XPS analysis of ATSM film, it appears to be stable during the bulk electrolysis. The O 1s signal increased in intensity after electrolysis and is attributed to

the presence of SO_4^{2-} into the film. The high proportion of C 1s signal was likely due to the carbon tape background.

4.2.2.2. GC-ZnATSM XPS Analysis before and after Electrolysis

The survey of ZnATSM (before) showed peaks associated with C, S, N, and Zn consistent with the expected formula (Figure 36). The small O peak observed in the XPS survey spectra is attributed to a contaminate species as observed in the ATSM spectrum. The XPS survey after electrolysis (after) also contains peaks associated with C, S, N and O. However, the peaks associated with the Zn signal are absent, and a more intense signal assigned to O is observed.

Figure 36. Structure of ZnATSM.

Figure 37. Survey of ZnATSM before and after electrolysis.

The atomic percentages calculated from two spots for ZnATSM (before) is consistent with the theoretical atomic percentages for the complex, Table 11. The atomic percentages for ZnATSM (after) were also calculated on two spots, Table 12. The data does not support the presence of ZnATSM because of the absence of the Zn 2p signal for the sample after electrolysis. The intense of O signal is attributed to the presences of SO_4^{2-} or HSO_4^- from the reaction solution. The large C signal intensity, relative to N, indicates a C source other than demetallated ATSM, which could be due to the carbon tape background.

Table 11. Atomic Percentage of ZnATSM before Electrolysis.

Elements: Theoretical At%	Spot 1	Spot 2
C 1s: 47%	45.2	47.0
N 1s: 35%	31.4	30.2
S 2p: 12%	9.8	10.0
Zn 2p: 6%	7.0	7.2

Table 12. Atomic Percentage of ZnATSM After Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2
---------------------------	--------	--------

C 1s: 47%	48	49.8
N 1s: 35%	21	22.1
S 2p: 12%	10.3	9.9
Zn 2p: 6%	<0.1	<0.1
O 1s:	20.6	18.2

The structure of ZnATSM shows the Zn coordinated to the ATSM ligand and the XPS analysis is shown in Figure 38 ($C_8H_{14}N_6S_2Zn$). Four carbon peaks were used to fit the carbon signal as for ATSM. Three of them, represented in the diagram of the complex, were fit with an area ratio of 2:1:1, and the inclusion of the fourth peak for C-O contaminate. The methyl C1 signal appeared at 284.85 eV, and the peaks of C2 and C3 peaks appear at 284.96 eV and 286.15 eV, respectively. The complex displays one broadened sulfur signal, which was fit with two peaks at 161.90 and 163.08 eV, respectively. As before, three peaks of equal area were used to fit the N 1s signal at 397.78, 398.38 and 398.78 eV, respectively. The Zn 2p signal was fit with two peaks at 1020.69 and 1043.74 eV for Zn 2p 3/2 and Zn 2p 1/2, respectively, clearly indicates the appearance of Zn on the GCE surface before electrolysis. O 1s peak was fit with two peaks at 531.82 eV and 533.24 eV which is assigned to sulfate and C-O contaminate, Figure 39.

Figure 38. XPS-HR data of ZnATSM before electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Zn 2p (bottom right).

Figure 39. XPS-HR-O of ZnATSM before electrolysis.

Same approach was used to analysis the XPS-HR data for ZnATSM on GCE surface after electrolysis, in Figure 40. Four carbon peaks were used to fit the C signal with an area ratio of 2:1:1, and those peaks were centered at 284.8, 285.33, 285.93, and 287.61 eV, respectively. The peak at the highest BE also assigned to the C-O or S-O contaminate. Two types of sulfur were observed in the ZnATSM sample after electrolysis, with one

signal appears at 161.92, and 163.09 eV, and the other at 164.63 and 165.78 eV. The second S signal is assigned to an oxidized sulfur (eg. SO_4^{2-} or HSO_4^-) from the reaction solution. Four peaks were used to modeled the N 1s signal. Three of them were fit with peaks with an equivalent area ratio at 398.15, 398.91 and 399.21 eV, respectively. The fourth peak appears at 400.72 eV is attributed to the N-O contamination. For O 1s signal, two peaks were used to fit at 532.09 and 533.31 eV which is assigned to sulfate signals. There is no Zn 2p signal observed for the ZnATSM sample on GCE surface after electrolysis., which indicates the demetallation of ZnATSM during the bulk electrolysis.

The UV-Vis spectra collected for ZnATSM before and after electrolysis in DCM solution is shown in Figure 41. After electrolysis, the UV-Vis spectra look identical to the ATSM ligand, which agrees with the XPS results showing the demetallation of ZnATSM during bulk electrolysis.

Figure 40. XPS-HR of ZnATSM after electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and O 1s (bottom right).

Figure 41. Solution electronic spectra of DCM washings before (blue) and after (gray) HER catalysis of GC-ZnATSM, and comparison with ATSM ligand (orange).

4.2.2.3. GC-CuATSM XPS Analysis before and after Electrolysis

The survey of CuATSM sample on GCE surface before electrolysis shows peaks associated with C, S, N, and Cu consistent with the expected formula: $C_8H_{14}N_6S_2Cu$ (Figure 42). A small O peak is observed as previous samples due to the C-O contamination. The XPS survey of CuATSM sample after electrolysis also contains peaks associated with C, S,

N and Cu. The intensity of all these peaks were decreased due to the decrease of the amount of testing sample as described for ATSM sample. As in ATSM, the signal of Q signal significantly increased due to the presence of SO_4^{2-} or HSO_4^- from the reaction system, and the intense of C signal is from the carbon tape background because of the small size of the sample.

Figure 42. Structure of CuATSM.

Figure 43. XPS Survey of ATSM before and after electrolysis.

The atomic percentages of CuATSM sample on the GCE surface before and after electrolysis is shown in Table 13 and Table 14. The data of CuATSM sample before electrolysis collected on three spots and consistent with the theoretical atomic

percentages for the complex. The atomic percentages for CuATSM sample after electrolysis collected on three spots and the calculated atom percentages also indicate the presence of CuATSM on the GC surface after electrolysis. The intensity of O 1s signal was increased after electrolysis because of the presences of SO_4^{2-} or HSO_4^- in the film, and the relatively large C intensity indicates a C source other than intact CuATSM ligand contributing to this signal, which is carbon tape background as discussed before.

Table 13. Atomic Percentage of CuATSM Before Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 47%	46.35	45.48	46.73
N 1s: 35%	33.98	33.96	33.93
S 2p: 12%	11.82	12.33	11.89
Cu 2p: 6%	7.85	8.23	7.44

Table 14. Atomic Percentage of CuATSM After Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 47%	59.34	55.52	58.62
N 1s: 35%	17	21.36	18.11
S 2p: 12%	10.28	8.91	10.11
Cu 2p: 6%	3.1	5.4	3.77
O 1s	12	8.74	12.41

The CuATSM structure is similar with ZnATSM, therefore, the same parameters have been used to fit the XPS-HR signals, in Figure 44. Three peaks were used to fit the carbon signal based on the CuATSM structure at 284.8, 285.53, and 286.45 eV, respectively. A peak assigned to C-O contamination appears at 288.86 eV. The peaks of C1:C2:C3 were fit with an area ratio of 2:1:1, which is consistent with the complex structure. The S 2p signal was fit with two peaks centered at 161.99 eV and 163,16 eV, respectively, represents one type of sulfur consistent with CuATSM structure. Four peaks

of equal area were used to fit the N 1s signal at 398.35, 399.25, 399.59 eV and at 401.41, and the peak at highest BE was attributed to the C-O contamination. Both Cu(I) and Cu(II) were observed in the XPS-HR spectra. The peak of Cu(I) was centered at 932.04 and 951.76 eV, while at 933.88 and 953.76 eV for Cu(II) signal. The presence of Cu(I) was expected because long X-ray exposure can reduce Cu(II) to Cu(I).¹⁴⁶

Figure 44. XPS-HR of CuATSM before electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Cu 2p (bottom right).

The same approach was used to fit the XPR-HR data for CuATSM after electrolysis, Figure 45. C 1s signal was fitted with 284.8, 285.49, 286.42 and C-O contamination at 288.66 eV with the same parameters as similar to those used to fit the C signal pf CuATSM before electrolysis. Two types of sulfur were observed in S 2p signal and each of them were fit with two peaks. The first S is appeared at 162.22 and 163.04 eV and the oxidized sulfur appears at 163.36 and 164.20 eV. Four peaks were used to fit the N 1s signal at 398.94, 399.80 eV, 400.84 -eV and one peak at 403.44 eV caused by C-O contamination. Cu(I) and Cu(II) were observed for CuATSM after electrolysis. The signal of Cu(I) was fit with two peaks at 932.37 and 951.80 eV, while Cu(II) was fit with two peaks at 934.09 and 953.93 eV. Based on the XPS analysis, both Cu(I) and Cu(II) signals are clearly observed.

