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DENSITY GRADIENT FILMS, LANTHANIDE ELECTROCHEMISTRY, AND MAGNETIC FIELD EFFECTS ON HYDROGEN EVOLUTION, OXYGEN REDUCTION, AND LANTHANIDE ELECTROCHEMISTRY

by Krysti Lynn Knoche

A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

May 2015

Thesis Supervisor: Associate Professor Johna Leddy

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Graduate College The University of Iowa Iowa City, Iowa

CERTIFICATE OF APPROVAL

PH.D. THESIS

This is to certify that the Ph.D. thesis of

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To my family and my best beloved. I am the luckiest.

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ABSTRACT

Electroanalytical techniques are used to investigate mass transport through density gradient films; lanthanide triflate reduction and oxidation in a Nafion/acetonitrile matrix; and magnetic field effects on hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and lanthanide electrochemistry.

Graded density films are more dense at the electrode surface and become less dense out into solution due to a brush polymer structure. Fick's second law expands to account for a diffusion coefficient that varies with distance x normal to the electrode surface. Confocal microscopy, cyclic voltammetry, and computer simulations are used to investigate density graded Ficoll^(R) films. Mass transport approaches steady state (scan rate independence) at slow scan rates where the diffusion length samples the entire film. The use of Ficoll to template an ion exchange polymer is explored by casting Nafion^(R) Ficoll composites.

Lanthanide electrochemistry is enabled in acetonitrile at a Nafion modified platinum electrode in the presence of triflate ligands. Formal potentials are shifted into the voltage window of acetonitrile accessible due to triflate complexation. The Nafion further solubilizes the compounds. The mechanism (ECEC) is studied with cyclic voltammetry and x-ray photoelectron spectroscopy.

Magnetic field effects on electrochemical systems have been of interest to researchers for the past 65 years. Mass transport effects, such as magnetohydrodynamics and magnetic field gradient effects have been reported, but the Leddy group focuses on electron transfer effects. Electrode surfaces are modified with composite films of magnetic microparticles suspended in ion exchange polymer Nafion. Effects are verified to be electron transfer related and due to the magnetization of chemically inert microparticles. The magnets catalyze the rates of important electron transfer reactions such as hydrogen evolution and oxygen reduction.

Magnetic field effects on HER at various noncatalytic metal electrodes are explored with linear scan voltammetry. There is a correlation between the magnetic susceptibility of the electrode metals and the HER exchange currents (reaction rates). Exchange currents are $10^3 \times$ larger for a paramagnetic metal electrode than a diamagnetic one with the same work function. The overpotential at diamagnetic electrodes is decreased by modification with a Nafion + magnetic microparticle composite film. A decrease in overpotential of ~70 % for all electrodes except platinum is observed. The overpotential decrease correlates with the magnetic susceptibility of the particles.

Magnets can enhance differences between lanthanide cyclic voltammograms by shifting current densities at a given potential and enhancing current based on the number of 4f electrons and magnetic moment of each lanthanide ion.

Magnetic field effects on ORR in acetonitrile are investigated with cyclic voltammetry. In aprotic solvents, ORR proceeds by a one electron transfer reaction to paramagnetic $O_2^{\cdot-}$. Enhanced reversibility and electron transfer kinetics are observed as well as a decrease in overpotential of ~100 mV. Magnetic field effects on ORR in a lanthanide triflate solution are also examined. Electron transfer kinetics and reversibility are further enhanced in the presence of lanthanide triflate.

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PUBLIC ABSTRACT

Electrochemical reactions are processes that involve the transfer of an electron. These reactions are critical to the operation of many common devices such as batteries and fuel cells. Electrochemical techniques such as cyclic voltammetry evaluate how fast the electrons and molecules move (electron transfer and mass transport, respectively). Here, several systems are electrochemically investigated.

Lanthanides are heavy elements generated as nuclear waste products decay. Lanthanides are nonradioactive and can be recycled for applications in lasers, medical imaging, and high power magnets. When magnets are added to the electrode, enhanced electron transfer rates are observed as increases in current and decreases in the energy required to drive the reaction.

In energy technologies, hydrogen evolution reaction (HER) generates hydrogen as a fuel and the oxygen reduction reaction (ORR) drives metal air batteries and fuel cells. Electrochemical systems generate H_2 and O_2 by splitting water and consume H_2 and O_2 as fuels that provide clean (no pollutants) sources of renewable energy. Metal air batteries have significantly more inherent energy than lithium ion batteries. Addition of magnetic microparticles to the electrodes increases current (rates) of HER and ORR.

Ficoll^{\mathbb{R}} is a polymer that forms a graded density film, where the film is more viscous at one edge, then gradually becomes less viscous. When molecules move through the film along this gradient, they can be delivered to the most dense side at a steady, fixed rate. This has applications for coatings and stabilizers and steady

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delivery of pharmaceuticals such as time release hormones, insulin, nicotine, and mood enhancers. Microscopy, cyclic voltammetry, mathematical equations, and computer simulations are used to explore the properties of these films. Methods to make films with density gradients out of other materials are also explored.

This work contributes to important technologies in energy generation and storage, nuclear waster remediation, and the time release of pharmaceuticals.

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CHAPTER 1

INTRODUCTION

Electroanalytical techniques are used to investigate mass transport through density gradient films; lanthanide triflate reduction and oxidation in a Nafion/acetonitrile matrix; and magnetic field effects on hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and lanthanide electrochemistry.

Energy limits everything humans do. Currently, 80 % of the world's energy comes from fossil fuels like coal, natural gas, and petroleum. These are limited, nonrenewable resources with a huge pollutive toll on the environment. Alternative methods for energy production are needed. However, present alternative methods do not provide the same energy efficiency and low cost as fossil fuels. New ways to catalyze alternative methods are needed to improve efficiencies to parity or better with fossil fuel methods [1]. Thermodynamics predict the ideal amount of energy that can be generated by a system. However, there are energy losses in any technology (e.g., heat loss in combustion engines), inefficiencies in conversion (e.g., only \sim 12% of energy from the sun is harnessed into electrical energy in solar cells), and kinetic considerations (e.g., kinetic losses in oxygen reduction in proton exchange membrane fuel cells). Catalysts help overcome some of these issues by decreasing the energy needed for the reactions and increasing reaction rates [2].

Physical catalysts catalyze reactions without any net chemical interaction. These include phenomena such as heat, sound waves, and magnetic fields. Physical catalysts are often reusable and can translate across many chemical systems. Research in the Leddy group shows that magnetic fields enhance the efficiencies of electron transfer reactions, thereby increasing efficiencies closer to the ideal thermodynamic values. Magnetic field effects on fundamental electrochemical systems have been investigated, including redox reactions of transition metal complexes and organic complexes, and homogeneous and heterogeneous electron transfer [3–5]. Magnetic field effects have also been applied to electrochemical power systems such as p-Si and dye sensitized solar cells, proton exchange membrane fuel cells, primary alkaline batteries, manganese dioxide supercapacitors, and nickel hydroxide batteries [4–10]. In each case, electrodes are modified with magnetic microparticles suspended in a polymer film. Observed effects include increases in currents and efficiencies and decreases in the reaction overpotentials. The magnetic particles are chemically inert; similar size glass beads suspended in a polymer film do not have the same effect [8]. The effects scale with the magnetic field strength of the particles and the percent loading of the particles [4]. The magnetic properties of the redox species also impacts behaviors.

Here, magnetic field effects on hydrogen evolution reaction, oxygen reduction reaction, and lanthanide electrochemistry are investigated. Additional fundamental experiments to further explore the nature of the magnetic effect are conducted, including comparison of particle magnetization methods and comparison of local (particle based) versus external (outside the beaker) magnetic fields.

Low temperature proton exchange membrane (PEM) fuel cells display the greatest efficiency with H_2 fuel. Electrolysis of water generates high purity hydrogen, but efficiency is limited by poor oxygen evolution kinetics and the use of expensive noble metal electrodes such as platinum [11]. Platinum is needed because other metals have higher overpotentials for hydrogen evolution.

In nonaqueous, aprotic solvents, a quasireversible one electron reduction of O_2 is observed that produces the paramagnetic superoxide radical O_2^{--} [2, 12, 13]. Nonaqueous ORR is important for metal air batteries [12–16]. Lithium air batteries involve the oxidation of lithium at the anode and the reduction of oxygen at the cathode. Lithium air batteries have extremely high thermodynamic values of specific energy (5-15 × lithium ion batteries). Most of the present limitations in Li air battery development are at the cathode due to high overpotential of ORR and slow oxygen kinetics [17–19].

Nuclear energy is cleaner than fossil fuels, but produces radioactive waste. Lanthanide isotopes are produced during fission of ²³⁵U, most of which decay to stable nonradioactive lanthanide elements in a relatively short amount of time. If lanthanides can be separated out from the waste, nuclear waste is decreased and expensive rare earth metals are recycled for uses such as lasers, medical imaging, chemical catalysts, and permanent magnets [20]. Present lanthanide detection and separation methods are costly, tedious, and time-consuming. Lanthanide elements are difficult to separate from each other in solution because they have extremely similar properties, including masses, ionic radii, oxidation states, and standard potentials [21]. Electrochemically, lanthanide analysis is limited because their standard potentials fall outside the potential window of common electrolyte solutions [20]. Here, a method is developed to analyze lanthanides electrochemically in common solvents on the benchtop where a second reductive wave is observed. This allows magnetic field effects on lanthanide electrochemistry to be investigated. Film structures are important for applications such as pharmaceutical long term, controlled, drug delivery of molecules like insulin, serotonin, dopamine, and birth control hormones, paint drying and release of anti-mold compounds over time in paint, and chemical engineering polymerization through the controlled release of monomers, oxygen inhibitors, and initiators. Adsorbed polymers affect the flux of molecules due to differences in viscosity relative to the solution. Usually, flux in solution or across a uniformly dense polymer film decays over time. The full expression of Fick's second law reveals a way to achieve steady state flux by changing the physical structure of a film. Experimentally, the density graded polymer Ficoll is characterized and its mass transport properties investigated. Ficoll is a polymer that forms a graded density film, where the film is more viscous at one edge, then gradually becomes less viscous. When molecules move through the film along this gradient, they can be delivered to the most dense side at a steady, fixed rate. The use of Ficoll to template graded density ion exchange polymer films is also explored.

CHAPTER 2

MAGNETIC EFFECTS ON HYDROGEN EVOLUTION REACTION (HER)

Magnetic field effects on HER at various noncatalytic metal electrodes are explored. The efficiency of electrochemical hydrogen evolution varies widely with the electrode material. Trasatti made a careful study of the efficiency of HER on a wide variety of single element electrodes. Here, Trasatti's data are used to examine impacts of magnetic properties of the electrodes on the rate and efficiency of HER. A detailed analysis of Trasatti's data is made. Based on the apparent pattern in the data, the addition of magnetic particles to the electrode surfaces is explored. The addition of magnetic particles is shown to increase the rates of HER for several diamagnetic electrodes. These electrodes include gold, glassy carbon, and mercury.

2.1 Background

Magnetic properties of materials, the mechanism of HER, and work by Sergio Trasatti are discussed.

2.1.1 Magnetic Properties of Materials and Molecules

Materials have magnetic properties based on whether they have unpaired electrons. This means magnetic properties are commonly observed in compounds of transition metals that have unpaired d orbital electrons and lanthanides that have unpaired f orbital electrons [22]. Magnetic behavior is classified by whether the electrons are paired or unpaired and, if unpaired, whether the parallel orientation of the unpaired electrons established by an externally applied magnetic field persists once the external field is removed. Diamagnetic compounds have no unpaired electrons and, therefore, are neither attracted nor aligned by an external magnetic field. Paramagnetic compounds have unpaired electrons oriented at random that will align in the presence of an external magnetic field but that alignment is not sustained once the external magnetic field is removed. Ferromagnetic compounds have unpaired electrons oriented parallel to each other once subjected to a magnetic field; the unpaired electrons retain this alignment once the external magnetic field is removed and, thus, ferromagnetic materials have an overall net magnetic moment. When the applied magnetic field strength is sufficient to establish parallel orientation for all unpaired electrons, the material is at saturation magnetization and the maximum net magnetic moment is achieved. Antiferromagnetic compounds have unpaired electrons oriented antiparallel to each other such that the magnetic moment is less than it would be if the spins were all aligned parallel. Antiferromagnetic materials can have a zero net magnetic moment. In antiferromagnet and ferromagnetic states, aligned magnetic dipoles occur spontaneously. There is a positive energy of interaction between neighboring spins that allows this to occur (spin coupling), either parallel or antiparallel. Magnetic susceptibility (χ) provides a measurement of the strength of the magnetic field generated by the coupled spins. Diamagnetic compounds have small and negative magnetic susceptibilities such that $\chi_{diamagnetic} \ll 1$. Paramagnetic compounds have small, positive magnetic susceptibilities (still < 1), but compared to diamagnetic compounds, $\chi_{paramagnetic} >> |\chi_{diamagnetic}|$. Ferromagnetic compounds have large, positive magnetic susceptibilities (>>1).

Antiferromagnetic χ s can be small and comparable to paramagnetic χ s when nonzero [22].