Figure 45. XPS-HR of ATSM after electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Cu 2p (bottom right).

Based on the XPS analysis, CuATSM appears to be stable on GC surface during bulk electrolysis. The experimental data of atom percentages before electrolysis indicates the presence of CuATSM on the GC surface. After electrolysis, the calculated atom percentages also indicate the presence of CuATSM on the GCE surface with an higher intense O 1s signal due to the presence of SO_4^{2-} , and the expected high intense of C signal. Unlike the ZnATSM film, the Cu 2p signals displays in the sample after electrolysis, indicates the presence of CuATSM. The UV-Vis spectra of CuATSM before and after electrolysis collected in DCM solution agree with the result concluded from XPS analysis, in Figure 46.

Figure 46. Solution electronic spectra of DCM washings before and after HER catalysis of GC-CuATSM.

4.2.2.4. GC-ATSP XPS Analysis before and after Electrolysis

A similar approach is used to analyze the ATSP modified electrode in this dissertation. The XPS survey data of ATSP before electrolysis is shown in Figure 47 with peaks associated with C, S and N, and consistent with the expected formula: $C_{18}H_{14}N_6S_2$ (Figure 48). The XPS survey after electrolysis also contains peaks associated with C, S, and N, with an intense peak assigned to O, which is at the same position observed for ATSM.

Figure 47. Structure of ATSP Ligand.

Figure 48. XPS-Survey of ATSP before and after electrolysis.

The atomic percentages calculated on three spots for ATSP on GCE surface before electrolysis is consistent with the theoretical atomic percentages for the complex, Table 3. The atomic percentages for ATSP after electrolysis were calculated on two spots, Table 4. After electrolysis, the intensity of C 1s signal and O signal was increased as observed in ATSP systems.

Table 15. Atomic Percentage of ATSP Before Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 69%	69.08	70.22	68.81
N 1s: 23%	23.03	22.09	23.83
S 2p: 7.6%	7.89	7.7	7.37

Table 16. Atomic Percentage of ATSP After Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2
C 1s: 69%	58.13	66.84
N 1s: 23%	13.15	12.59
S 2p: 7.6%	10.16	6.96
O 1s:	18.56	13.62

The XPS-HR data were fit (Figure 49) with following parameters: Four carbons in different electronic environments with the ratio of C1:C2:C3:C4 = 3:1:1:1 should be observed based on the structure, where C1 is the sp² carbon in phenol ring, and C2 is the hydrocarbon, which should be at 284.8 eV. Generally, C1 and C2 have close BE energy which can be fit with one peak. C3 is the C with carbon double bond with one nitrogen and single bond with another carbon, and C4 is assigned to the one double bonded with nitrogen and single bonded with one sulfur. Thus, for C signal, three peaks represent the carbons from ATSP ligand appear at 284.8, 285.63, and 286.33 eV with a peak at 287.74 eV assigned to the C-O contamination. One type of sulfur was observed and fit with two peaks at 161.99 eV and 163.15 eV with an area ratio of 1: 0.51. Three peaks were used to fit the N 2s signal at 400.10, 400.37 and 400.82 eV, respectively, with an equivalent peak area based on the structure. O 1s signal was fit by two peaks at 532.34 and 533.94 eV.

Figure 49. XPS-HR of ATSP before electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and O 1s (bottom right).

The same approach has been used to fit the XPS-HR data of ATSP sample on GCE surface after electrolysis, Figure 50. Four C peaks were used to fit C 1s signal at 284.8, 285.43, 286.06 and 288.34 eV, respectively. Two types of sulfur were observed for the ATSP sample after electrolysis with one at 162.06 and 163.02 eV and eV and the other appears at 164.14 and 165.30 eV, where the S peak at high BE is due to the SO_4^{2-} from the reaction solution. Three peaks were used to fit the N 1s signal at 400.21, 400.40 and 401.45 eV, respectively.

Figure 50. XPS-HR of ATSP after electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and O 1s (bottom right).

The XPS analysis indicates that ATSP displays stable on the GCE surface during bulk electrolysis. The atom percentages of each atom agree the presence of the ATSP on electrode surface before electrolysis. After electrolysis, the intensity of O 1s peak increased due to the presence of H_2SO_4 in the film and the higher C 1s signal was caused by the carbon tape background as explained before

4.2.2.5. GC-ZnATSP XPS Analysis before and after Electrolysis

The survey of ZnATSP on GCE surface before electrolysis shows peaks associated with C, S, N, and Zn, which is consistent with the expected formula: $C_{18}H_{14}N_6S_2Zn$ (Figure 51). The XPS survey after electrolysis still contains peaks associated with C, S, and N. However, the Zn peak is absent and a peak assigned to O is observed with high intensity.

Figure 51. Structure of ZnATSP.

Figure 52. XPS-Survey of ZnATSP before and after electrolysis.

The atomic percentages for ZnATSP before electrolysis were calculated on two spots, which were agreed with the theoretical atomic percentages for ZnATSP, Table 17. The atomic percentages for ZnATSP after electrolysis was also calculated on two spots,

Table 18, and these data do not show the presence of ZnATSP on electrode surface due to the absence of Zn 2p signal. The increase of O signal caused by the presences of SO_4^{2-} or HSO_4^- in the film from the reaction solution, and the relatively large C intensity is due to the carbon tape background.

Table 17. Atomic percentage of ZnATSP before electrolysis.

Elements: theoretical At%	Spot 1	Spot 2
C 1s: 66.6%	65.21	63.93
N 1s: 22.2%	22.31	24.11
S 2p: 7.4%	8.61	8.31
Zn 2p: 3.7%	3.88	3.65

Table 18. Atomic percentage of ZnATSP after electrolysis.

Elements: theoretical At%	Spot 1	Spot 2
C 1s: 66.6%	62.75	59.39
N 1s: 22.2%	16.95	20.12
S 2p: 7.4%	7.41	8.00
Zn 2p: 3.7%	< 0.1	< 0.1
O 1s:	12.89	18.2

By using the same parameter as ATSP, the XPR-HR data for ZnATSP before electrolysis was fit and shown in Figure 53. The C 1s signal was fit by four peaks at 284.8, 285.47, 286.03 and 287.00 eV, respectively, and the peak at highest BE is assigned to the C-O contamination as previous systems. One type of sulfur appears at 162.57 and 163.72 eV, and four peaks were used to fit the N 1s signal at 398.87, 399.71, and 399.91 eV with equivalent peak area and the fourth peak at 401.37 eV is assigned to the C-O contamination. The Zn 2p signal was fit with two peaks centered at 1021.96 eV and 1045.00 eV.

Figure 53. XPS-HR of ZnATSP before electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Zn 2p (bottom right).

The XPS data for ZnATSM after electrolysis was collected and analyzed, Figure 54. Four peaks were used to fit C 1s signal at 284.8, 285.27, 285.97 and 287.71 eV, respectively. Two types of sulfur were observed and each sulfur was fit with two peaks with area ration of 1: 0.51. One sulfur appears at 162.10 and 163.42 eV, while the other at 163.17, and 164.33 eV, which due to the presence of SO_4^{2-} . Four peaks were used to fit the N 1s signal at 400.02, 400.49, 400.74 and 401.57 eV. The peak at the highest BE is

assigned to N-O contamination. For O signal, two peaks were appeared at 532.18 and 533.69 eV.

Figure 54. XPS-HR of ZnATSP after electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and O 1s (bottom right).

A weak signal of Zn 2p was observed for the ZnATSP sample after electrolysis Figure 55, but the calculation of atom percentage for Zn is less than 0.1%, which indicates the demetallation of Zn ATSP during bulk electrolysis. An O 1s peak appears after

electrolysis due to the presence of HSO_4^- or SO_4^{2-} in the ZnATSP film from reaction solution, Figure 54(bottom right).

Figure 55. XPS-HR-Zn of ZnATSP after electrolysis

The UV-Vis spectra (Figure 56) of ZnATSP before and after electrolysis in DCM further indicates that ZnATSP was not stable during the electrolysis. After electrolysis, the spectra of ZnATSP (orange) looks similar with the ATSP ligand (gray), which agrees with the results of XPS analysis.

Figure 56. Solution electronic spectra of DCM washings before (blue) and after (orange) HER catalysis of GC-ZnATSP.

4.2.2.6. GC-CuATSP XPS Analysis before and after Electrolysis

The XPS survey (Figure 58) of CuATSP before electrolysis shows peaks associated with C, S, N and Cu consistent with the expected formula: $C_{18}H_{14}N_6S_2Cu$ (Figure 57), and those peaks were also observed in the XPS survey of CuATSP sample after electrolysis.

Figure 57. Structure of CuATSP.

Figure 58. XPS-Survey of CuATSP before and after electrolysis.

The atomic percentage calculated on three spots for CuATSP sample on GCE surface before electrolysis is consistent with the theoretical atomic percentages for the complex, Table 19. The atomic percentages for CuATSP sample after electrolysis was

calculated on three spots, in Table 20, and the data indicate the presence of CuATSP on the GCE surface before and after electrolysis.

Table 19. Atomic Percentage of ATSP Before Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 66.6%	69.8	71.13	69.94
N 1s: 22.2%	20.09	18.94	19.99
S 2p: 7.4%	6.91	6.79	6.60
Cu 2p: 3.7%	3.20	3.05	3.47

Table 20. Atomic Percentage of ATSP After Electrolysis.

Elements: theoretical At%	Spot 1	Spot 2	Spot 3
C 1s: 66.6%	56.13	58.77	57.43
N 1s: 22.2%	18.15	20.67	18.10
S 2p: 7.4%	8.97	8.42	8.87
Cu 2p: 3.7%	3.68	3.55	3.28
O 1s	13.07	8.42	12.32

The XPS-HR analysis has been processed by following the same parameters as ATSP and ZnATSP, Figure 59. Four peaks were used to fit carbon signal at 284.8, 285.34, 286.00 and 287.21 eV. S 2p signal was fitted with one sulfur at 162.8 and 164.1 eV. N signal was fit with three peaks at 399.32, 400.12 and 400.75 eV. Cu(I) and Cu(II) was observed in CuATSP sample before electrolysis. The signal of Cu(I) was fit with two peaks at 932.63 and 952.48 eV; and Cu(II) at 934.21 and 954.39 eV. The Cu(I) and Cu(II) satellite appears in the range of 937-950 eV, which is a prove of the oxidation state of the Cu.

Figure 59. XPS-HR of CuATSP before electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Cu 2p (bottom right).

The XPS data of CuATSM after electrolysis were collected and analyzed with the same parameters for CuATSM before electrolysis, Figure 60. Four peaks were used to fit carbon signal at 284.4, 285.50, 286.38 and 288.13 eV. . Two types of sulfur were observed with one at 162.72 and 163.88 eV, and the other at 164.53 and 165.69 eV for SO_4^{2-} . Three peaks were used to fit the N 1s signal at 399.39, 400.18, 400.96 and 401.57 eV. The most important is Cu 2p signals appears and fit with Cu(I) at 932.60 and 952.31 eV, and Cu(II) at 934.55 and 954.33 eV.

Figure 60. XPS-HR of CuATSP after electrolysis: C 1s (top left), S 2p (top right), N 1s (bottom left) and Cu 2p (bottom right).

The XPS data indicates that CuATSP is stable on the GC surface during bulk electrolysis. Before electrolysis, the atom percentage of C, N, S and Cu matches the theoretical atomic percentages of CuATSP, which is a strong evidence of the presence of catalyst on the modified GC electrode. After electrolysis, the atom percentage also indicates the presence of CuATSP with an intense C signal due to the carbon tape background and an intense O 1s peak attributed to the SO_4^{2-} and HSO_4^- . The results of UV-

Vis for CuATSP sample in DCM before and after electrolysis agrees the result of XPS analysis, Figure 61.

Figure 61. Solution electronic spectra of DCM washings before (orange) and after (blue) HER catalysis of GC-CuATSP.

4.2.3. Polarization Curves and overpotential calculation

GC-ATSM, GC-ZnATSM and GC-CuATSM

To evaluate the HER activity of the ATSM ligand and its metal complexes under heterogeneous conditions, polarization curves were recorded for GC-ATSM, GC-CuATSM and GC-ZnATSM in 0.5 M H₂SO₄. Overpotentials were recorded at a current density of 10 mA/cm² using modified electrodes at their optimum loadings level. To determine the optimum loading quality for surface modification, a series of modified GC electrode were prepared with different loading capacity, and the polarization curves were measured. The comparison of overpotentials and Tafel slopes are shown in Table 1.

For GC-ATSM, the lowest overpotential appears using 10 nmol and displayed an overpotential at 1.12 V (Figure 62). The optimal loading capacity for GC-ZnATSM and GC-

CuATSM were found to be 40 and 50 nmol, respectively, with overpotentials of 923 and 774 mV, respectively, in Figure 63 and 64. The Tafel slopes were calculated and showed in Table 21, which will be discussed later.

Figure 62. Polarization curves for GC-ATSM at different loading amounts

Figure 63. Polarization curves for GC-ZnATSM at different loading amounts recorded in 0.5 M $\text{H}_2\text{SO}_4(\text{aq})$ with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Figure 64. Polarization curves for GC-CuATSM at different loading amounts recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

The comparison of polarization curves for GC-ATSM, GC-ZnATSM and GC-ATSP are shown in Figure 65. The lowest overpotential was observed for GC-CuATSM at 774 mV, which is 349 mV lower than GC-ATSM, while the GC-ZnATSM appeared in the middle at 923 mV.

Figure 65. Polarization curves of GC-ATSM, GC-ZnATSM and GC-CuATSM recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Table 21. HER Overpotentials (η) and Tafel Slopes of the GC-ATSM, GC-ZnATSM and GC-CuATSM.

Electrode	Loading/nmol	η / mV	Tafel Slop mV/dec
GC-ATSM	10	1123	427
GC-ZnATSM	40	923	235
GC-CuATSM	50	774	150

GC-ATSP, GC-ZnATSP and GC-CuATSP

The polarization curves for GC-ATSP, GC-ZnATSP and CuATSP were collected under the same conditions use for the GC-ATSMs, in Figure 66-68. As well, the optimal surface loading amounts for ATSP, ZnATSP and CuATSP were determined and are listed in Table 22. The results indicated that after replacing two methyl amino groups with aniline groups, the HER electrocatalytic activity does not change much. Overpotentials of ATSP compounds are smaller compare to ATSM compounds (30-70 mV). For GC-ATSP and GC-ZnATSP resulting in overpotential of 1090 and 853 mV, and their optimal loadings are 10 and 40 nmol, respectively. GC-CuATSP, on the other hand, performs better than the other two catalysts with an optimal loading of 40 nmol and overpotential of 745 mV. In both systems, Cu- compounds show the best electrocatalytic activity.

Figure 66. Polarization curves for GC-ATSP at different loading amounts recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Figure 67. Polarization curves for GC-ZnATSP at different loading amounts recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Figure 68. Polarization curves for GC-CuATSP at different loading amounts recorded in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Table 22. HER Overpotentials (η) and Tafel Slopes of the GC-ATSP, GC-ZnATSP and GC-CuATSP.

Electrode	Loading/nmol	η / mV	Tafel Slop mV/dec
GC-ATSP	10	1090	268
GC-ZnATSP	40	853	217
GC-CuATSP	40	745	192

4.2.4. Impedance Studies.

Electrochemical impedance spectroscopy have been used to study the correlation between film resistance and HER overpotential. Data were collected over a frequency range of 10^{-2} to 10^5 Hz at an applied overpotential of 1.3 V at optimal loading capacity is compared. Nyquist plots of the EIS data (Figure 70) were simulated using the model in Figure 69. Simulation parameters are provided in Table 23. Similarity between the responses of all fabricated GC electrodes suggests a similar mechanism for hydrogen

evolution. The lack of Warburg impedance indicates that mass transport is rapid enough so that the reaction is kinetically controlled.

The Nyquist plots of GC-ATSM, GC-ZnATSM and GC-CuATSM are shown in Figure X. The plots contain a semicircle in the low frequency range and the data has been fitted to a model (Figure X) with a resistor (R_s) in series with a module comprised of a second resistor (R_{ct}) in parallel with a constant phase element (CPE), where R_s represent the contact resistance between electrolyte and electrode surface, R_{ct} represents the charge transfer resistance within the catalyst film, and CPE is a constant phase element representing the capacitive behavior of the electrodes. The simulated Nyquist plot parameters has been shown in Table 23.

Figure 69. Electrical equivalent circuit model for EIS data interpretation for the GC-ATSMs and GC-ATSPs.