2.1.2 Hydrogen Evolution Reaction

Hydrogen (H_2) is a high energy density molecule that finds use in fuel cells. Low temperature proton exchange membrane (PEM) fuel cells display the greatest efficiency with H₂ fuel. High purity hydrogen provides better efficiencies than reformates. Industrially, high purity hydrogen is produced commercially by steam reformation of natural gas. Not only is this an energy taxing endeavor, but it requires a nonrenewable resource. Production and environmental cost is higher than for petroleum based energy. The high cost of hydrogen production labels H_2 as an energy carrier rather than a fuel. Electrolysis of water generates high purity hydrogen, but is limited by poor oxygen evolution kinetics and the use of expensive noble metal electrodes such as platinum [11]. Platinum is used because other metals have higher overpotentials for hydrogen evolution. Overpotential is the experimentally observed voltage above the thermodynamic potential that is required to drive a reaction at a given rate [2]. Overvoltage is an energy tax. A method to reduce the overpotential at inexpensive electrodes is needed. Chemical catalysts explored by other researchers include molybdenum sulfide electrodes, molybdenum sulfide nanoparticles, and biomimetic organometallic compounds [23].

The mechanism for HER is thought to involve the adsorption of protons to the electrode surface. When a potential is applied, adsorbed protons are reduced to radical hydrogens (H^{\cdot}) as described in Equation 1 and two adsorbed H[·]s combine



Figure 1. Diagram depicting hydrogen evolution reaction (HER). Proton H^+ adsorbs to electrode surface where it is reduced to radical H^- . Two adsorbed H is combine to form hydrogen gas H_2 which diffuses away from the electrode.

to form hydrogen (H_2) gas as described in Equation 2. Then, H_2 (g) desorbs and diffuses away from the electrode surface [11, 23–25].

$$H_{ads}^+ + e \ \rightleftharpoons \ H_{ads}^. \tag{1}$$

$$2H_{ads}^{\cdot} \rightleftharpoons H_{2,ads}$$
 (2)

Figure 1 is a diagram depicting this hydrogen evolution reaction mechanism. HER at platinum is the half reaction for the normal hydrogen electrode (NHE) and its formal potential at platinum is set to zero as the standard against which other redox reactions are compared. This translates to an E^0 for HER at platinum of 0.00 V vs NHE or -0.241 V vs SCE (saturated calomel reference electrode).

Among noncatalytic, single metal electrodes, platinum has the best efficiency for HER, but it is expensive, so researchers investigate HER at other metals, alloys, and chemically modified electrodes [23]. To compare and evaluate hydrogen evolution across different electrode materials, electrochemists refer to exchange currents, i_0 . Tafel plots allow exploration of the relationship between the log of the current, $\log i(E)$, and the overpotential (described in Equation 3 as the difference between the experimental potential and the reaction standard potential). η (V) is the overpotential, E (V) is the experimental potential, E^0 (V) is the standard potential, i (A) is the current, i_0 (A) is the exchange current, α is the transfer coefficient, R is the gas constant, T is the temperature, and F is the Faraday constant [26].

$$\eta = \frac{RT}{2.3\alpha F} \log i_0 - \frac{RT}{2.3\alpha F} \log i \tag{3}$$

$$\eta = E - E^0 \tag{4}$$


Figure 2. Example Tafel plot of log cathodic current i (A) versus overpotential η (V). Extrapolation provides exchange current i_0 at $\eta = 0$.

Mass transport effects are ignored, so the overpotential associated with the current is solely dependent on the activation energy required to drive the electron transfer. A Tafel plot is used to extrapolate the current at no overpotential ($E = E^0$, $\eta = 0$); this current is called the exchange current i_0 . The lower the exchange current, the slower the electron transfer kinetics. An example Tafel plot is provided in Figure 2.

2.1.3 Trasatti Data

Sergio Trasatti compiled data for exchange currents at 31 metals, critically compiling data by identifying carefully determined i_0 values from the literature. The criteria are as follows: 1) i_0 extrapolated from lowest detectable portion of Tafel line, 2) high purity polycrystalline metal surfaces, and 3) acidic solutions at room temperature, with either 0.5-1.0 M sulfuric acid when possible or 0.05 M sulfuric acid or 0.05 M hypochloric acid [24, 27–30]. Trasatti found strong correlations in plots of the negative log of the exchange currents with the work functions of the electrode metals. Trasatti states that this makes sense, considering that the work function (eV) is the energy with which electrons near the Fermi level are bound to the interior of a solid; these are the electrons most likely to exchange during an electrochemical reaction. This correlation occurs on two distinct, parallel lines. Trasatti hypothesized the bifurcation was established by whether the electrodes were sp or transition metals. Here, the data are considered in terms of the magnetic properties of the electrodes (diamagnetic, paramagnetic, or ferromagnetic) in Figure 3. The difference in the electronic structures of sp and transition metals dictates the magnetic properties of the metals. The trend with magnetic properties can be

Metal	$-\log i_0 (\mathrm{A/cm^2})$	Φ (eV)	$\chi_m \; (\times 10^{-10} \; {\rm cm}^3/{\rm mol})$
Au	6.5	4.78	-3.55
Cu	7.8	4.70	-0.686
\mathbf{Sb}	8.6	4.56	-13.3
Sn	10.0	4.35	-3.68
Bi	10.4	4.36	-36.0
Ga	10.4	4.25	-2.09
Zn	10.5	4.30	-1.45
Ag	11.0	4.30	-2.48
In	11.3	4.08	-1.61
\mathbf{Pb}	11.4	4.18	-3.11
Tl	11.5	4.02	-6.13
Cd	11.6	4.12	-2.59
Hg	12.3	4.50	-4.21

Table 1. HER exchange currents, work functions, and molar magnetic susceptibilities for diamagnetic metal electrodes

checked by plotting the exchange current versus the molar magnetic susceptibility of electrodes with the same work function. Ag, Zn, and Mo all have the same work function of 4.3 eV. The negative log exchange currents versus molar magnetic susceptibilities for Ag, Zn, and Mo are plotted in Figure 4; there is a linear correlation of $R^2 = 0.9967$ with slope $= -(2.6_3 \pm 0.1_5) \times 10^9$ decades $i_0/10^{-10}$ cm³mol⁻¹ and intercept $= 10.2 \pm 0.1$ decades i_0 .

Values for negative log exchange current, work function, and molar magnetic susceptibility are listed in Tables 1 and 2 for all elements plotted in Figure 3. The paramagnetic/ferromagnetic line has slope $-6.4_4 \pm 0.2_4$ decades i_0/eV and intercept $35._4 \pm 1._1$ decades i_0 with R² 0.9787. The diamagnetic line has slope $-6.5_6 \pm 0.5_6$ decades i_0/eV and intercept $38._5 \pm 2._4$ decades i_0 with R² 0.9317. For elements with the same work function, a paramagnetic element has an exchange current $3._1 \pm 1._6$ orders of magnitude larger than that of a diamagnetic element.



Figure 3. Trasatti data replotted with attention to magnetic properties of the metals. Data falls on two parallel lines. One consists of ferromagnetic (blue triangles) and paramagnetic (red squares) metals. The other consists of the diamagnetic metals (green diamonds). The paramagnetic/ferromagnetic line has slope $-6.4_4 \pm 0.2_4$ decades i_0/eV and intercept $35._4 \pm 1._1$ decades i_0 with R² 0.9787. The diamagnetic line has slope $-6.5_6 \pm 0.5_6$ decades i_0/eV and intercept $38._5 \pm 2._4$ decades i_0 with R² 0.9317. $\Delta \log i_0 = 3._1 \pm 1._6$.



Figure 4. Plot of log exchange current $i_0 \text{ (mA/cm}^2)$ versus molar magnetic susceptibility $\chi_m (10^{-10} \text{ cm}^3/\text{mol})$ for metal electrodes with the same work function $\phi = 4.3 \ eV$. Regression analysis yields slope $-(2.6_3 \pm 0.1_5) \times 10^9$ decades $i_0/10^{-10} \text{ cm}^3 \text{mol}^{-1}$, intercept 10.2 ± 0.1 decades i_0 , and $\mathbb{R}^2 0.9967$. Ag and Zn are diamagnetic, and Mo is paramagnetic.

Metal	$-\log i_0 (\mathrm{A/cm^2})$	Φ (eV)	$\chi_m \; (\times 10^{-10} \; {\rm cm}^3/{\rm mol})$
Pt	3.0	5.03	23.8
Re	3.0	4.95	8.57
Pd	3.1	5.01	69.9
$\mathbf{R}\mathbf{h}$	3.5	4.99	13.6
Ir	3.6	4.97	4.42
Os	4.1	4.83	1.10
Ru	4.2	4.80	5.46
Ni	5.25	4.73	
Co	5.3	4.70	
Fe	5.6	4.65	
W	6.4	4.55	7.17
Cr	7.0	4.40	23.1
Mo	7.3	4.30	11.2
Al	8.0	4.19	2.10
Ti	8.3	4.10	19.2
Nb	8.4	4.20	26.1
Ta	8.5	4.22	19.4
Mn	10.9	3.90	66.5

Table 2. HER exchange currents, work functions, and molar magnetic susceptibilities for paramagnetic and ferromagnetic metal electrodes

This leads to a question: Given its dependence on magnetic properties, can we catalyze HER at diamagnetic electrodes by introduction of localized magnetic fields at the electrode surface with magnetic microparticles?

2.2 Methods and Materials

Glassy carbon, gold, platinum, and mercury electrodes are modified with composite films of chemically inert, magnetic microparticles suspended in a Nafion^{\mathbb{R}} film and magnetized with an external NdFeB ring magnet. Analysis is done by linear scan voltammetry in a three electrode setup. Controls of unmodified electrodes, electrodes modified with Nafion only films, and electrodes modified with demagnetized particles are analyzed for comparison. The magnetic particles, film preparation, magnetization, and electrochemical analysis are described below. All methods and materials are the same for glassy carbon, platinum, and gold. Slightly different methods and materials are required to evaluate mercury electrodes because mercury is a liquid at room temperature and forms alloys.

2.2.1 Magnetic Microparticles

Commercially produced magnetic microparticles, called SiMag-Cx, are purchased from Chemicell, GmbH. The SiMag-Cx particles consist of a maghemite (Fe₂O₃) core with an alkyl-siloxane coating that renders them chemically inert. The core particles are 1 μ m in diameter. Effectively, SiMag-Cx microparticles serve as non-porous magnetic silica particles. Three types of coatings with different lengths of alkyl chains (number of carbons = x = 1, 3, or 8) are used. SiMag-C1 particles have a methyl-siloxane coating, SiMag-C3 particles have a propyl-siloxane coating, and SiMag-C8 particles have an octyl-siloxane coating. Figure 6 is a schematic representation of a SiMag-C3 particle. Maghemite is paramagnetic and able to sustain a permanent magnetic field. Once magnetized, cores of >1 μ m diameter are of sufficient size to sustain a permanent magnetic field in the absence of an applied field.

The volumetric magnetic susceptibility of Nafion only and the particles suspended in Nafion are measured in a Gouy balance. Table 3 lists the volumetric magnetic susceptibility of the particles in cgs and μ B (Bohr magneton) and Figure 5 plots the volumetric magnetic susceptibility of the SiMag-Cx particles versus the number of carbons in the alkyl-siloxane coating. To analyze demagnetized particles as a control,

# Carbons	$\chi_v ~(\mathrm{cgs})$	$\chi_v \ (\mu B)$
8	$(8.7_8 \pm 0.1_2) \times 10^{-6}$	1.44 ± 0.02
3	$(1.02 \pm 0.08) \times 10^{-5}$	$1.8_5 \pm 0.1_4$
1	$(1.61 \pm 0.08) \times 10^{-5}$	$2.4_8 \pm 0.1_2$

Table 3. Number of carbons in alkyl-siloxane coatings and volumetric magnetic susceptibility of SiMag-Cx particles

the particles are vortexed (see the film preparation subsection for more details). Due to extensive mechanical stress, sustained (≥ 2 hours) vortexing demagnetizes the particles. Thus, unless the particles are premagnetized prior to composite formation, they do not provide a magnetic field.

2.2.2 Film Preparation

All electrodes are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. Nafion[®] (DuPont) is a perfluorosulfonic acid polymer; it has a Teflon[®] fluorocarbon backbone with sulfonic acid side chains. Cations (e.g., protons) can exchange between the sulfonic acid sites in the polymer film and the acidic electrolyte solution. Electrodes are modified with either a Nafion only film or a composite of alkyl-siloxane coated maghemite microparticles (SiMag-Cx) in Nafion where the microparticles are either demagnetized prior to composite formation or magnetized while the composite film dried. Nafion films are made by casting an aliquot of Nafion solution (5 % w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface, then allowing the casting



Figure 5. Plot of the volumetric magnetic susceptibility of SiMag-Cx particles versus the number of carbons in the alkyl-siloxane coating. Error bars are standard deviation for triplicate measurements.



Figure 6. Representation of SiMag-C3 magnetic microparticle. A maghemite core is coated in propyl-siloxane molecules (only one pictured). Coverage is so complete that the particles are chemically inert; effectively non-porous magnetic silica particles. The length of the alkyl chain in the coating (methyl, propyl, or octyl) changes the magnetic susceptibility of the particle.

solvents to evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. The aliquot volume is calculated so that the film will be $\sim 7 \ \mu m$ thick when immersed in the acidic solution [31]. For the platinum electrode with area 0.452 cm², this is 5.0 μL .

To prepare magnetized composites of Nafion and SiMag-Cx particles, an aqueous suspension of particles is mixed in a microcentrifuge tube with the Nafion solution in a 1:20 volumetric ratio to yield a 6 % w/w loading of particles in the dry film. Immediately before casting the film, the solution is briefly vortexed (5 seconds) to ensure complete and even suspension of the particles and Nafion. An aliquot of the Nafion + SiMag-Cx solution is cast onto the surface of the electrode held in a stand so that the planar electrode surface faces up, parallel to the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. As shown in the diagram in Figure 7, a NdFeB ring magnet (o.d. = 7.6 cm, i.d. = 3.8cm, 1.3 cm height) is placed around the electrode as the film dries such that the electrode is in the center of the ring and the electrode surface is in the same plane as the magnet. The film air dries for ≥ 24 hours. The ring magnet is removed after the first hour of drying. A photograph of the Teflon cylinder with ring magnet drying setup is provided in Figure 8. Again, the aliquot volume is calculated so that the film will be $\sim 7 \ \mu m$ thick when immersed in acidic solution. On visual inspection, the Nafion and Nafion + SiMag-Cx films look the same.

To prepare composites of Nafion + demagnetized SiMag-Cx particles, the same



Figure 7. Diagram of casting magnetization procedure. A NdFeB ring magnet is placed around the electrode for one hour while the cast film dries. Total drying time is 24 hours. SiMag-Cx particles are suspended in a Nafion film that is $\sim 7 \ \mu m$ thick when immersed in acidic solution.

Label	Film Composition	Magnetization State
U		
N	Nafion only	
C1	Nafion + SiMag-C1	magnetized
C3	Nafion $+$ SiMag-C3	magnetized
C8	Nafion $+$ SiMag-C8	magnetized
xC1	Nafion $+$ SiMag-C1	demagnetized
xC3	Nafion $+$ SiMag-C3	demagnetized
xC8	Nafion $+$ SiMag-C8	demagnetized

Table 4. Data labels for film composition and magetization state of various modified electrodes

procedure described above is followed, except after the Nafion + SiMag-Cx solution is made, it is vortexed continuously for ≥ 2 hours and the ring magnet is not employed while the film dries. Sustained (≥ 2 hours) vortexing is thought to demagnetize the particles due to extensive mechanical stress. Data are also collected for unmodified electrodes.

Henceforth, data for unmodified electrodes will be referred to by the label U, data for electrodes modified with Nafion films will be referred to by the label N, data for electrodes modified with magnetized Nafion + SiMag-C1 composites will be referred to by the label C1, and data for electrodes modified with Nafion + demagnetized SiMag-C1 composites will be referred to by the label xC1. Data labels for the Nafion + SiMag-C3 and Nafion + SiMag-C8 composites will follow the same pattern (C3, xC3, C8, xC8). Refer to Table 4 for a summary of these labels.

2.2.3 Linear Scan Voltammetry

Linear scan voltammetry is an electrochemical measurement in which a linearly



Figure 8. Photograph of drying setup for film preparation. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. If the film is magnetized, a NdFeB ring magnet is placed around the electrode in the same plane as the surface.

varying potential (V) is applied to the electrode. The potential sweeps from the initial potential to the final potential at a fixed scan rate v (V/s), and the current (A) is measured as a function of the potential. The standard potential E^0 for the redox probe is typically between the initial and final potential.

An aqueous solution of 0.10 M nitric acid (HNO₃, Fisher Chemical) is prepared and sparged with nitrogen gas for 20 minutes. The H⁺ of the HNO₃ is the redox probe as well as HNO₃ being the electrolyte. A three electrode setup is used. The working electrodes are either glassy carbon (Pine Instruments, $A = 0.452 \text{ cm}^2$), gold (CH Instruments, $A = 0.126 \text{ cm}^2$), or platinum (Pine Instruments, $A = 0.452 \text{ cm}^2$); the counter electrode is platinum mesh; and the reference electrode is saturated calomel (SCE), which has a standard potential of +0.241 V vs NHE. Linear scan voltammetry is performed (CH Instruments 760B potentiostat) at scan rate 50 mV/s from 0 V to -1.0 V vs. SCE. Films equilibrate for ≥ 24 hours in the solution before a potential is applied and reequilibrate for one hour between each subsequent scan. A minimum of three films of each type are cast and analyzed in triplicate.

2.2.4 Mercury Electrode Setup

Mercury is a liquid metal at room temperature, so a different setup and different materials are needed than for the other, solid electrodes. A 1000 μ L pipette tip is used as the cell. A mercury (Aldrich) pool sits in the bottom of the pipette tip. A platinum wire is inserted in the bottom opening of the tip to provide conduction between the mercury and the potentiostat alligator clip outside the cell. The wire and tip are wrapped in Teflon tape to seal the bottom of the cell. A Ag/AgSO₄



Figure 9. Diagram of mercury HER setup. A mercury pool sits in the bottom of a 1000 μ L pipette tip. A platinum wire provides conduction between the mercury and an alligator clip outside the cell. A Ag/AgSO₄ reference electrode and Pt mesh counter electrode are used.

(+0.713 V vs NHE) wire reference electrode is used because the SCE is too large to fit in the cell. The Ag/AgSO₄ electrode is made by holding a silver wire at a potential of 1.5 V in 1 M H₂SO₄ until a AgSO₄ layer forms (approximately one minute). A platinum mesh counter electrode made from a coiled wire is the counter electrode. A solution of 0.10 M sulfuric acid (H₂SO₄) is prepared instead of another acid because mercury tends to adsorb other ions such as nitrate and chloride. The exposed area of the mercury electrode is calculated to be 0.283 cm² using the height filled by the pool and the formula for the area of the base of a cone. A fresh mercury pool is used in each experiment. An unmodified mercury electrode, a mercury electrode modified with a Nafion film, and a mercury electrode modified with a magnetized Nafion + SiMag-C1 composite are evaluated. The films are cast within a dry cell on top of the mercury pool and dried \geq 24 hours. Films are magnetized by placing a NdFeB ring magnet around the pipette in the plane of the mercury pool surface for the first hour of drying.

2.3 Results and Discussion

Magnetic field effects on HER at glassy carbon, platinum, gold, and mercury metal electrodes are evaluated by linear scan voltammetry.

2.3.1 Glassy Carbon

Figure 10a is an overlay of 50 mV/s voltammograms for hydrogen evolution reaction at glassy carbon electrodes modified with no film, a Nafion film, a magnetized Nafion + SiMag-C1 composite, a magnetized Nafion + SiMag-C3 composite, and

a magnetized Nafion + SiMag-C8 composite. Figure 10b is an overlay of 50 mV/s voltammograms for hydrogen evolution reaction at glassy carbon electrodes modified with no film, a Nafion film, a Nafion + demagnetized SiMag-C1 composite, a Nafion + demagnetized SiMag-C3 composite, and a Nafion + demagnetized SiMag-C8 composite. There is a statistically significant decrease in the HER overpotential at electrodes modified with the magnetized Nafion + SiMag-Cx composites compared to electrodes modified with Nafion films. The rises are also steeper, indicating faster electron transfer kinetics. Demagnetized films have higher overpotentials than Nafion, consistent with slower kinetics with demagnetized electrodes. The current is higher for Nafion as compared to unmodified electrodes and is ascribed to higher proton concentration in Nafion as compared to solution. Analysis focuses on the potential at a low current density where electron transfer effects dominate mass transport effects. Figure 11 plots the change in HER overpotential at magnetic composite modified electrodes relative to Nafion (ΔE (V) from N) at 0.4 mA/cm² versus the volume magnetic susceptibility of the SiMag-Cx particles. There is a linear correlation. Regression analysis yields slope $(1.18 \pm 0.003) \times 10^4 \text{ V}/\mu \text{cgs}$, intercept $(2.9_4 \pm 3.2) \times 10^{-2}$ V, and R² 0.9987. Table 5 lists volume magnetic susceptibilities for the particles in each composite film and the ΔE (V) from N at 0.4 mA/cm² and the ΔE (V) from N at 0.1 mA/cm² for each modified electrode. There is also a linear correlation for the change in HER overpotential at magnetic composite modified electrodes relative to Nafion (ΔE (V) from N) at 0.1 mA/cm² versus the volume magnetic susceptibility of the SiMag-Cx particles, for which regression analysis yields slope $(0.655 \pm 0.04_8) \times 10^4 \text{ V}/\mu\text{cgs}$, intercept $(2.85 \pm 5.00) \times 10^{-3} \text{ V}$,



Figure 10. Overlays of 50 mV/s linear scan voltammograms for hydrogen evolution at unmodified glassy carbon electrodes (U, yellow long dashed line), and glassy carbon electrodes modified with a Nafion film (N, purple long dashed line), Nafion + SiMag-C1 composite (C1, blue solid line), Nafion + SiMag-C3 composite (C3, red dotted line), and Nafion + SiMag-C8 composite (C8, green dashed line). Films containing magnetized particles are magnetized in overlay a) and demagnetized particles in overlay b).



Figure 11. Plot of change in overpotential ΔE (V) from Nafion at 0.4 mA/cm² versus magnetic susceptibility of the SiMag particles from glassy carbon HER voltammograms above. Regression analysis yields slope $(1.180 \pm 0.003) \times 10^4 \text{ V}/\mu \text{cgs}$, intercept $(2.9_4 \pm 3.2) \times 10^{-2} \text{ V}$, and R² 0.9987. Error bars are standard deviation.

Table 5. Volume magnetic susceptibility and potentials at low current density for HER at modified glassy carbon electrodes (n = 3)

Film	$\chi_v (cgs)$	$\Delta E (V)$ from N @ 0.10 mA/cm ²	ΔE (V) from N @ 0.40 mA/cm ²
C1	1.61×10^{-5}	$0.10_4 \pm 0.01_3$	$0.19_1 \pm 0.01_9$
C3	1.02×10^{-5}	$0.076_0 \pm 0.008$	$0.12_3 \pm 0.02_2$
C8	$8.7_8 \times 10^{-6}$	$0.060_0 \pm 0.003$	$0.11_1 \pm 0.02_8$
Ν	-1.00×10^{-7}		

and R^2 0.9893. The overpotential decreases with the magnetic susceptibility of the magnetized particles. For C1 particles, the overpotential is decreased by 200 mV relative to Nafion only films at 0.4 mA/cm². When the particles are demagnetized, the overpotential is around 50 mV larger for all composites as compared to Nafion at 0.4 mA/cm².

2.3.2 Gold

There is also a decrease in the overpotential of HER at gold electrodes when modified with micromagnets. Gold electrodes modified with N, C3, C8, xC1, and xC8 are evaluated. Figure 12 is an overlay of 50 mV/s voltammograms for hydrogen evolution reaction at gold electrodes modified with a Nafion film, a magnetized Nafion + SiMag-C3 composite, a magnetized Nafion + SiMag-C8 composite, a Nafion + demagnetized SiMag-C1 composite, and a Nafion + demagnetized SiMag-C8 composite. Table 6 lists volume magnetic susceptibilities for the particles in each composite film and the ΔE (V) from Nafion at two low current densities, 0.10 mA/cm^2 and 1.25 mA/cm^2 , for each modified electrode.



Figure 12. Overlay of 50 mV/s voltammograms for hydrogen evolution reaction at gold electrodes modified with a Nafion film (N, purple medium dashed line), Nafion + magnetized SiMag-C3 composite (C3, red dotted line), Nafion + magnetized SiMag-C8 composite (C8, green short dashed line), Nafion + demagnetized SiMag-C1 composite (C1, blue solid line), and Nafion + demagnetized SiMag-C8 composite (C8, red long dashed line).