Table 23. Simulated Nyquist Plot Parameters for GC-ATSM, GC-ZnATSM and GC-CuATSM from the Impedance Spectra at 1.3 V.

Electrode	$R_s(\Omega)$	$R_{ct}(\Omega)$	CPE-T (sP/ $\mu\Omega$)	CPE-P (sP/ $\mu\Omega$)
GC-ATSM	5.4	1.15E+05	6.24E-06	0.74
GC-ZnATSM	9.87	7.00E+04	1.50E-05	0.81
GC-CuATSM	7.82	5.75E+03	3.08E-05	0.76

Figure 70. Nyquist plots of GC-ATSM, GC-ZnATSM and GC-CuATSM at $\eta=1.3$ V in 0.5 M H_2SO_4 . Insert: zoom in of high frequency area.

The same model has been used to fit the EIS data of ATSP system. The similar behavior was observed in ASYP and its metal complexes. The CuATSP displays the lowest semicircle in low frequency range, indicates the lowest charge transfer resistance in the film. The ATSP displays the largest charge transfer resistance compare to ZnATSP and CuATSP. The Nyquist plot is shown in Figure 71 and simulated parameters are shown in Table 24.

Figure 71. Nyquist plots of GC-ATSP, GC-ZnATSP and GC-CuATSP at $\eta=1.3$ V in 0.5 M H_2SO_4 .

Table 24. Simulated Nyquist Plot Parameters for GC-ATSP, GC-ZnATSP and GC-CuATSP from the Impedance Spectra at 1.0 V.

Electrode	$R_s(\Omega)$	$R_{ct}(\Omega)$	CPE-T (sP/ $\mu\Omega$)	CPE-P (sP/ $\mu\Omega$)
GC-ATSP	8.7	1.90E+05	3.68E-06	0.65
GC-ZnATSP	6.85	7.50E+04	4.20E-06	0.57
GC-CuATSP	2.08	6.70E+03	7.60E-06	0.66

This results agree with the results of the polarization measurements. Based on studies, changing the methyl amine groups with aniline groups do not change the resistances significantly. Thus, ATSMs and ATSPs have close overpotentials, which has been discussed before.

4.2.5. Long-term Stability Studies.

The stability of the modified GC electrodes with ATSM and ATSP and their metal complexes was evaluated by chronopotentiometry at a fixed catalytic current density of 10 mA cm⁻² over 24 hours. The results of the GC-ATSMs (Figure 72) indicate overpotentials increase for both GC-ATSM and GC-CuATSM during catalysis. The overpotential of GC-ATSM increased by 520 mV over the first 4 h and stabilized for the duration of the catalysis, and GC-CuATSM increased by 320 mV over the first 5 hours and then remains constant over the reminder of the experiment. Apparently, some of the desorbed from the electrode surface during the several hours conditioning period, which caused an increase in the overpotential required to maintain current densities at 10 mA cm⁻².

Figure 72. Long-term stability studies for GC-ATSM and GC-CuATSM at 10 mA cm^{-2} for 24 h in $0.5 \text{ M H}_2\text{SO}_4$.

The same behavior has been observed for GC-ATSP and GC-CuATSP, Figure 73. Over the first 4 hours, GC-ATSP and GC-CuATSP increased about 460 mV and 350 mV, respectively. After that period, the overpotentials remained stable for the electrodes during the electrocatalysis. The H_2 gas identification was determined by GC-MS with a molecular sieve column, with retention time of 3.1 min.

Figure 73. Long-term stability studies for GC-ATSP and GC-CuATSP at 10 mA cm^{-2} for 24 h in $0.5 \text{ M H}_2\text{SO}_4$.

4.2.6. Tafel Slope Calculations and Mechanism Studies.

The Tafel slopes of GC electrodes modified with ATSM, ATSP and their metal complexes were plotted in Figure 74 (ATSM) and Figure 75 (ATSP), and the Tafel slopes for each electrode at their optimal loading capacities were calculated, listed in Table 24

(ATSP) and Table 25 (ATSP), respectively. For GC-ATSMs, the GC-CuATSM displays the lowest Tafel slope of 150 mV/dec, indicates a faster electron transfer process on the modified electrode than GC-ATSM and GC-ZnATSM. The same behavior was observed for GC-ATSPs, where the GC-CuATSP displays the lowest Tafel slope of 192 mV/dec. For both systems, the values of Tafel slope were higher than 120 mV/dec which indicates the Volmer step is the rate determine step in these systems.

Figure 74. Tafel slope plots for GC-ATSM, GC-ZnATSM and GC-CuATSM.

Figure 75. Tafel slope plots for GC-ATSP, GC-ZnATSP and GC-CuATSP.

Table 25. Tafel slope of GC-ATSM, GC-ZnATSM and CuTASM at their optimal loading capacity.

Electrode	Loading/nmol	η / mV	Tafel Slop mV/dec
GC-ATSM	10	1123	427
GC-ZnATSM	40	923	235
GC-CuATSM	50	774	150

Table 26. Tafel slope of GC-ATSP, GC-ZnATSP and CuTASP at their optimal loading capacity.

Electrode	Loading/nmol	η / mV	Tafel Slop mV/dec
GC-ATSP	10	1090	268
GC-ZnATSP	40	853	217
GC-CuATSP	40	745	192

4.3. Conclusion

In summary, a series of GC electrodes modified with ATSM, ATSP and their Cu- and Zn- complexes were prepared and evaluated in 0.5 M H₂SO₄ for their HER electrocatalytic activity. The modified electrodes were used as working electrodes, with Pt as counter electrode and Ag/AgCl as reference, within a three-electrode cell as described before.

The morphology of modified electrodes was studied by SEM. For GC-ATSM, the surface did not change much before and after electrolysis. However, for GC-ZnATSM and GC-CuATSM, the surfaces were roughened and aggregated after electrolysis. For GC-ATSP, an smooth and uniform film was formed by drop casting on the surface, and after electrolysis, the film lost its uniformity by holes on the surface due to the generation of H₂ gas during the electrolysis. Similar to GC-ATSP, GC-ZnATSP and GC-CuATSP showed a

uniform film on the modified GC surface before electrolysis, and the surfaces were roughened after reaction.

The XPS and UV-Vis were used to determine the active species on the GC electrodes, and the atomic percentage was calculated to determine the composition of each compound. Based on the XPS analysis, ATSM remains stable on the GC surface during bulk electrolysis, as well as CuATSM. For ZnATSM, a process of de-metallation was observed due to the absence of Zn 2p signal in the sample after electrolysis. The same trend was observed for ATSP and its metal complexes. The ATSP and CuATSP was stable on GC surface during bulk electrolysis while the ZnATSP demetallated during the reaction. The long-term stability properties for each electrode were evaluated by chronopotentiometry. All modified electrodes demonstrate good, long-term stability in overpotential following an initial conditioning period. The polarization curves were collected to determine the optimal loading capacities for all modified electrodes. For Gc-ATSM, GC-ZnATSM and GC-CuATSM, their optimal loadings were observed at 10, 40 and 50 nmol with overpotential at 1123, 923 and 774 mV, respectively. For GC-ATSP, GC-ZnATSP and GC-CuATSP, the optimal loading capacities were observed at 10, 40 and 40 nmol at overpotential of 1090, 853 and 745 mV. All these modified electrodes exhibit good long-term stability properties over 24 hours. The general mechanism for these catalysts were determined by Tafel slopes. The CuATSM and CuATSP display the lowest Tafel slope value than ATSM, ATSP, and their Zn complexes, indicate a faster electron transfer inside the film. The high values of Tafel slope for all catalysts indicate the Volmer step as the rate determine step.

CHAPTER V

CARBON PASTE ELECTRODE APPLICATION IN ReL_3 , ATSM and CuATSM

5.1 Background

As discussed in Chapters III and IV, carbon is a useful material for fabricating electrodes. Glassy carbon is resistant to corrosion, displaying high temperature resistance, hardness (7Mohms), low density and low temperature resistance, low friction and low thermal resistance (refs). However, compare to metallic electrodes, the overpotential of HER is higher on glassy carbon. To improve HER activity much effort has focused on surface modification of glassy carbon. In many cases, deposition or surface confinement of catalysts improves overpotential and charge transfer between target substrates (H^+ for HER) and the electrode surface.^{72, 136, 147-156}

An attractive alternative to deposition and derivatization of carbon electrode surfaces is the inclusion of electrocatalysts in a carbon paste matrix.¹⁵⁷ Carbon paste electrodes (CPEs) are widely used in electroanalysis as sensors,¹⁵⁸⁻¹⁶² but have found limited use in HER catalysis.

CPEs are generally easy to fabricate using a mixture of carbon materials and pasting liquids. The most commonly used carbon material is graphite powder.¹⁶³

however, recently more advance materials such as carbon nanotubes (CNT) have been used to make paste electrodes (CNTPEs).¹⁶⁴⁻¹⁶⁸

The most common method for preparing CPEs is to mix the catalyst in the appropriate carbon material to form a homogeneous paste, which gives the CPEs some pre-determined properties.¹⁶⁹⁻¹⁷¹ CPEs have been employed for the analysis of inorganic and organic species.¹⁷² However, CPEs have some disadvantages, which limit their application. The biggest problem is the properties and success in working depends on the process of preparation. CPEs are not commercially available and require preconditioning before use. However, a major advantage of this type of electrode is the catalyst is easily refreshed by abrasion resulting in a mechanically stable surface.

One of the first reports of use of CPEs was reported by Abdolkarim Abbaspour¹⁷³ using Ni ferrite nanoparticles embedded in carbon paste. The nanoparticles were composed of mixed oxide Fe and Ni and prepared at low temperature by co-precipitation and mixed in graphite powders. The electrocatalytic activity of Ni-Fe NPs for HER was evaluated under varying acidic conditions and Tafel slopes were found to vary between 97.75 and 122.19 mV/dec, which indicates the rate determining step is the Volmer step. Abbaspour later reported HER activity for CPEs impregnated with nano sized Ni and Zn phthalocyanines (nano NiPc and nanoZnPC) (ref), which also showed good electrocatalytic activity.¹⁷⁴

Recently, Hu et al, evaluated HER activity of MoS₃ and MoS₂ CPEs.¹⁷⁵ They reported several deposition methods employed to fabricate modified electrodes with

MoSn particles. The MoSn CPEs gave the highest current densities compared to modified GEs and fluorine-doped tin-oxide (FTO) glass electrodes. However, it was difficult to determine the weight-average activity of these CPEs because of the unknown surface coverage of the electrodes. Polarization curves of blank CPEs and MoS₃ modified electrodes were generated at pH=0 in 1.0 M H₂SO₄ at 5 mV/s.

In the previous chapter, four strategies were used to prepare ReL₃ modified electrodes. The first two involved direct coating of ReL₃ and [ReL₃]⁺ on the surface of clean and polished GC, and the latter two involved adding CB layers on the electrode surface first and then depositing the catalyst on top of the CB layer. The results showed that by adding a CB layer first, the charge transfer resistance decreased by 100 times, while the overpotential decreased about 500 mV, indicating the carbon layer functions as a conducting matrix reducing the resistance inside the catalyst film. This observation suggests that CPEs may experience similar reduction in overpotential leading to active HER electrocatalysts.¹³²

5.2. Results and Discussion

5.2.1. Electrode preparation

CPE-ReL₃:

CPE electrodes were prepared by mixing certain amount of ReL₃ with graphite particles that was suspended in a DCM solution (10 ml DCM solution for 1 g solid) that was magnetically stirred until complete evaporation of the solvent. Then the sample was sonicated for 10 mins. The homogeneous mixture will be dried under a heating lamp for

1-2 hours to assume complete evaporation of DCM. The solid mixture was then mixed with paraffin oil (20 w/w%) in a mortar and the emulsion was mulled for 15 min to obtain a uniformly wetted paste. The proportion of Paraffin oil has been optimized by measuring the background potential for CPEs with 10% - 40% of paraffin oil. With addition of 10% paraffin oil, the carbon paste could not stick tightly inside the syringe and was very easy to fell off during the electrolysis. With 20% of paraffin oil, a stable CPE surface was generated for the HER electrolysis measurement. However, with the addition of the paraffin oil, which is nonconductive and would increase the resistance in the paste, the blank overpotential increased, and based on the polarization curves, the CPE with 20% paraffin oil shows a stable surface with the lowest overpotential, Figure 76.

Figure 76. Polarization curves of CPE with paraffin oil: graphite ratio of 10%, 20% ,30% and 40% recorded in 0.5 M H₂SO₄ (aq) with the unmodified CPE electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl (3.5 M KCl) as the reference electrode.

The paste was tightly packed into plastic syringe tubes with inner diameters normally between 0.5 -3 mm, Figure 77. Electrical contact with the paste was established by inserting a copper wire down the length of the plastic syringe tube into the paste. The

final step is to smooth the CPE surface using weighting paper and the surface was coated with Nafion film by drop casting 2 μ L of Nafion solution and allowed to dry for 30 min under a heating lamp prior to use. The CPE is stable at room temperature in the air and the surface can be renewed by cutting off the old surface with spatula and depressing the plunger. For CPE-ReL₃, different ratios of ReL₃: carbon black has been studied to optimized loading capacity from 0.5% to 2.0%.

Figure 77. Scheme of Carbon Paste Electrode.

CPE-ATSM/CuATSM:

ATSM and CuATSM CPEs were prepared in a method similar to CPE-ReL₃. For CPE-ATSM, 0.3 – 4.5 mg of ATSM ligand was mixed with 3 mg of graphite and suspended in 10 mL DCM with stirring. After evaporation of DCM, the dry solid mixture will be mixed with paraffin oil (20 w/w%) in mortar and mulled for 15 min to obtain a uniform wetted paste. For CPE-CuATSM, 0.3 – 4.5 mg of ATSM ligand was mixed with 3 mg of graphite and suspended in 10 mL DCM with stirring. The suspension was sonicated for 10 mins and

then dried under a heating lamp. Then the dry solid mixture is mixed with paraffin oil (20 w/w%) in mortar and mulled for 15 min to obtain a uniform wetted paste. The uniform pastes were tightly packed into plastic tubes as described before. As with the CPE-ReL₃ system, different ratios (0.5%, 1% and 1.5%) of ATSM and CuATSM: carbon black were evaluated to determine the optimum loading capacities.

5.2.2. Surface Morphology studies

CPE-ReL₃:

Microscopy studies has been employed to study the morphology of the modified CPE surfaces. In Figure 78, the SEM images of CPE-ReL₃ shows good uniformity of the surface, which is smoother than the film generated by directly drop casting on the GC electrode. After electrolysis, the uniformity of the surface decreased due to the forming of H₂ gas in the film, however, the CPE surface exhibits more stable than observed on modified GC surfaces.

Figure 78. SEM image of CPE-ReL₃ before (left) and after (right) electrolysis with Nafion layer.

CPE-ATSM and CPE-CuATSM:

Microscopy studies have been done to investigate the morphology of the films before and after electrolysis for CPE-ATSM and CPE-CuATSM. As it shown in Figure 79, before electrolysis, both CPEs showed good uniformity and smooth surfaces. Bulk electrolysis using both electrodes in 0.5 M H₂SO₄ at a scan rate of 20 mV/s was conducted. The SEM images of the surfaces after electrolysis are shown in Figure 80. In the SEM images, the CPE surfaces appear to have lost some uniformity after electrolysis. Both electrodes show the presence of pores, likely caused by the generating of H₂ gas during the reaction. However, the surface looks more stable than the drop casting GC surfaces based on the SEM images, and this is because in CPE system, catalysts were uniformly mixed throughout the carbon paste matrix. The long-term stability study of CPE systems also indicated that overpotential increases after 24 hours of chronopotentiometry, however, the change is smaller than observed for GC systems, which showed in chapter IV. Generally, the paraffin binder for the carbon-paste electrodes could be gradually dissolved in solutions and the generating of H₂ will destroy the CPE surface, so the CPE surfaces are not very stable during the long-term electrolysis. However, in this system, a layer of Nafion film was added on the top of the CPE surface, which improved the stability of CPE-ATSM and CPE-CuATSM during the reaction. Evolution of hydrogen roughens the CPE surfaces upon prolonged electrolysis leading to a decline in electrode stability.

Deposition of a Nafion layer significantly improved the stability of the CPE-ATSM and CPE-CuATSM during HER electrolysis.

Figure 79. SEM image of CPE-ATSM(left) and CPE-CuATSM(right) electrode surface before electrolysis with Nafion layer.

Figure 80. SEM image of CPE-ATSM(left) and CPE-CuATSM(right) electrode surface after electrolysis with Nafion layer.

5.2.3. Polarization Curves and Overpotential Calculation

The electrochemical set up employed the same three-electrode cell as described in chapter III, with modified CPE as working electrode, a Pt wire as counter electrode and Ag/AgCl (3.5 M KCl) as the reference electrode, Figure 81.