Table 6. Volume magnetic susceptibility and potentials at various current densities for HER at modified gold electrodes (n = 3)

Film	$\chi_v (cgs)$	ΔE (V) from N @ 0.10 mA/cm ²	ΔE (V) from N @ 1.25 mA/cm ²
C3	1.02×10^{-5}	$0.056_7 \pm 0.003_6$	$0.03_{25} \pm 0.01_{45}$
C8	$8.7_8 \times 10^{-6}$	$0.04_{25} \pm 0.01_{39}$	$0.01_{83} \pm 0.01_{70}$
Ν	-1.00×10^{-7}		
xC1		$0.00_{253} \pm 0.01_{270}$	$-0.020_9 \pm 0.001_3$
xC8		$0.01_{50} \pm 0.02_{94}$	$-0.024_6 \pm 0.003_7$

Table 7. Volume magnetic susceptibility and potentials at various current densities for HER at modified platinum electrodes (n = 3)

Film	$\chi_v (cgs)$	ΔE (V) from N @ 0.10 mA/cm ²	ΔE (V) from N @ 0.40 mA/cm ²
C1	1.61×10^{-5}	$0.025_0 \pm 0.001$	$0.025_0 \pm 0.001$
C3	$1.02 imes 10^{-5}$	$0.023_0 \pm 0.001$	$0.022_7 \pm 0.001$
C8	$8.7_8 imes10^{-6}$	$0.023_3 \pm 0.002$	$0.021_3 \pm 0.001$
N	-1.00×10^{-7}		

2.3.3 Platinum

Platinum is paramagnetic and already has fast, reversible hydrogen kinetics. A minimal statistical difference is observed in the HER overpotential (< 25 mV) between Nafion only and magnetized composite modified electrodes. There is no statistical difference between the demagnetized composites and Nafion only. Platinum electrodes modified with N, C1, C3, and C8 are evaluated. Figure 13 is an overlay of 50 mV/s voltammograms for hydrogen evolution reaction at platinum electrodes modified with no film, a Nafion film, a magnetized Nafion + SiMag-C1 composite, a magnetized Nafion + SiMag-C3 composite, and a magnetized Nafion + SiMag-C8 composite. Table 7 lists volume magnetic susceptibilities for the particles in each composite and the ΔE (V) from Nafion at low current densities of 0.1 mA/cm² and 0.4 mA/cm² for each modified electrode. At higher current densities (> 5 mA/cm²), there is some evidence of decreased overpotential with magnetized C1 and C3 particles.



Figure 13. Overlay of 50 mV/s voltammograms for hydrogen evolution reaction at platinum electrodes modified with no film (U, yellow long dashed line), a Nafion film (N, purple medium dashed line), Nafion + SiMag-C1 composite (C1, blue solid line), Nafion + SiMag-C3 composite (C3, red dotted line), and Nafion + SiMag-C8 composite (C8, green short dashed line). Inset is enlargement of -0.25 to -0.35 V portion of voltammogram.

Film	$\chi_v ~({ m cgs})$	$E (V) @ 0.10 mA/cm^2$	ΔE (V) from N @ 0.10 mA/cm ²
C1	1.61×10^{-5}	$-0.8_{63} \pm 0.2_{11}$	$0.4_{38} \pm 0.3_{81}$
Ν	-1.00×10^{-7}	$-1.3_{01} \pm 0.3_{18}$	
U		$-1.2_{42} \pm 0.3_{04}$	$0.0_{59} \pm 0.4_{40}$

Table 8. Volume magnetic susceptibility and potentials at various current densities for HER at modified mercury electrodes (n = 3)

2.3.4 Mercury

Mercury electrodes modified with U, N, and C1 are evaluated. Figure 14 is an overlay of 50 mV/s voltammograms for hydrogen evolution reaction at mercury electrodes modified with no film, a Nafion film, and a magnetized Nafion + SiMag-C1 composite. Table 8 lists volume magnetic susceptibilities for the particles in each composite film, the potential at which low current density 0.1 mA/cm² is reached, and the ΔE (V) from N at 0.1 mA/cm² for each modified electrode. The mercury pool electrode is difficult to replicate without large variations, and the sides of the pipette wall attract Nafion, making it difficult to cast uniform films. However, there still seems to be a decrease in overpotential between the magnetized composite modified electrode and the Nafion modified electrode with a 72 % confidence level based on a t-test to compare two means.

2.4 Conclusions

A decrease in the hydrogen evolution overpotential is observed for magnetically modified glassy carbon, gold, mercury, and p-Si electrodes. Glassy carbon is a poor electrode for hydrogen evolution. On modification with magnetic composites, the



Figure 14. Overlay of 50 mV/s voltammograms for hydrogen evolution reaction at mercury electrodes modified with no film (U, yellow long dashed line), a Nafion film (N, purple medium dashed line), and magnetized Nafion + SiMag-C1 composite (C1, blue solid line).

-					
Ele	ctrode	E^0 (V)	Overpotential of N (V)	$E(V) @ 0.10 mA/cm^2$	ΔE (V) from N
Glass	y Carbon	-0.241	$0.26_6 \pm 0.02_1$	$-0.52_0 \pm 0.01_9$	$0.19_1 \pm 0.01_9$
	Gold	-0.241	$0.29_1 \pm 0.01_2$	$-0.47_5 \pm 0.03_6$	$0.056_7 \pm 0.003_6$
Me	ercury	-0.713	$0.60_1 \pm 0.05_0$	$-0.8_{63} \pm 0.2_{11}$	$0.4_{38} \pm 0.3_{81}$
Pla	tinum	-0.241	$0.075_7 \pm 0.003_0$	$-0.29_2 \pm 0.01_2$	$0.0025_0 \pm 0.0001$
	p-Si		$0.40_0 \pm 0.02_9$	$-0.10_6 \pm 0.05_1$	$0.27_0 \pm 0.05_0$

Table 9. Comparison of change in overpotential measured at 0.4 mA/cm^2 for HER at various magnetized C1 modified electrodes relative to Nafion (n = 3)

overpotential for the onset of H_2 evolution decreases. At any potential where HER occurs on glassy carbon, current is higher under magnetic modification. The onset of H_2 evolution occurs at more positive potentials as the magnetic susceptibility of the microparticles increases. Platinum is paramagnetic and already has fast, reversible hydrogen kinetics. Almost no statistical difference in the HER overpotential between electrodes modified with magnetized composites and Nafion films is observed at low current densities.

Table 9 lists the average change in overpotential for magnetized C1 modified p-Si, glassy carbon, gold, and mercury electrodes. Data for p-Si included in Table 9 are from work by Heung Chan Lee [8]. Control electrodes modified with demagnetized particles have larger overpotentials than electrodes modified with Nafion only. Addition of magnetic microparticles impacts the onset potential and current at a given potential for the HER at diamagnetic electrodes so that the rate is faster and more similar to Pt electrodes. An average decrease in overpotential of about 70% at diamagnetic electrodes is observed. Demagnetized particles do not have the same effect as magnetized particles. This indicates that magnetization of the particles is an important step. The Trasatti data suggest the effects from addition of magnetic fields are electron transfer related.

CHAPTER 3

MAGNETIC EFFECT VERIFICATION

There is clear evidence that magnetization increases the currents for academically interesting redox probes at magnetic composites relative to Nafion only films. Here, evidence is provided by examination of demagnetized and magnetized composites. Two questions are investigated: Do the magnetic fields affect mass transport and/or electron transfer? What role does magnetization of the microparticles play?

3.1 Introduction and Theory

From the Trasatti plot (Figure 3 in Chapter 2), magnetic fields affect electron transfer rates. But, many groups study mass transport effects of external magnetic fields, such as magnetohydrodynamics and magnetic field gradients. Under magnetohydrodynamics, magnetic fields generate forces on ions in condensed fluids that induce fluid flow (convection). Gradient fields interact with paramagnetic species in a fluid to induce currents associated with motion of the paramagnetic species into the field [32,33]. Here, introduction of magnetic microparticles into the microstructured ion exchange polymer Nafion is shown to impact electron transfer rather than mass transport.

The Leddy group has examined fundamental effects of magnetic modification on transition metals; the effects are well-documented [3–10]. Results are consistent with microparticle magnetization generating the observed enhancements in current and reductions in overpotentials. A clear demonstration that magnetization is the critical key to enhanced electrocatalysis is presented.

3.1.1 Self Exchange

The apparent diffusion coefficient D_{app} of outer sphere, transition metal redox probes in Nafion is measured voltammetrically from peak currents. The apparent diffusion coefficient is enhanced by a self exchange reaction between the halves of the redox couple that occurs in the bulk Nafion phase. The self exchange reaction is a homogeneous electron transfer process.

Two different oxidation states of the same chemical species $(M^n \text{ and } M^{n\pm 1})$ transfer an electron rather than exchange positions by physical motion. The reactants and products are the same, but they undergo an effective spatial switch through exchange of an electron as in Equation 5.

$$M^n + M^{n\pm 1} \rightleftharpoons M^{n\pm 1} + M^n \tag{5}$$

The Dahms Ruff equation describes the apparent diffusion coefficient D_{app} (cm²/s) in terms of the physical diffusion coefficient D_{mt} (cm²/s) due to mass transport (physical motion), the self exchange rate k_{ex} (s⁻¹), the distance of closest approach between two species δ (cm), and the probe concentration c^* (mol/cm³) [34].

$$D_{app} = D_{mt} + \frac{\delta^2 k_{ex} c^*}{6} \tag{6}$$

The hopping diffusion coefficient $D_{hopp} = \frac{\delta^2 k_{ex} c^*}{6}$ measures the effectiveness of the hopping rate and increases with k_{ex} . The physical diffusion coefficient D_{mt} reflects why Nafion films must equilibrate in solution for so long (≥ 24 hours) before

measurement. D_{mt} is on the order of 10^{-10} cm²/s, so extraction of the probe into Nafion is slow. But, during electrochemical analysis, apparent diffusion is fast because the probe does not move but just transfers electrons.

3.2 Methods and Materials

Platinum electrodes are modified with composites of chemically inert, magnetic microparticles suspended in Nafion^{\mathbb{R}}. Premagnetized and demagnetized particles are compared, as well as unmagnetized and magnetized composite films. Analysis is done by cyclic voltammetry in a three electrode setup. Measurements are taken both in the absence of an external magnetic field and in the presence of an external magnetic field. Controls of unmodified electrodes and electrodes modified with Nafion only films are analyzed for comparison. The film preparation, magnetization, and electrochemical analysis are described below.

3.2.1 Film Preparation

All electrodes are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. Electrodes are modified with either a Nafion film or a composite of methyl-siloxane coated maghemite microparticles (SiMag-C1, volume magnetic susceptibility 16.1 ± 0.8 μ cgs) in Nafion where 1) the microparticles are either demagnetized or premagnetized prior to composite formation and 2) the composite film is either dried in the absence of an external magnetic field or dried in the presence of a magnetic field. Nafion films are made by casting 5.0 μ L of Nafion solution (5 % w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface, then allowing the casting solvents to evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 5.0 μ L, the density of Nafion in acidic solution, and the electrode area, the film will be ~7 μ m thick when immersed in the acidic solution [31].

To prepare composites of Nafion and SiMag-C1 particles, an aqueous suspension of particles (50 mg/mL) is mixed in a microcentrifuge tube with the Nafion suspension in a 1:20 volumetric ratio to yield a 6 % w/w loading of particles in the dry film. Immediately before casting the film, the composite solution is briefly vortexed (5 seconds) to ensure complete and even suspension of the particles. 5 μ L of the Nafion + SiMag-C1 solution is cast onto the electrode surface. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. The film air dries for \geq 24 hours. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow.

To prepare composites of Nafion and premagnetized SiMag-C1 particles, the Nafion + SiMag-C1 solution sits in a microcentrifuge tube in the center of a NdFeB ring magnet for one hour. Before the premagnetization, the particles are suspended in an even distribution in the solution from vortexing. After premagnetization, all particles have aggregated in the bottom of the tube. Brief vortexing (5 seconds) in the microcentrifuge tube resuspends the microparticles without disturbing individual



Figure 15. Photograph of setup for control experiment in which a NdFeB ring magnet is placed around the beaker to provide an external magnetic field, in the same plane as the electrode surface. The platinum working electrode is labelled WE, the platinum mesh counter electrode is labelled CE, and the SCE reference electrode is labelled RE.

particle magnetization.

To prepare composites of Nafion and demagnetized SiMag-C1 particles, the Nafion + SiMag-C1 solution is vortexed in the microcentrifuge tube for ≥ 2 hours. Sustained vortexing is thought to demagnetize the particles due to extensive mechanical stress. Magnetized composite films are prepared by placing them in the presence of an external magnetic field for the first hour of drying. As shown in the diagram in Figure 7, a NdFeB ring magnet (o.d. = 7.6 cm, i.d. = 3.8 cm, 1.3 cm height) is placed around the electrode such that the electrode is in the center of the ring and the electrode surface is in the same plane. A Teflon cylinder is still placed around the electrode to protect it from dust but still allow air flow, and the film air dries for ≥ 24 hours. The ring magnet is removed after the first hour. A photograph of the Teflon cylinder with ring magnet drying setup is provided in Figure 8. On visual inspection, the Nafion only films and all Nafion + SiMag-C1 films look the same. Data are also collected for unmodified electrodes.

Henceforth, data for unmodified electrodes will be referred to by the label U; data for electrodes modified with Nafion films will be referred to by the label N; data for electrodes modified with Nafion + demagnetized SiMag-C1 composites will be referred to with the label D; and data for electrodes modified with Nafion + premagnetized SiMag-C1 composites will be referred to with the label P. If the composite was magnetized with a ring magnet while drying, an F is added to the label. If the composite was not magnetized, an x is added to the label. Thus, for a composite film dried in a ring magnet and cast from a mixture of Nafion + demagnetized SiMag-C1particles, the full label would be DF. Refer to Table 10 for a

Label	Film	Particle Magnetization State	Film Magnetized?
U			
N	Nation only		No
Dx	Nafion $+$ SiMag-C1	demagnetized	No
DF	Nafion + SiMag-C1	demagnetized	Yes
Px	Nafion $+$ SiMag-C1	premagnetized	No
PF	Nafion + SiMag-C1	premagnetized	Yes

Table 10. Data labels for film composition and magetization state of the particles and film for various modified electrodes

summary of all labels.