Figure 81. Electrochemical set for CPE system.

CPE-ReL₃:

To evaluate the HER electrocatalytic activity under heterogeneous condition, polarization curves have been recorded for CPE-ReL₃ in 0.5 M H₂SO₄ solution under ambient conditions. Linear sweep measurements were recorded from 0.5 V – -1.7 V to obtain polarization curves.

For CPE-ReL₃, different graphite: ReL₃ ratios (0.1%, 0.5%, 1.0% and 1.5%) were evaluated to determine the optimal loading amount to prepare the CPE-ReL₃ working electrode. The polarization curves of CPE-ReL₃ electrodes with different ratios are shown in Figure 82. Overpotential data are listed in Table 27. The optimum graphite: ReL₃ ratio

was determined to be 1% with the lowest overpotential at 472 mV. With increasing ration of ReL_3 in carbon paste, the overpotential decreased from 0.5% to 1.0% and then started to increase and jumped to 970 mV when the ratio reached 5%.

Figure 82. Polarization curves of CPE- ReL_3 with graphite: ReL_3 ratio of 0.5%, 1.0% ,1.5% and 5% recorded in 0.5 M H_2SO_4 (aq) with the modified electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Thus, the electrocatalytic activity of CPE- ReL_3 (1% loading) and GC- ReL_3 (60 nmol loading) are compared in Figure 83. The overpotential at 10 mA cm^{-2} is 472 mV for CPE- ReL_3 , which is 439 mV less than observed for GC- ReL_3 ($\eta = 911 \text{ mV}$ at 10 mA cm^{-2}). As discussed in Chapter III, the GC-CB- ReL_3 which contains a layer of CB, has an overpotential at 487 mV, which is only 29 mV different than CPE- ReL_3 , showing that carbon coated electrode surfaces show better electrochemical properties than bare glassy carbon surfaces. The carbon materials not only generate higher surface areas containing more catalyst exposed to the solution, but also provide a highly conductive film with faster electron transfer within the catalysts film, resulting of the reduction of the overpotential required for the HER.

Figure 83. Polarization curves of GC-ReL₃ and CPE-ReL₃ recorded in 0.5 M H₂SO₄ (aq) with the modified electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl (3.5 M KCl) as the reference.

Table 27. Overpotential for CPE-ReL₃ with different loadings.

Electrode	Potential (mV) vs. RHE
CPE-ReL ₃ -0.5%	543
CPE-ReL ₃ -1.0%	472
CPE-ReL ₃ -1.5%	543
CPE-ReL ₃ -5.0%	947

CPE-ATSM:

The polarization curves of CPE-ATSM has been recorded by linear sweep voltammetry from 0.72 V - -1.48 V at 20 mV/s in 0.5 M H₂SO₄(aq) with the modified electrode as the working electrode, a Pt wire as the counter electrode, and Ag/AgCl (3.5 M KCl) as the reference, Figure 84. The optimal graphite to ATSM ration was figured by measuring the polarization curves of CPE-ATSMs at 0.1%, 0.5%, 1% and 1.5%. The CPE-ATSM-1% exhibits the lowest overpotential at 531 mV, which is 278 mV lower than the highest value of 809 mV for CPE-ATSM 1.5%. The overpotential value for each ratio is

listed in Table 28. Compare to GC-ATSM, the overpotential of CPE-ATSM-1% is 499 mV lower than GC-ATSM ($\eta = 1.03$ V).

Figure 84. Polarization curves of CPE-ATSM at different ratios of ATSM:graphite, recorded in 0.5 M H₂SO₄ (aq) with the modified electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl (3.5 M KCl) as the reference electrode.

Table 28. Overpotentials of CPE-ATSM

Electrode	Potential (mV) vs. RHE
CPE-ATSM-0.1%	726
CPE-ATSM-0.5%	681
CPE-ATSM-1.0%	531
CPE-ATSM-1.5%	809

CPE-CuATSM:

The polarization curves of CPE-CuATSM were recorded under the same condition as CPE-ATSM, and carbon paste electrode with different ratios of graphite to CuATSM was studied to determine the optimal loading capacities (Figure 85). The lowest overpotential appeared at CPE-CuATSM-1% for 546 mV, which is 30 mV lower than CPE-CuATSM-0.5%

and CPE-CuATSM-1.5%. Compared to GC-CuATSM, the overpotential of CuATSM was reduced by 228 mV.

Figure 85. Polarization curves of CPE-CuATSM at different ratios of CuATSM to graphite, recorded in 0.5 M H_2SO_4 (aq) with the modified electrode as working electrode, a Pt wire as counter electrode, and Ag/AgCl (3.5 M KCl) as the reference electrode.

Figure 86. Polarization curves for GC-CuATSM (orange) and CPE-CuATSM (blue). Scan rate: 20 mV/s sweep scan from 0.5 V to -1.0 V in 0.5 M H_2SO_4 .

Table 29. Overpotentials of GC-CuATSM and CPE-CuATSM at a current density of 10 mA cm⁻² in 0.5 M H₂SO₄.

	GC-CuATSM	CPE-CuATSM
Overpotential (mV)	774	599

5.2.4. Electrochemical Impedance Studies

Electrochemical impedance spectroscopy (EIS) provides valuable information on the kinetics of electron transport in the CP electrodes and greater understanding of interfacial reactions at CPE surfaces.

CPE-ReL₃:

The EIS data and fitting are presented in Nyquist plots, such as in Figure 87. The blue dots are the real data from EIS measurements, and the yellow line is the fitting results based on a circuit model and parameters in equation x, y in the line are shown in Figure 88. The circuit model includes three parts for CPE-ReL₃ system. The first parameter is R_1 , which represents R_s , the contact resistance between electrode surface and electrolyte in solution.

Figure 87. Nyquist plot of CPE-ReL₃: real data (blue dots) and fitted data (orange line) at $\eta = 1.3$ V in 0.5 M H₂SO₄.

As shown in Figure 87, two semicircles are observed in the impedance fitted plot. In the circuit, R_3 represents the surface activation resistance, which cause by the diffusion of ions into the films and it is very typical for embedded electrodes. R_2 , the semicircle appears in low frequency range, is assigned to the charge transfer resistance on the surface.¹⁷⁶ The results of circuit analysis based on the model are shown in Table 30.

The CPE is defined by the following equation:

$$Z = 1/[Y_0(i\omega)^\alpha]$$

where Y_0 is the CPE constant, ω is the angular frequency, and α is the CPE power ($0 \leq \alpha \leq 1$). If α is equal to 1, the equation is identical to that of a capacitor, and an ideal capacitor is obtained:

$$Z = 1/(i\omega C)$$

If α is equal to 0, the CPE represents an ideal resistor. Often, a CPE is used as a model in place of a capacitor to compensate for inhomogeneity in the system.

Figure 88. Electrical equivalent circuit model for EIS data interpretation for the ReL₃ modified GC electrodes.

Compare with GC-ReL₃, where the R_s of GC-ReL₃ (41.1 Ω) is much lower than CPE-ReL₃, the higher contact resistance is probably caused by the Nafion film over layer on the CPE surface, which slows the charge transfer rate. The activation resistance (R_3) for CPEs are not observed in the GC-ReL₃ system. The charge transfer resistance of CPE-ReL₃ is 3828 Ω , which is over 100 times lower than in the GC system. Moreover, this value is even lower than the observation for GC-CB-ReL₃, which is around 6000 Ω . Thus, the charge transfer resistance was dramatically decreased in CPE system, leading to improving of the performance of ReL₃ for HER electrocatalysis.

Table 30. EIS calculation of CPE-ReL₃.

	R_1 / Ω	R_3 / Ω	CPE2-T (sP/ $\mu\Omega$)	CPE2-P (sP/ $\mu\Omega$)	R_2 / Ω	CPE1-T (sP/ $\mu\Omega$)	CPE1-P (sP/ $\mu\Omega$)
CPE-ReL₃	71.1	360	1.5 E-4	0.72	3828	7.8 E-4	0.93

CPE-ATSM:

The EIS measurement was conducted under the same condition as used in the CPE-ReL₃ study. The EIS measurements were made using the frequency sweep from 10⁵ to 0.01 Hz. Z' and Z'' are the real and imaginary parts of experimental data. The blue dots are the real data, and the yellow line is the fitted results (Figure 89) based on a circuit model shown in Figure 90. This model will also be used to fit CPE-CuATSM. Four parameters have been applied in this model. The first parameter is R_1 , which represents the contact resistance between solid surface and electrolyte in solution. The next parameter, R_2 can be assigned to the surface activation resistance. The surface activation usually appears in heterogeneous systems because the films behave as inhomogeneous

resistors result in a “kinetic” semicircle. The resistance is proportional to pore size and surface. A W_1 (Warburg diffusion element) was inserted after R_2 , which is an equivalent electrical circuit component that models the charge diffusion process. The last part contains a resistance (R_3) parallel with a capacitor (C_1), where R_3 represents the charge transfer resistance on the CPE-ATSM surface while C_1 represents a double layer capacitance. The double layer effect appears at the interface between a solid particle/a porous body and an adjacent liquid electrolyte, and two layers of ions with opposing polarity at the interface when a potential is applied, Figure 91.

Figure 89. Nyquist plot of CPE-ATSM: real data (blue dots) and fitted data (orange line) at $\eta = 1.3$ V in 0.5 M H_2SO_4 .

Figure 90. Electrical equivalent circuit used to model the system of CPE-ATSM investigated with EIS.

The EIS fitting was processed in ZView and the equivalent circuit parameters are shown in Table 31. As discussed in Chapter IV, for GC-ATSM, the contact resistance is $5.4\ \Omega$, which is close to the value for CPE-ATSM. However, the charge transfer resistance for GC-ATSM is $115\ \text{k}\Omega$, which is over 100 times higher than observed for CPE system ($893\ \Omega$). These data indicate that for the CPE system, the charge transfer resistance has been reduced significantly similar to CPE- ReL_3 .

Table 31. EIS calculation of CPE-ATSM

	R_1 / Ω	R_2 / Ω	CPE1-T ($\text{sP}/\mu\Omega$)	CPE1-P ($\text{sP}/\mu\Omega$)	R_3 / Ω	C1
CPE-ATSM	10	29.29	2.86 E-8	1.08	893	0.001

Figure 91. Schematic of double layer in liquid at contact with solid surface.

CPE-CuATSM:

The EIS measurements were performed under the same condition used for CPE-ATSM. The same equivalent circuit model was used to fit the CPE-ATSM EIS data, in Figure 92. The blue dots are the real data and the orange line is the fitting data generated by the ZView software.

Figure 92. Nyquist plot of CPE-CuATSM: real data (blue dots) and fitting data (orange line) at $\eta = 1.3$ V in 0.5 M H_2SO_4 .

As discussed in Chapter IV, the contact resistance is $7.82 \, \Omega$ for GC-CuATSM, which is close to the value determined for CPE-CuATSM. However, the charge transfer resistance for GC-CuATSM is $5750 \, \Omega$, which is about 10 times higher for the CPE-CuATSM ($508 \, \Omega$). With CPE- ReL_3 and CPE-ATSM, the charge transfer resistance is significantly reduced (Table 32).

Table 32. EIS calculation of CPE-CuATSM

	R_1 / Ω	R_2 / Ω	CPE1-T (sP/ $\mu\Omega$)	CPE1-P (sP/ $\mu\Omega$)	R_3 / Ω	C1
CPE-CuATSM	10	12.31	3.17 E-2	0.22	508	0.002

5.2.5. Stability Studies for CPEs

Initial CPE studies showed the electrodes were unstable in strong acidic solutions. However, the addition of a Nafion over layer produced stable electrode surfaces that do not degrade upon prolonged HER catalysis. Chronopotentiometry has been conducted to study the long-term stability of the CPE-ReL₃, CPE-ATSM and CPE-CuATSM. The current was fixed at 10 mA cm⁻² and the change in overpotential was monitored during 24 h. The long-term stability study for CPE-ReL₃ is shown in Figure 93. The overpotential increased about 320 mV over 24 h period. Compare to GC-ReL₃, there was no obvious conditioning period for CPE-ReL₃, which indicated that the interaction between catalyst and matrix is stronger and more stable than GC-ReL₃. The overpotential increased slowly and a total increasing of 320 mV was observed in 24 h for CPE-ReL₃, which is 190 mV lower than observed for GC-ReL₃. These data indicate a stable surface during the electrolysis for CPE-ReL₃.

Figure 93. Long-term stability study for CPE-ReL₃ for 24 h in 0.5 M H₂SO₄.

The long-term stability studies of CPE-ATSM is shown in Figure 94. The initial applied potential for CPE-ATSM was 0.64 V, and surprisingly reduced by 11 mV over 24 h

measurement. Compare to the value for GC-ATSM, where the potential increased about 520 mV, indicated that by using carbon paste electrode, the stability of electrode was improved significantly.

Figure 94. Long-term stability study for CPE-ATSM for 24 h in 0.5 M H₂SO₄.

The long-term stability study for CPE-CuATSM is shown in Figure 95. The initial potential is at 0.75 V vs. RHE, and the same behavior as CPE-ATSM has been observed for CPE-CuATSM. The potential increased gradually over 24 h and reached 0.813 V at the end. The total increasing of the potential is only 95 mV, while the potential increased around 500 mV for GC-CuATSM.

Figure 95. Long-term stability study for CPE-CuATSM for 24 h in 0.5 M H₂SO₄.

5.3. Conclusions

In this part, CPE system has been employed to prepare the modified working electrodes by mixing catalysts with graphite powder. The optimum ratio of catalyst:graphite has been found by polarization curve measurement. For all modified CPEs, they all showed the lowest overpotential at catalyst to graphite ratio of 1 w/w%. The morphology studies for CPE surfaces before and after electrolysis, and the SEM images of CPE-ReL₃, CPE-ATSM and CPE-CuATSM all indicate a smooth and uniform surface before electrolysis, and after electrolysis, all the films lost their uniformity and pores were forming during the reaction because of the generating of the H₂ gas. The EIS studies indicate by using CPE, the charge transfer resistance (R_s) is greatly reduced than the GC system while the contact resistance didn't change a lot. For CPE-ReL₃, the R_s is 3238 Ω , which is over 100 times less than GC-ReL₃, and its overpotential is 528 mV which is 383 mV less than GC-ReL₃; for CPE-ATSM, the R_s is 893 mV and compare the GC-ATSM, it also reduced by 100 times. The overpotential for CEP-ATSM is 531 at 10 mA cm⁻², which is also lower than the GC-ATSM. For CPE-CuATSM, the R_s is 508 Ω and it is about 10 times less than the GC-CuATSM (5750 Ω), and the overpotential was reduced for 210 mV compare to GC-CuTASM. The stability study was conducted at last by chronopotentiometry. By keeping the current density at 10 mA cm⁻², the potential change during 24 h has been recorded. The results indicate a more stable surface and smaller potential increase for CPE system. Thus, for ReL₃, ATSM and CuATSM catalysts in heterogeneous HER conditions, they reach better electrocatalytic performance and stabilities in CPE system than in GC system.

CHAPTER VI

CONCLUSIONS

6.1 Translation of Ligand-Centered HER Activity and Mechanism of a Rhenium-Thiolate from Solution to Modified Electrodes

A rhenium-thiolate complex $[\text{ReL}_3]^{n+}$ ($n = 0$ and 1) has been modified on the GC electrode surfaces, and carbon black has been used to increase the surface area and provided a high conductive support for catalysts by preparing GC-CB- $[\text{ReL}_3]^{n+}$ ($n = 0$ and 1). These modified electrodes were studied in $0.5 \text{ M H}_2\text{SO}_4$ as heterogeneous HER electrocatalysts. The GC-CB- $[\text{ReL}_3]^+$ showed the lowest overpotential at 357 mV with a Tafel slope of 155 mV/dec . The electrochemical impedance study further confirmed the correlation between film resistance and HER overpotential. The Nyquist plot of GC-CB- $[\text{ReL}_3]^+$ showed the smallest charge transfer resistant at $4 \text{ k}\Omega$, which is over 300 times better than GC- ReL_3 . The durability study for all modified GC electrodes was conducted by chronopotentiometry. The potential was kept at -1.48 V vs. RHE over 24 h , and the potential that required for keeping the current density at 10 mA cm^{-2} has been recorded. For GC- ReL_3 , the overpotential increased by 510 mV over the first 3 h and then kept constant over the remainder of the experiment. The initial increase in overpotential can be attributed to a decrease in the number of active sites on the surface. The total

overpotential change for all the modified electrodes are relatively large. The evaluation of active sites on the surface during the electrolysis was conducted by diffuse reflectance spectra in solution and solid state. At the end, the Tafel slope has been calculated from polarization curves which indicates the rate determine steps and mechanism of HER on the interface. The value of Tafel slope indicates the Volmer step is the rate determine step for all the catalysts. Combined with the study of ReL_3 in homogeneous, the proposed mechanism was going through a ligand-centered pathway with no metal hydride involved in. The DFT studies for ReL_3 further proves that the metal hydride pathway is not favorable in this system.