3.2.2 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical measurement in which a changing potential (V) is applied to the electrode. The potential sweeps from the initial potential to the final potential, then back to the initial potential at a fixed scan rate v (V/s), and the current (A) is measured as a function of the potential.

An aqueous solution of 0.640 mM tris(bipyridine) ruthenium(II) chloride $(\operatorname{Ru}[\operatorname{bpy}]_3^{2+}, \operatorname{Sigma})$ and 0.10 M nitric acid (HNO₃, Fisher Chemical) is prepared and sparged with N₂ (g). A three electrode setup is used. The working electrode is platinum (Pine Instruments, $A = 0.452 \text{ cm}^2$), the counter electrode is platinum mesh, and the reference electrode is saturated calomel (SCE), which has a standard potential of +0.241 V vs NHE. Cyclic voltammetry is performed (CH Instruments 760B potentiostat) at scan rates 20, 50, 100, and 200 mV/s in a randomized order from 0.7 V to 1.3 V to 0.7 V vs. SCE. Films equilibrate for ≥ 24 hours in the solution before a potential is applied and reequilibrate for one hour between each subsequent scan. A minimum of three films of each type are cast and analyzed in

triplicate. Measurements are made in the absence of an external magnetic field and then repeated in the presence of an external magnetic field. The external magnetic field is provided by a NdFeB ring magnet seated around the beaker in the plane of the electrode surface as shown in the photograph in Figure 15.

3.3 Results and Discussion

Figure 16 is an overlay of 200 mV/s cyclic voltammograms of $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ at an unmodified electrode (U) and electrodes modified with a Nafion film (N), a magnetized Nafion + demagnetized SiMag-C1 composite (DF), a magnetized Nafion + premagnetized SiMag-C1 composite (PF), a nonmagnetized Nafion + demagnetized SiMag-C1 film (Dx), and a nonmagnetized Nafion + premagnetized SiMag-C1 composite (Px). All measurements in Figure 16 are made in the absence of an external magnetic field. Table 11 lists the percent increase in current between the composite modified electrodes and Nafion modified electrode.

Dx (particles are demagnetized and the composite film is not magnetized during drying) currents are almost the same as N (Nafion film), but DF (composite of demagnetized particles is magnetized during drying) currents are larger than N. Px and PF (premagnetized particles) currents are even larger. Electrodes modified with premagnetized particle composites have higher currents than demagnetized particle composites. Film magnetization lines up the particles in vertical columns within the film, resulting in a lower percentage of particles being present on the electrode surface. Previous group members saw that the magnetic effect scales with the percent loading of particles, so this makes sense that PF has lower currents than



Figure 16. Overlay of 200 mV/s cyclic voltammograms of $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ at an unmodified electrode (U, black solid line) and electrodes modified with a Nafion film (N, red dashed line), a magnetized Nafion + demagnetized SiMag-C1 composite (DF, green solid line), a magnetized Nafion + premagnetized SiMag-C1 composite (PF, blue solid line), a nonmagnetized Nafion + demagnetized SiMag-C1 composite (Dx, green dashed line), and a nonmagnetized Nafion + premagnetized SiMag-C1 composite (Px, blue dashed line).
Electrode	i _{pf} @ 200 mV/s	% Increase in Current	% Increase in Current
Label	(μA)	from N @ 200 mV/s	from N @ All Scan Rates
U	-130 ± 4	-77 ± 3	-81 ± 3
N	-570 ± 20		
PF	-800 ± 10	40 ± 1	72 ± 26
DF	-720 ± 20	26 ± 1	43 ± 11
Px	-890 ± 90	56 ± 6	95 ± 32
Dx	-600 ± 50	5 ± 1	4 ± 2

Table 11. Comparison of percent change in current in the absence of an external magnetic field between electrodes modified with Nafion films and Nafion + SiMag-C1 compositess with different magnetization states (n = 3)

Px. The lack of change between Dx and N rules out the possibility that a chemical interaction causes the observed effects; the effect does not happen unless there is a magnetization step. Therefore, the effect is due to the presence of local magnetic fields. Percent loadings are well below the percolation limit.

T-tests to compare two means yield 98.5 % confidence that Px differs from N; $99.9_8 \%$ confidence that PF differs from N; $99.9_6 \%$ confidence that DF differs from N; and 75.6 % confidence that Dx differs from N. There is 99.6 % confidence that PF differs from DF; 99.1 % confidence that Px differs from Dx; 88.4 % confidence that PF differs from Px; and 96.1 % confidence that DF differs from Dx.

Figure 17a is an overlay of 200 mV/s cyclic voltammograms for an unmodified electrode in the absence and presence of an external magnetic field. Figure 17b is an overlay of 200 mV/s cyclic voltammograms for an electrode modified with a Nafion film in the absence and presence of an external magnetic field. The external magnetic field has an effect at the unmodified electrode, increasing the current by ~65 %. However, there is no significant effect of the external magnet



Figure 17. Overlays of 200 mV/s cyclic voltammograms for $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ measured in the absence of an external magnetic field (solid black line) and in the presence of an external magnetic field (dashed red line). a) Data for an unmodified platinum electrode; b) data for a platinum electrode modified with a Nafion film.



Figure 18. Overlays of 200 mV/s cyclic voltammograms for $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ measured in the absence of an external magnetic field (solid black line) and in the presence of an external magnetic field (dashed red line). Data for platinum electrodes modified with a) a nonmagnetized Nafion + demagnetized SiMag-C1 composite (Dx), b) a nonmagnetized Nafion + premagnetized SiMag-C1 composite (Px), c) a magnetized Nafion + demagnetized SiMag-C1 composite (DF), and d) a magnetized Nafion + premagnetized SiMag-C1 composite (PF).

on the Nafion modified electrode as the voltammograms are nearly superimposed. The enhanced currents at the unmodified electrode on application of the external magnetic field are consistent with enhanced transport of $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ and perhaps chloride by magnetohydrodynamics. For the Nafion film, the voltammograms are invariant on application of the external magnet during voltammetric measurements. In the microstructured Nafion film, the transport of $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ is not enhanced by magnetohydrodynamics. The water filled domains of Nafion are too small to allow the bulk fluid motion necessary to magnetohydrodynamic transport. Also, given the same peak splittings for Nafion with and without an external magnet, the external magnet does not impact the heterogeneous electron transfer rate or the homogeneous (electron hopping) electron transfer rate of Dahms and Ruff.

Figure 18 shows overlays for a magnetized Nafion + demagnetized SiMag-C1 composite (DF), a magnetized Nafion + premagnetized SiMag-C1 composite (PF), a nonmagnetized Nafion + demagnetized SiMag-C1 composite (Dx), and a nonmagnetized Nafion + premagnetized SiMag-C1 composite (Px) in the absence and presence of an external magnetic field. There is also no statistical effect by the external magnetic field on the composite modified electrodes. This is because there is a magnetohydrodynamic (mass transport) effect on the system, but it is negated when a Nafion film is present. Apparent diffusion of $\operatorname{Ru}[\operatorname{bpy}]_3^{2+}$ in Nafion occurs by self exchange, not by actual physical diffusion of molecules. Therefore, the effects seen from localized magnetic fields on microparticles are electron transfer related. The steeper rises observed for magnetically modified HER also indicate there is an effect on electron transfer kinetics. Trasatti data are also consistent with a magnetic effect on the electron transfer in formation of hydrogen gas from hydrogen ions in solution. In the presence of an external magnetic field, Dx current is slightly larger than in the absence of external magnetic field. The particles may become slightly magnetized by the ring magnet during the time period of analysis.

3.4 Conclusions

Mass transport effects from magnetic fields are precluded by the Nafion in the system. Apparent diffusion proceeds by self exchange; the redox molecules do not actually move but rather the electrons hop. Therefore, observed effects of decreased overpotential and enhanced current must be electron transfer related. Magnetizing the particles versus demagnetizing them greatly influences the magnitude of the effect. The particles are coated so they are chemically inert and loadings do not exceed the 15 % percolation limit. Thus, observed effects are due to the magnetic fields of the particles, not a chemical interaction or percolation.

CHAPTER 4

LANTHANIDE ELECTROCHEMISTRY

Voltammetric access to lanthanide ions is available in ionic liquids [21, 35] but not in common room temperature solvents. Here, lanthanide triflate compounds are electrochemically analyzed in acetonitrile at Nafion modified electrodes. The mechanism, potential shifts, simulations, and x-ray photoelectron spectroscopy are considered.

4.1 Background

The literature on lanthanide voltammetry is reviewed. How the electroanalysis of lanthanide compounds in common electrochemical solvents developed is described. X-ray photoelectron spectroscopy is reviewed.

4.1.1 Evolution of the Method

Lanthanides (referred to generally as Ln) are the rare earth elements group at the bottom of the periodic table, above the actinides, that have 4f electrons. In nuclear power plants, lanthanide isotopes are produced during fission of ²³⁵U; most lanthanide isotopes decay to stable nonradioactive lanthanide elements in a relatively short amount of time (many with half lives shorter than a day [36]). If the lanthanides can be separated out, nuclear waste is reduced and expensive rare earth metals are recycled for uses such as lasers, medical imaging, chemical catalysts, and permanent magnets [20]. Present lanthanide detection and separation methods are costly, tedious, and time-consuming. The lanthanide elements are difficult to separate from each other in solution because they have near identical properties, including masses, ionic radii, oxidation states, and standard potentials [21]. Lanthanides do have different numbers of unpaired 4f electrons that result in distinct magnetic properties. The 4f orbitals in Ln^{3+} ions are well shielded; they do not participate directly in bonding and, therefore, their spectroscopic and magnetic properties are largely unperturbed by ligands or the environment. Electrochemically, lanthanide analysis is limited by standard potentials in the range of -1.99 and -3.90 V vs NHE [20]. These potentials fall outside of the potential window of common electrolyte solutions. For example, in aqueous solutions at platinum, the potential window is limited by solvent electrolysis between +1.3 and -0.7 V vs NHE. Previously, researchers attempted to broaden the electrolyte potential window by 1) using either mercury drop electrodes or chemically modified carbon paste electrodes to increase the overpotential of the solvent electrolysis and/or 2) using expensive ionic liquids or molten salts with inherently wide solvent windows [35, 37-44]. Researchers also commonly encounter solubility problems because lanthanides are so large. Even in nonaqueous systems, oxygen reduction reaction (ORR) often occurs at a similar potential as lanthanide reduction/oxidation, which causes interference even though it does not narrow the potential window.

Here, several methods for electrochemical analysis of lanthanides were attempted before the triflate ligand, Nafion, and acetonitrile combination was evolved. First, boron-doped diamond (BDD) electrodes in both an aqueous system and an acetonitrile system were evaluated because of the wide potential window of BDD. Second, an attempt was made to follow a paper that reported voltammetric analysis of lanthanide trifluoromethanesulfonate (-OTf, known as triflate) compounds in acetonitrile, but we were unable to reproduce the result; the paper likely reports a mistaken interpretation of ORR and electrolysis of the I and Br electrolyte [45]. Third, in a paper by Koval, et al., copper (I) triflate is reacted with vinyl sulfonate to solubilize Cu (I) in water [46]. This paper led to the development of the system of a Nafion film modified platinum electrode and lanthanide triflate redox probes in acetonitrile.

4.1.2 X-Ray Photoelectron Spectroscopy

In x-ray photoelectron spectroscopy (XPS), x-rays probe core level binding energies of electrons. Upon bombardment of matter with high energy electrons, inner shell electrons are ejected from atoms [22]. Analysis of the kinetic energy of these emitted electrons identifies composition and electronic states of the atoms in the surface region (< 5 nm) of a sample. More specifically, a photon is absorbed by an atom M^n which leads to ionization M^{n+1} and emission of a core (inner shell) electron from the atom (Equation 7) [47].

$$M^n + hv \to M^{n+1} + e \tag{7}$$

Because of conservation of energy, the kinetic energy of the photon (hv) and kinetic energy of the emitted electron $(KE = E_e)$ yield the electron binding energy (BE).

$$E_{M^n} + hv = E_{M^{n+1}} + E_e (8)$$

$$E_e = KE = hv - (E_{M^{n+1}} - E_{M^n}) = hv - BE$$
(9)

The difference in energy $(E_{M^{n+1}} - E_{M^n})$ between the ionized and nonionized atoms is the binding energy. Binding energy can also be thought of as the energy required to remove an electron from its initial (bound state) energy level to vacuum level. A correction for the specific element's work function is required to convert from vacuum level minus initial level to BE, which is calculated from a reference analyzed with the sample [48].

Each core atomic orbital has characteristic binding energies; each element will yield a characteristic set of peaks in the photoelectron spectrum based on the electronic configuration of the element. The intensity of the peaks is related to the element concentration in the sampled region. p, d, and f orbitals have non zero orbital angular momenta. This leads to coupling between unpaired spin and orbital angular momenta and, therefore, spin-orbit splitting. Degenerate states $(J = L \pm S)$ arise from coupling L and S and result in characteristic spin-orbit doublets in the spectra [47, 48]. J is the total angular momentum, L is the orbital angular momentum and S is the spin angular momentum.

The exact binding energy of an electron depends on its local chemical and physical environment and formal oxidation state. A higher positive oxidation state of the same element leads to higher electron binding energies due to extra coulombic interactions between the emitted electron and the ion core [47]. There will also be a change in the binding energy of the core electrons of an element due to changes in the chemical bonding of the element. Lanthanide $4d_{3/2}$ and $4d_{5/2}$ doublets are the most commonly analyzed in XPS [49, 50] because the 4d electron binding energies change dependent on oxidation state and ligand environment. No matter what changes in lanthanide ligand bonding or oxidation state, 4f electrons are calculated to have the same binding energy [51].

4.2 Methods and Materials

Platinum electrodes are modified with Nafion^(R) films. Lanthanide trifluoromethanesulfonate compounds are electrochemically evaluated in an acetonitrile system. X-ray photoelectron spectroscopy (XPS) is performed to investigate oxidation states. The film and solution preparation, system setup, electrochemical analysis, and XPS analysis are described below.

4.2.1 Electrode and Solution Preparation

Platinum electrodes (Pine Instruments, $A = 0.452 \text{ cm}^2$) are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. Nafion films are made by casting 5.0 μ L of Nafion solution (5 % w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface, then allowing the casting solvents to evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 5.0 μ L, the density of Nafion in acetonitrile, and the electrode area, the film will be ~7 μ m thick when immersed in the acetonitrile solution [52].

Redox probes are all anhydrous lanthanide (III) trifluoromethanesulfonate compounds (99.9+ % pure, Sigma), referred to generally as LnOTf. Solutions of



Figure 19. Chemical structures of lanthanide trifluoromethanesulfonate and Nafion, a polymer with a Teflon fluorocarbon backbone and sulfonate side chains.

LnOTf and electrolyte tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma) in acetonitrile (Fisher, dried over 4A molecular sieves) are used for all electrochemical measurements. Trifluoromethanesulfonate (short name triflate) is a ligand that closely resembles Nafion side chains as shown in Figure 19. Three triflate ligands chelate one lanthanide atom in its 3⁺ oxidation state. For most experiments, solutions are 1.00 mM LnOTf and 0.10 M TBABF₄. When other concentrations are noted, the ratio of electrolyte to redox probe remains 100:1. Lanthanide trivalent cations are investigated as triflate salts of ytterbium (Yb), samarium (Sm), dysprosium (Dy), praseodymium (Pr), and gadolinium (Gd). Copper (II) triflate is also investigated.

Background/blank measurements are made in acetonitrile with 0.10 M TBABF₄ only. A blank solution saturated with oxygen is analyzed as well. The concentration of saturated O_2 (g) in acetonitrile is calculated to be 8 mM based on the value for O_2 (g) concentration in acetonitrile in air [53] and experimentally measured currents for a solution equilibrated in air and one saturated with O_2 (g). This saturated O_2 (g) concentration agrees with the value reported by Abraham et al. [54].

4.2.2 Electrochemical Measurements

A three electrode setup is used for all electrochemical measurements. All measurements are made in the LnOTF and TBABF₄ acetonitrile solutions except as noted. Films equilibrate for ≥ 5 hours before applying a potential, and reequilibrate for 30 minutes between each scan. The redox probe takes less time to equilibrate into Nafion in acetonitrile than in water. This is confirmed by measurements taken at intervals after the Nafion modified electrode is placed in the probe solution until a reproducible maximum current is achieved. Nitrogen is bubbled into the solution between scans and a nitrogen blanket is maintained during scans. A three neck flask is modified with an additional inlet. Each electrode is inserted through one of the joints. A gas line is fed through the fourth joint. All openings are parafilmed to maintain an inert atmosphere under nitrogen sparge. See Figure 20 for a diagram of the cell. Triplicate measurements are completed for each lanthanide triflate and at each scan rate. The working electrode is a platinum disk (Pine Instruments, $A = 0.452 \text{ cm}^2$), the counter electrode is platinum mesh, and the reference electrode is a Ag/AgO quasireference electrode (QRE) made by immersion of a freshly sanded Ag wire in concentrated HNO₃ for 10 minutes. Ferrocene (+0.64 V vs NHE) is used as an internal reference.

Cyclic voltammetry is performed (CH Instruments 760B potentiostat) at scan rates 20, 50, 75, 150, and 200 mV/s in a randomized order. The potential is swept from +1.5 V to -2.0 V to +2.0 V vs. Ag/AgO QRE; the forward sweep is then immediately repeated from +2.0 V to -2.0 V. Cyclic voltammograms that focus on the first reductive wave scan from +1.5 V to -0.8 V to +1.5 V.

For the concentration study, a solution of 0.490 mM YbOTf is prepared and a Nafion film modified electrode is equilibrated and analyzed as described above. Then, a mass of YbOTf is added to the solution such that the new concentration is 1.89 mM. The film is reequilibrated for ≥ 5 hours and the same measurements performed. This is repeated for concentrations of 3.31 mM and 5.00 mM YbOTf as well.



Figure 20. Diagram of experimental setup for lanthanide voltammetry. A three neck flask is modified with a fourth inlet. Each electrode is inserted in one of the necks. A gas line is fed into the fourth inlet. All openings are parafilmed to promote an inert atmosphere under nitrogen sparge.

For the experiment to evaluate water effects, an initial volume of 100 mL of 1.00 mM YbOTf and 0.10 M TBABF₄ in dry acetonitrile is analyzed as described above. Then, 1.00 mL of water is added for a 1.27 w/w % concentration of water in the solution, the solution reequilibrates for 30 minutes with N₂ (g) and the measurements are repeated. Another 1.00 mL of water is added for a total of 2.00 mL water or 2.54 w/w % water in the system, the solution reequilibrates, and the measurements are repeated. These steps are repeated again for totals of 5.00 mL and 10.00 mL of water (6.35 and 12.7 w/w % water) as well.

An additional experiment to investigate the role of the Nafion film is performed by equilibrating an electrode modified with a Nafion film in 1.00 mM YbOTf for 5 hours, then removing it to a blank solution of N_2 (g) sparged 0.10 M TBABF₄ electrolyte in acetonitrile. A voltammogram at 200 mV/s cyclic voltammetry is immediately undertaken. The scan is repeated 5 times continuously to see if a minimum current threshold is reached, then electrolyzed at -0.4 V for 10 minutes.

4.2.3 X-Ray Photoelectron Spectroscopy

Platinum foil (Sigma) electrodes approximately 0.5×1.0 cm are soaked in concentrated HNO₃ for one hour, then rinsed with 18 M Ω water and air dried in air. $1.0 \ \mu$ L Nafion films are cast for an end thickness of ~2 μ m and the films are dried in air ≥ 24 hours. The foil electrodes are equilibrated in a 1.00 mM YbOTf and $0.10 \ M \ TBABF_4$ acetonitrile solution. Then, either the electrodes are removed from the solution or they are electrolyzed at -0.4 V for ten minutes before removal from solution. The electrodes are then rinsed with acetonitrile and stored in a vacuum

4.3 Results and Discussion

Electrochemical measurements of YbOTf, PrOTf, SmOTf, GdOTf, and DyOTf are analyzed. XPS and computer simulation results are considered in view of the proposed voltammetric mechanism.

4.3.1 Electrochemical Measurements

Five lanthanide triflates are examined. The first is ytterbium triflate.

4.3.1.1 Voltammetry of Ytterbium Triflate

Figure 21 is a 20 mV/s cyclic voltammogram of the first and second sweep for a Nafion modified platinum electrode equilibrated in ytterbium triflate. The inset is a 200 mV/s cyclic voltammogram of the first reductive wave. Upon the first sweep, there are two main reduction peaks, which will be called A and B as shown in Figure 22. Figure 22 also demonstrates how the peak current for peak A (called i_{pA1} for the first sweep and i_{pA2} for the second sweep) is measured from the baseline current and the B peak current (i_{pB1} and i_{pB2}) is measured from the extrapolated mass transport decay of peak A. The potential at which i_{pA} occurs is called E_A and the potential at which i_{pB} occurs is called E_B . The potential difference between peaks A and B is called ΔE_{AB} and calculated as shown in Equation 10.

$$\Delta E_{AB} = |E_B - E_A| \tag{10}$$



Figure 21. 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in ytterbium triflate. Inset is a 200 mV/s cyclic voltammogram of the first reductive wave.



Figure 22. Demonstration of how lanthanide cyclic voltammograms are analyzed with a 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in ytterbium triflate.

Analysis focuses on the reductive waves and first sweeps. ΔE_{AB} is used as a characteristic because the oxidative waves are so poorly resolved that half wave potentials are difficult to determine. $E_{p/2}$ is an experimental estimate of the standard potential E^0 calculated as halfway between E_f and E_r . $E_{p/2}$ values are calculated for peak A from the cyclic voltammograms that only scan the first redox reaction; similarly, forward and reverse peak current ratios and peak splittings are also drawn from voltammograms that record only peak A.

Voltammetric morphology is considered qualitatively. Consider Figure 23. The near linear in current past peak A, especially at high scan rates, is atypical and not consistent with mass transport limited processes. A chemical step likely impacts the current response past peak A. On the second sweep, a dip around 0.5 V may indicate that an adsorbed species blocks an oxidation reaction on the first sweep but is removed on the second sweep so that an oxidation occurs even when sweeping in the reductive direction. The relative heights of peaks A and B change between the first and second sweep. On the second sweep, peak A is smaller, while peak B is approximately the same size but better resolved (see Figure 22). This also indicates there is a limiting chemical step in the mechanism, especially as the difference in second sweep peak heights is even more pronounced at higher scan rates. A slight shoulder before the first reductive peak could indicate an additional redox reaction is occurring at a similar E^0 . When the potential is only scanned far enough to look at peak A (Figure 21 inset), it appears chemically irreversible as well as electron transfer quasireversible at high scan rates and electron transfer irreversible at low scan rates. At 200 mV/s, peak forward currents are five times greater than reverse



Figure 23. Overlay of first sweep cyclic voltammograms for a Nafion modified platinum electrode in 3.31 mM ytterbium triflate, 0.30 M TBABF₄ for scan rates 20 mV/s (green short dash line), 50 mV/s (red medium dash line), and 200 mV/s (blue solid line). Additional scan rates 75 mV/s and 150 mV/s are not shown for clarity sake.



Figure 24. Plot of peak current (μ A) versus square root scan rate (V/s)^{1/2} ytterbium triflate for peak A on first sweep (i_{pA1} , blue circle), peak A on second sweep (i_{pA2} , red triangle), peak B on first sweep (i_{pB1} , green square), and peak B on second sweep (i_{pB2} , purple diamond) for scan rate 20, 50, 75, 150, and 200 mV/s. Regression data are provided in Table 12. Error bars are standard deviation. They are only shown for one series for clarity sake; error bars are comparable for the other series.

Table 12. Ytterbium triflate cyclic voltammetry regression data for the peak forward current of A and B on the first sweep versus square root of scan rate

Peak	Slope ($\mu As^{1/2}V^{-1/2}$)	Intercept (μA)	\mathbf{R}^2
i _{pA1}	1130 ± 20	-2.2 ± 0.6	0.9990
$ i_{pB1}$	1050 ± 40	-2.9 ± 0.1	0.9960

peak currents and peak splittings are more than 600 mV. At 20 mV/s, peak forward currents are ten times greater than reverse peak currents and peak splittings are around 400 mV. These results are consistent with a following chemical reaction of moderate rate.

Quantitatively, on the first sweep, i_{pA1} and i_{pB1} are linear with the square root of the scan rate, v (V/s). Because there are likely chemical reactions involved, interpretation of this linearity is difficult beyond acknowledging that there is at least some mass transport component in the response and any chemical steps are of a rate comparable to the rate of mass transport. Figure 24 is a plot of peak currents i_p (μ A) vs square root of the scan rate \sqrt{v} (V/s)^{1/2}. Regression data are given in Table 12. Figure 23 is an overlay of 20, 50, and 200 mV/s scan rate first sweep cyclic voltammograms of both reductive peaks for a 3.3 mM ytterbium triflate, 0.3 M TBABF₄ solution. Additional scan rates 75 mV/s and 150 mV/s are analyzed but not shown for clarity sake. The first sweep peak currents are linear with \sqrt{v} while the second sweep peak currents are not. Lack of linearity can mark a chemical step or quasireversible electron transfer kinetics.