6.2 Study of ATSM, ATSP and Their Zn- and Cu- Derivatives on GC electrode as HER electrocatalysts.

A series of modified GC electrodes have been prepared by drop casting ATSM, ATSP and their Cu- and Zn- complexes on the GCE surface. These electrodes were used as working electrode in a three-electrode cell for testing their HER activities in 0.5 M H_2SO_4 solution. The GC-ATSM and GC-CuATSM electrodes exhibited good, long-term stability in overpotential following an initial conditioning period. The lowest overpotentials appear on GC-CuATSM and GC-CuATSP, at 1123 mV and 774 mV, respectively. The GC-ATM and GC-ATSP exhibit the largest overpotential at 1123 and 1090 mV, while the GC-ZnATSM and GC-ZnATSP at 923 and 853 mV.

Table 33. HER Overpotentials (η) and Tafel Slopes of the Modified Electrodes

Electrode	Loading/nmol	η / mV	Tafel Slop / mV dec ⁻¹
GC-ATSM	10	1123	427
GC-ZnATSM	40	923	235
GC-CuATSM	50	774	150
GC-ATSP	30	1095	268
GC-ZnATSP	40	823	217
GC-CuATSP	60	723	192

The impedance study indicated the correlation between overpotential and charge transfer resistance. The GC-CuATSM and GC-CuATSP exhibit the smallest charge transfer resistance of 5.75 k Ω and 6.70 k Ω , while the GC-ATSM and GC-ATSP at 115k Ω and 190 k Ω , Table 34. The XPS data has been collected for evaluation of the active species on the GCE surface during the electrolysis, and the results show that ATSM and CuATSM is stable during the electrolysis while ZnATSM is demetallated during the reaction. The XPS analysis for ATSP and its derivatives shows the same behaviors as ATSM systems. The ATSP and CuATSP displays stable on the GCE surface while the ZnATSM demetalled during the electrolysis. The GC-ATSP and GC-CuATSP electrodes exhibit good, long-term stability during the electrolysis with a conditioning period over the first 5 hours, and then kept stable during the remaining time.

Table 34. Simulated Nyquist plot parameters for modified GC electrodes.

Electrode	$R_s(\Omega)$	$R_{ct}(\Omega)$	CPE-T (sP/ $\mu\Omega$)	CPE-T (sP/ $\mu\Omega$)
GC-ATSM	5.4	1.15E+05	6.24E-06	0.74
GC-ZnATSM	9.87	7.00E+04	1.50E-05	0.81
GC-CuATSM	7.82	5.75E+03	3.08E-05	0.76
GC-ATSP	8.7	1.90E+05	3.68E-06	0.65
GC-ZnATSP	6.85	7.50E+04	4.20E-06	0.57
GC-CuATSP	2.08	6.70E+03	7.60E-06	0.66

In Chapter 4, ATSM and ATSP ligand was proved to function as heterogeneous HER catalysts in acidic condition, which indicated that their Cu- complexes, CuATSM and CuATSP, could go through a ligand-centered mechanism when functioning as HER catalyst which needs further study. Even the overpotentials of these catalysts are relatively large to other catalysts, this thiosemicarbazone frameworks displays a huge potential for hydrogen evolution catalysis.

6.3 ReL_3 , ATSM and CuATSM Modified Carbon Paste Electrode

Catalyst modified carbon paste electrodes have been prepared by mixing catalysts with graphite powder together as the paste. The optimal ratio of catalyst to graphite has been determined by polarization curves, and the lowest overpotential for CPE- ReL_3 , CPE-

ATSM and CPS-CuATSM are all appeared at 1 w/w%. Compare to modified GC systems, the overpotential of modified CPEs were improved significantly (Table 35). The overpotential decreased by 452 mV for ReL_3 , 499 mV for ATSM and 228 for CuATSM.

Table 35. Overpotential comparison between GC and CPE systems.

Catalyst	Overpotential in GC system(mV)	Overpotential in CPE system(mV)
ReL₃	910	458
ATSM	1030	531
CuATSM	774	546

The morphology study of CPE surface before and after electrolysis were evaluated. All the CPE surfaces exhibited smooth and uniform properties before electrolysis, and after electrolysis, the uniformity decreased due to the hydrogen generation in the film. However, the CPE surfaces still look more stable than modified GC surface based on the SEM images, which influence the stability properties if these CPEs during the long-term stability study. The impedance study furtherly revealed the correlation between charge transfer resistance and overpotential. The Nyquist plots were fit and simulated with a circuit model shown .

The charge transfer resistance, which represents the resistance within the catalyst film, is the one of the most important parameters to evaluate the catalytic activity of the catalyst on the electrode surface. For CPE- ReL_3 , the R_s is 3238 Ω , which is over 100 times less than GC- ReL_3 , which related to the decrease of the overpotential for CPE- ReL_3 . The R_{ct} is 893 Ω For CPE-ATSM which is 100 times less than R_{ct} in GC-ATSM. For CPE-CuATSM, the R_{ct} is 508 Ω , which is also about 10 times less than the GC-CuATSM (5750 Ω).

The Stability study of CPEs are conducted with chronopotentiometry by recording potential required for maintaining current density at 10 mA cm^{-2} over 24 hours. The results of CPEs indicate an excellent stable surface for CPE systems, and a smaller potential change compare to GC system, which has been shown in Table 38.

Table 36. Comparison of overpotential increasing over 24 h for GC and CPE system.

Catalyst	Overpotential increased for GC	Overpotential increased for CPE
ReL₃	510 mV	320 mV
ATSM	520 mV	-11 mV
CuATSM	320 mV	95 mV

In summary, The modified carbon paste electrodes show smaller overpotentials and lower charge transfer resistance for all three catalysts, with excellent stability properties during long-term electrolysis.

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APPENDIX A:

Figure A1. Surface UVs of $[\text{ReL}_3]^n$ ($n=0,1$) before 1CV cycle in 0.5 M H_2SO_4 . Scan rate: 200 mV/s.

Figure A2. Surface UVs of $[\text{ReL}_3]^n$ ($n=0,1$) after 1CV cycle in 0.5 M H_2SO_4 . Scan rate: 200 mV/s.

Figure A3. SEM images of GC- ReL_3 after CV cycles in 0.5 M H_2SO_4 at 200 mV/s.

Figure A4. SEM images of GC- GC- $[\text{ReL}_3]^+$ after CV cycles in 0.5 M H_2SO_4 at 200 mV/s.

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Publications and Presentations

1. Translation of Rhenium-Thiolate HER activity and mechanism from Solution to Electrode surfaces: Experimental and DFT study

Wuyu Zhang, Andrew Z. Haddad, Brady D. Garabato, Pawel M. Kozlowski, Robert M. Buchanan, and Craig A. Grapperhaus.

Inorganic Chemistry **2017** 56 (4), pp 2177–2187

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2. Reversible methanol addition to copper Schiff base complexes: a kinetic, structural and spectroscopic study of reactions at azomethine C=N bonds.

Wuyu Zhang , Nina Saraei , Hanlin Nie , John R. Vaughn , Alexis S. Jones , Mark S. Mashuta , Robert M. Buchanan and Craig A. Grapperhaus.

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DOI: 10.1039/C6DT01955B

3. ATSM, ATSP and their Cu- and Zn- Derivatives Working as HER electrocatalysts on GC electrode surface in Heterogeneous Conditions

Wuyu Zhang, Robert M. Buchanan, Craig A. Grapperhaus.

4. Influence of pH of gelatin solution on cycle performance of the sulfur cathode

Wuyu Zhang, Yaqin Huang.

J. Electrochem. Soc. **2010** 157, 4, A443-A446

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5. Metal ATSM Complexes Modified Carbon Paste Electrode for Hydrogen Evolution Reaction

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Oral presentation. April 2017.

6. Heterogeneous Catalysts for Hydrogen Evolution Reaction in Aqueous Solution.

Wuyu Zhang, Robert M. Buchanan, Craig A. Grapperhaus.

Kentucky Academy Society.

Oral Presentation. Nov 2016.

7. Reversible addition of alcohols across C=N bonds of a N₄ Schiff base ligand coordinated to copper (II).

Wuyu. Zhang, H. Nie, M.S. Mashuta, C.A. Grapperhaus, R.M. Buchanan.
249th American Chemical Society National Meeting.
Poster presentation. April 2015.