Figure 25 is an overlay of 20 mV/s first sweep cyclic voltammograms for a Nafion

modified platinum electrode in electrolyte only TBABF_4 solution and ytterbium triflate concentrations of 0.49 mM, 1.9 mM, 3.3 mM, and 5.0 mM (TBABF₄ concentrations are always $100 \times$ the ytterbium triflate concentration). Current increases linearly with increasing concentration of YbOTf, which confirms that the observed electrochemical behavior is due to the ytterbium triflate in the system. Figure 26 is a plot of peak currents i_p (μA) versus concentration (mM) of ytterbium triflate. Regression data are provided in Table 13. All peak currents are linear with concentration. For peak A, the slopes of i_{pA1} and i_{pA2} versus concentration are statistically the same. If there is a chemical step about peak A, the linearity is consistent with a reaction that is neither catalytic, second order, nor a dimerization. For peak A, the reactions are the same for the first and second sweeps. For peak B, the linearity of i_{pB1} and i_{pB2} versus concentration discounts catalytic, second order, and dimerization reactions. That the slopes for peak B on the first and second sweeps are different does not identify the reaction on the second sweep as the same as the first. However, the lower \mathbb{R}^2 values for the B peaks are most likely an artifact of human analysis error; the peak A mass transport decay is extrapolated by hand to measure i_{pB} . There are no faradaic peaks in the electrolyte only cyclic voltammogram. An experiment in which the concentration of triflate was increased in the same manner as the ytterbium triflate concentration study by addition of tetrabutylammonium trifluoromethanesulfonate showed no effect on the current response. Because there was no change in current on addition of triflate ligand, it is probable that the triflate is not electroactive and that the triflate is well bound to the metal ions in various oxidation states.



Figure 25. Overlay of 20 mV/s first sweep cyclic voltammograms for a Nafion modified platinum electrode in electrolyte TBABF_4 only solution (black solid line), and ytterbium triflate concentrations of 0.490 mM (red medium dash line), 1.89 mM (yellow long dash line), 3.31 mM (green short dash line), and 5.00 mM (blue solid line).



Figure 26. Plot of peak current (μ A) versus concentration (mM) ytterbium triflate for peak A on first sweep (i_{pA1} , blue circle), peak A on second sweep (i_{pA2} , red triangle), peak B on first sweep (i_{pB1} , green square), and peak B on second sweep (i_{pB2} , purple diamond). Regression data provided in Table 12. Error bars are standard deviation. They are only shown for one series for clarity sake; error bars are comparable for the other series.

Table 13. Regression data for the 20 mV/s peak forward current of A and B on the first and second sweep versus concentration of yt-terbium triflate

Peak	Slope ($\mu A/mM$)	Intercept (μA)	\mathbf{R}^2
ipA1	210 ± 10	39 ± 35	0.9944
ipB1	140 ± 30	11 ± 8	0.9433
ipA2	204 ± 5	-24 ± 15	0.9989
ipB2	180 ± 20	45 ± 61	0.9771

Figure 27 is an overlay of 20 mV/s cyclic voltammograms for copper triflate and ytterbium triflate. Other than replacing the ytterbium with copper, the system is the same. Copper triflate voltammetry differs from ytterbium triflate voltammetry. Potentials are normalized to NHE to be certain the observed peaks are at different potentials. This is another confirmation that the observed currents are due to lanthanide redox behavior.

An O_2 (g) saturated (~8 mM) electrolyte only solution overlaid with an N_2 (g) sparged electrolyte only solution in Figure 28 demonstrates that the peaks observed in ytterbium triflate systems are not due to oxygen reduction reaction. An O_2 (g) saturated ytterbium triflate solution is shown in the inset. The two LnOTf reductive peaks are distinct from the ORR peak although the ORR occurs near the same potential.

When the electrode is equilibrated in YbOTf then removed to a blank electrolyte solution, the current is immediately lower. Repetitive scans do not decrease below a threshold current level. This indicates that some YbOTf remains in the film and is recycled by the cyclic voltammetry. When still in a bulk solution of YbOTf, redox



Figure 27. Overlay of 200 mV/s cyclic voltammograms of Nafion modified platinum electrodes in 1.00 mM copper triflate and 1.00 mM ytterbium triflate solutions. Electrolyte is 0.10 M TBABF₄ for both.



Figure 28. Overlay of 200 mV/s cyclic voltammograms for a 0.10 M TBABF₄ only solution saturated with O_2 (g) (blue dashed line) and sparged with N_2 (g) (black solid line). Inset is a 200 mV/s cyclic voltammogram for a 1.00 mM ytterbium triflate and 0.10 M TBABF₄ solution saturated with O_2 (g).



Figure 29. Overlays of 200 mV/s cyclic voltammograms for electrodes modified with Nafion films in 1.00 mM YbOTf and 0.10 M TBABF₄ in acetonitrile with water concentrations of 0 (black solid line), 1 (red long dashed line), 3 (green short dashed line), 6 (yellow dotted line), and 13 (blue solid line) w/w %. a) full cyclic voltammograms are shown, b) an enlargement of the main peaks.

probe from the solution must be readily available to exchange into the film during analysis to maintain the higher currents.

Because of the way films are prepared, there is a chance some water is present in the film even after it is dried. An experiment is performed in which water is gradually introduced to the Nafion/LnOTf/acetonitrile system. This also serves as an evaluation to determine if the Nafion film would work for electroanalysis of lanthanide ions in water or if the acetonitrile is equally important to the system. Figure 29a is an overlay of 200 mV/s cyclic voltammograms for YbOTf and TBABF₄ in acetonitrile with water concentrations of 0, 1.27, 2.54, 6.35, and 12.7 w/w %. Figure 29b is an enlargement of Figure 29a main peaks. Adding water gradually shows a marked difference. The potential window shrinks as hydrogen evolution of the water can now occur. The lanthanide peaks shift and eventually disappear.

4.3.1.2 Voltammetry of Various Lanthanide Triflates

Figures 30, 31, 32, and 33 are 20 mV/s cyclic voltammograms of SmOTf, DyOTf, GdOTf, and PrOTf, respectively, with insets of 200 mV/s scans of the first redox reactions. The cyclic voltammograms for all lanthanides are similar. See Figure 35 for all lanthanide voltammograms on the same potential axis. Values of ΔE_{AB} vary slightly with lanthanide. Samarium appears more reversible than the others. The praseodymium B peak (Figure 33) exhibits evidence of two consecutive reduction reactions, which may be $Pr^{3+} + e \rightleftharpoons Pr^{2+}$ and $Pr^{2+} + e \rightleftharpoons Pr^{1+}$. Figure 34 is an overlay of 10, 50, and 200 mV/s scan rate first sweep cyclic voltammograms of the first reductive peak for a 1.45 mM dysprosium triflate, 0.15 M TBABF₄ solution.



Figure 30. 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in 1.42 mM samarium triflate, 0.15 M TBABF₄. Inset is a 200 mV/s cyclic voltammogram of only the first reductive wave.



Figure 31. 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in 1.45 mM dysprosium triflate, 0.15 M TBABF₄. Inset is a 200 mV/s cyclic voltammogram of only the first reductive wave.



Figure 32. 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in 0.904 mM gadolinium triflate, 0.10 M TBABF₄. Inset is a 200 mV/s cyclic voltammogram of only the first reductive wave.



Figure 33. 20 mV/s cyclic voltammogram of first and second sweep for Nafion modified platinum electrode in 1.44 mM praseodymium triflate, 0.15 M TBABF₄. Inset is a 200 mV/s cyclic voltammogram of only the first reductive wave.



Figure 34. Overlay of first sweep cyclic voltammograms for a Nafion modified platinum electrode in 1.45 mM dysprosium triflate, 0.15 M TBABF₄ for scan rates 10 (green short dash line), 50 (red medium dash line), and 200 mV/s (blue solid line). Additional scan rates 20 and 150 mV/s are not shown for clarity sake. Inset is an enlargement of the 10 mV/s scan.

Ln	E_{pf}	E_{pr}	$E_{p/2}$ (V)	$\Delta E_p (\mathrm{mV})$	i _{pf}	i _{pr}	i _{pf} /i _{pr}
					$(\mu A/mM)$	$(\mu A/mM)$	
Yb	$-0.46_3 \pm 0.02$	$0.30_2 \pm 0.02$	$-0.08_{10} \pm 0.02$	770 ± 30	308 ± 5	-112 ± 5	2.7 ± 0.1
Sm	$-0.41_9 \pm 0.03$	$0.17_5 \pm 0.03$	$-0.12_2 \pm 0.05$	590 ± 20	243 ± 4	-63.9 ± 5	3.8 ± 0.2
Dy	$-0.38_2 \pm 0.01$	$0.22_9 \pm 0.03$	$-0.07_{60} \pm 0.02$	610 ± 40	418 ± 4	-71.9 ± 4	5.8 ± 0.4
Gd	$-0.38_4 \pm 0.02$	$0.20_0 \pm 0.02$	$-0.09_{21} \pm 0.01$	580 ± 20	355 ± 6	-96.2 ± 4	3.7 ± 0.1
Pr	$-0.41_4 \pm 0.02$	$0.25_{6} \pm 0.01$	$-0.07_{92} \pm 0.02$	670 ± 30	429 ± 4	-147 ± 6	2.9 ± 0.2

Table 14. The 200 mV/s peak potentials and currents, peak splitting, and current ratios for the first redox reaction (peak A first sweep) of various lanthanides (n = 3)

Table 15. The 20 mV/s peak potentials, peak currents, and potential difference between forward peaks A and B for various lanthanides (n = 3)

			Peak Forward Currents (μ A/mM)				
Ln	E_A (V)	E_B (V)	$\Delta E_{AB} (\mathrm{mV})$	i_{pA1}	i_{pB1}	i_{pA2}	i_{pB2}
Yb	$-0.38_2 \pm 0.01$	-1.11 ± 0.01	730 ± 50	747 ± 15	78.0 ± 1.6	72.1 ± 1.3	76.5 ± 1.5
Sm	$-0.38_2 \pm 0.02$	-1.10 ± 0.02	720 ± 50	89.8 ± 1.8	87.5 ± 1.8	85.5 ± 2.0	80.8 ± 1.5
Dy	$-0.33_2 \pm 0.01$	-1.06 ± 0.01	700 ± 50	88.1 ± 1.7	94.0 ± 2.1	977 ± 30	97.4 ± 1.6
Gd	$-0.41_0 \pm 0.05$	-1.12 ± 0.02	710 ± 50	92.4 ± 2.0	106 ± 3	89.5 ± 1.6	94.2 ± 2.1
Pr	$-0.36_1 \pm 0.01$	-1.42 ± 0.10	1060 ± 70	917 ± 23	130 ± 5	95.1 ± 2.1	98.6 ± 2.8

The inset is a larger view of the 10 mV/s scan. Regression analysis yields slope $(1.3_9 \pm 0.1_6) \times 10^3 \ \mu \text{As}^{1/2} \text{V}^{-1/2}$, intercept $-4.8_0 \pm 0.4_6 \ \mu \text{A}$, and $\text{R}^2 \ 0.9873$.

Table 14 lists forward and reverse peak currents, i_{pf} and i_{pr} , and their corresponding peak potentials, E_{pf} and E_{pr} , along with $E_{p/2}$ s, peak splitting ΔE_p , and i_p ratios for the 200 mV/s scans of the first redox reactions (only peak A scanned) for all LnOTfs. Table 15 lists peak potentials for the reductive wave peaks A and B, E_A and E_B , and their corresponding peak currents for the first and second sweeps, i_{pA1} , i_{pB1} , i_{pA2} , and i_{pB2} , along with ΔE_{AB} s for the 20 mV/s scans of the first and second redox reactions for all LnOTfs. Table 16 lists peak currents for the first E_A and E_B . Currents are normalized to 1 mM concentrations of LnOTf in all tables.


Figure 35. 20 mV/s cyclic voltammograms of full potential window first sweeps for Nafion modified platinum electrodes in praesodymium triflate (purple), gadolinium triflate (yellow), dysprosium triflate (red), samarium triflate (green), and ytterbium triflate (blue). Electrolyte is TBABF₄ in acetonitrile for all. Voltammograms are plotted at a vertical offset for clarity, so a 100 μ A current scale is shown at left.



Figure 36. 200 mV/s cyclic voltammograms of peak A only for Nafion modified platinum electrodes in praesodymium triflate (purple), gadolinium triflate (yellow), dysprosium triflate (red), samarium triflate (green), and ytterbium triflate (blue). Electrolyte is TBABF₄ in acetonitrile for all. Voltammograms are plotted at a vertical offset for clarity, so a 400 μ A current scale is shown at left.

In Figure 35, the voltammograms for all lanthanides are shown together; the morphologies for all are much the same. In Figure 36, the first redox waves (only peak A scanned) are also shown to have common morphologies. Similar morphologies and potentials for the first reductive wave (peak A) are observed in molten salts [35, 40, 41] and ionic liquids for Yb, Sm, and Eu [38, 39, 43, 44]. Authors assign peak A to the $3^+/2^+$ redox couple but provide no evidence. For ionic liquids, most papers also use lanthanide triflate compounds and triflate related anions [21, 38, 39]. Triflate compounds seem to be especially soluble in ionic liquids where the anion is either tetrafluoroborate (BF_4^-) or a trifluoromethanesulfonyl derivative (OTf-, TFSI-, bis(trifluoromethanesulfonyl)amide) [35]. Ohno, et al. bind Yb(OTf)₃ to a sodium sulfonate compound and determine that one of the triflates is replaced by the sodium sulfonate compound [49]. It seems likely that the sulfonates in Nafion may do the same thing in this system. Toyoshima, et al. design a flow cell to detect lanthanides using Nafion films on carbon cloth, which may work in a similar way to the system here, where the Nafion binds the lanthanides near the electrode surface 55.

4.3.2 X-Ray Photoelectron Spectroscopy

Figure 37 is an XPS spectrum for a Nafion modified platinum foil electrode equilibrated in a 1.00 mM YbOTf, 0.10 M TBABF₄ acetonitrile solution. Binding energy values are calibrated to carbon 1s = 284.6 eV as a reference. The Yb³⁺ $4d_{3/2}$ and $4d_{5/2}$ peaks are at 186.5 and 202.6 eV, respectively, which correspond with literature values [49, 50]. Figure 38 is an XPS spectrum for a Nafion modified



Figure 37. X-ray photoelectron spectrum for a Nafion film modified platinum foil electrode equilibrated in a 1.00 mM YbOTf, 0.10 M $\rm TBABF_4$ solution.



Figure 38. X-ray photoelectron spectrum for a Nafion film modified platinum foil electrode equilibrated in a 1.00 mM YbOTf, 0.10 M TBABF₄ solution then electrolyzed at -0.4 V vs Ag/AgO QRE for ten minutes to reduce the Yb³⁺.

Table 16. Peak potentials and peak currents for foward peaks A and B for scan rates 20, 50, and 200 mV/s for various lanthanides at Nafion modified platinum electrodes (n = 3)

				Peak Forward Currents ($\mu A/mM$)			
Ln	v (mV/s)	E_A (V)	E_B (V)	i_{pA1}	i_{pB1}	i _{pA2}	i_{pB2}
Yb	200	$-0.55_3 \pm 0.01$	-1.37 ± 0.01	254 ± 5	252 ± 5	182 ± 4	219 ± 9
	50	$-0.40_3 \pm 0.01$	-1.15 ± 0.02	121 ± 5	127 ± 5	111 ± 4	131 ± 3
	20	$-0.38_2 \pm 0.01$	-1.11 ± 0.01	$74{7} \pm 1$	78.0 ± 1	72.1 ± 1	76.4 ± 1
Sm	200	$-0.61_8 \pm 0.02$	-1.25 ± 0.02	345 ± 9	205 ± 5	214 ± 6	190 ± 7
	50	$-0.37_4 \pm 0.02$	-1.17 ± 0.02	167 ± 5	156 ± 5	151 ± 5	138 ± 5
	20	$-0.38_2 \pm 0.02$	-1.10 ± 0.02	89.8 ± 1	87.5 ± 1	85.5 ± 2	80.8 ± 2
Dy	200	$-0.39_6 \pm 0.02$	-1.14 ± 0.01	320 ± 10	264 ± 5	208 ± 5	216 ± 6
	50	$-0.33_9 \pm 0.01$	-1.08 ± 0.03	170 ± 5	183 ± 5	144 ± 5	174 ± 5
	20	$-0.33_2 \pm 0.01$	-1.06 ± 0.01	88.1 ± 1	94.0 ± 2	$97{7} \pm 3$	97.4 ± 2
Gd	200	$-0.50_3 \pm 0.04$	-1.27 ± 0.01	320 ± 9	273 ± 5	195 ± 5	192 ± 7
	50	$-0.37_4 \pm 0.01$	-1.19 ± 0.03	158 ± 5	175 ± 2	131 ± 3	159 ± 5
	20	$-0.41_0 \pm 0.05$	-1.12 ± 0.02	92.4 ± 2	106 ± 2.5	89.5 ± 2	94.2 ± 2
Pr	200	$-0.43_2 \pm 0.01$	-1.35 ± 0.01	307 ± 7	397 ± 6	221 ± 8	246 ± 8
	50	$-0.37_4 \pm 0.01$	-1.25 ± 0.01	161 ± 3	173 ± 3	115 ± 5	148 ± 2
	20	$-0.36_1 \pm 0.01$	-1.42 ± 0.10	91.7 ± 2	130 ± 5.0	95.1 ± 2	98. $_6 \pm 3$

platinum foil electrode equilibrated in a 1.00 mM YbOTf, 0.10 M TBABF₄ acetonitrile solution then electrolyzed at -0.4 V vs Ag/Ag⁺ QRE for ten minutes to reduce the Yb³⁺. The XPS spectrum for the reduced sample has a shoulder on the 4d_{3/2} peak at ~4 eV more negative binding energy that is assigned to Yb²⁺, consistent with literature [49,50]. In the reduced sample, a high concentration of Yb³⁺ remains. XPS only probes 5 nm into the surface of the 2 μ m film. Yb²⁺ exchanges from the electrode far out into the film during electrolysis, however new Yb³⁺ also exchanges into the film from the solution throughout analysis so that the fractional concentration of divalent ytterbium compared to trivalent ytterbium is low at the outer edge of the film. It is concluded that the first reductive wave (at around -0.4 V vs Ag/AgO) is the result of the redox reaction $Yb^{3+} + e \rightleftharpoons Yb^{2+}$. There are no literature data for ytterbium triflate or ytterbium cation standard potentials in organic solvents. Aqueous Yb^{3+/2+}, Yb^{2+/0}, and Yb^{0/3+} potentials are listed at -1.05, -2.80, and -2.22 V vs NHE, respectively [20]. If the first reductive wave E⁰ is 0.0 V vs NHE for Yb^{3+/2+} and the second wave is -1.0 V vs NHE for Yb^{2+/0}, this indicates a ligand shift of \sim +1 V for triflate ligand in acetonitrile. The shift can be explained by both effects from nonaqueous solvation energy and ligand complexation. In nonaqueous electrochemistry, shifts in the standard potential from that in an aqueous system occur because solvation energy for M⁺ differs with solvent. On average, standard potentials for transition metal redox probes shift positively by 0.5 V in acetonitrile compared to water [56]. Solvation shifts are commonly observed in lanthanide electrochemistry in ionic liquids and molten salts [21, 35, 56]. The ferrocene/ferrocene⁺ couple does not shift, which is why ferrocene is used as an internal reference in nonaqueous systems.

Potential shifts due to ligand complexation are considered in terms of the Nernst equation (Equation 12) for the redox reaction and the rates of formation K_f for the trivalent and divalent ligand complexes (Equations 15 and 16) where R is the gas constant, T is the temperature, and F is Faraday constant.

$$Ln^{3+} + e \rightleftharpoons Ln^{2+} \tag{11}$$

$$E = E^{0} - \frac{RT}{nF} \ln \frac{[Ln^{2+}]}{[Ln^{3+}]}$$
(12)

$$Ln^{3+} + 3OTf \rightleftharpoons Ln^{3+}(OTf)_3 \tag{13}$$

$$Ln^{2+} + 2OTf \rightleftharpoons Ln^{2+}(OTf)_2$$
 (14)

$$K_{f,3} = \frac{[Ln^{3+}(OTf)_3]}{[Ln^{3+}][OTf]^3}$$
(15)

$$K_{f,2} = \frac{[Ln^{2+}(OTf)_3]}{[Ln^{2+}][OTf]^3}$$
(16)

Substitute the rates of formation into the Nernst equation and an additional term related to the ratio of the formation constants emerges: the potential shift due to the ligand, E_{ligand} .

$$E = E^{0} - \frac{RT}{nF} \ln \frac{[Ln^{2+}(OTf)_{3}]}{K_{f,2} [OTf]^{3}} \frac{K_{f,3} [OTf]^{3}}{[Ln^{3+}(OTf)_{3}]}$$
(17)

$$E = E^{0} - \frac{RT}{nF} \ln \frac{K_{f,3}}{K_{f,2}} - \frac{RT}{nF} \ln \frac{[Ln^{2+}(OTf)_{3}]}{[Ln^{3+}(OTf)_{3}]}$$
(18)

$$E_{ligand} = E^{0} - \frac{RT}{nF} \ln \frac{K_{f,3}}{K_{f,2}}$$
(19)

 E_{ligand} in this system is ~0.5 V, consistent with the formation constant for $Ln^{3+}(OTf)_3$ being greater than that for $Ln^{2+}(OTf)_3$ by 10⁵.

4.3.4 Mechanism

DigiSim^(R) (Bioanalytical Systems, Inc.) is a commercially available program to simulate electrochemical mechanisms for various voltammetric perturbations. From simulations with DigiSim that focus mainly on the reductive wave, a probable mechanism is an ECEC where there are two redox reactions, a one electron reaction $A + e \rightleftharpoons B$ at E_1^0 and a two electron reaction $B + 2e \rightleftharpoons C$ at E_2^0 . One of the chemical reactions is a disproportionation reaction $A + C \rightleftharpoons 2B$. And there is another chemical reaction B or $C \rightleftharpoons D$ where D is not electroactive about E_1^0 or E_2^0 .

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Figure 39 is a simulation of the first redox reaction with mechanism ECC in which $A + e \rightleftharpoons B$ (the E⁰ is -0.1 V vs NHE and homogeneous electron transfer rate is 0.0002 cm/s) and A and B can be affected by the disproportionation reaction $A + C \rightleftharpoons 2B$ (K_{dis} = k₁/k₂ = 5 × 10⁶) and B can also be affected by the chemical reaction $B \rightleftharpoons D$ (K_c = k₃/k₄ = 1 × 10⁸). Simulated voltammetric morphology and peak current ratios are similar to experimental results (see Figure 36).

Figure 40 is a simulation of the full lanthanide cyclic voltammogram with mechanism ECEC in which $A + e \rightleftharpoons B$ ($E_1^0 = -0.1$ V vs NHE and homogeneous electron transfer rate is 0.0002 cm/s) and $B + e \rightleftharpoons C$ (E₂⁰ = -1.0V vs NHE and homogeneous electron transfer rate is 0.0001 cm/s). A, B, and C are affected by the disproportionation reaction $A + C \rightleftharpoons 2B$ (K_{dis} = k₁/k₂ = 5 × 10⁶) and B is also affected by the chemical reaction $B \rightleftharpoons D$ (K_c = k₃/k₄ = 1 × 10⁸). Simulated voltammetric morphology reflects experimental results (see Figure 35), except for the relative heights of reductive peaks A and B. Limitations of the simulation software prevent changing the value of K_{dis} . When the mechanism is altered so that the second redox reaction is $B + 2e \rightleftharpoons C$, K_{dis} becomes set at 10^{-58} . The simulation thermodynamically disallows a two electron transfer and a disproportionation reaction. Most likely, a two electron transfer is more accurate and altering K_{dis} would solve the issue with peak heights. There is a good morphological match for this mechanism. The last chemical reaction is the formation of another lanthanide compound - perhaps a lanthanide hydroxide or lanthanide fluoride compound that is not electroactive in this potential range. In Nafion, this is likely sulfonate.

From the literature, the $Ln^{3+/2+}$ and $Ln^{2+/0}$ redox reactions are known [20]. The



Figure 39. DigiSim simulation of a cyclic voltammogram for an ECC mechanism in which $A + e \rightleftharpoons B$ ($E^0 = -0.1$ V vs NHE and homogeneous electron transfer rate is 0.0002 cm/s), $A + C \rightleftharpoons 2B$ ($K_{dis} = k_1/k_2 = 5 \times 10^6$), and $B \rightleftharpoons D$ ($K_c = k_3/k_4 = 1 \times 10^8$) where D is not electroactive in the potential range.



Figure 40. DigiSim simulation of a cyclic voltammogram for an ECEC mechanism in which $A + e \rightleftharpoons B$ ($E_1^0 = -0.1$ V vs NHE and homogeneous electron transfer rate is 0.0002 cm/s), $B + e \rightleftharpoons C$ ($E_2^0 = -1.0$ V vs NHE and homogeneous electron transfer rate is 0.0001 cm/s), $A + C \rightleftharpoons 2B$ ($K_{dis} = k_1/k_2 = 5 \times 10^6$), and $B \rightleftharpoons D$ ($K_c = k_3/k_4 = 1 \times 10^8$) where D is not electroactive in the potential range. The black line is the first sweep and the gray line is the second sweep.

voltammetric morphology does not suggest that lanthanide metal is plated on the electrode, nor is there visual evidence of plating. In Nafion, the concentration of sulfonate is ~ 1 M, so neutral species Ln^0 may be bound even with a very low binding constant.

There is literature precedent for disproportionation of lanthanide halides [20]. Disproportionation is a redox reaction in which a species is simultaneously reduced and oxidized to form two different oxidation states. In this case, Ln^{2+} goes to both Ln^{3+} and Ln^{0} where X⁻ is a generic halide anion.

$$3LnX_2 \rightleftharpoons 2LnX_3 + Ln \tag{20}$$

Thus, the following mechanism is proposed, where A is an unknown anion that forms new compounds with an Ln of oxidation state n.

$$Ln^{3+} + e \rightleftharpoons Ln^{2+} \tag{21}$$

$$Ln^{2+} + 2e \quad \rightleftharpoons \quad Ln^0 \tag{22}$$

$$2Ln^{2+} \rightleftharpoons Ln^{3+} + Ln^0 \tag{23}$$

$$Ln^n \rightleftharpoons LnA_n$$
 (24)

The mechanism interpretation is complicated by the strong influence of the chemical reactions on the electrochemical reactions. The concentration of Ln^{3+} can be affected by the reactions in Equations 21 and 22. The concentration of Ln^{2+} can be affected by the reactions in Equations 21, 22, and 23. The concentration of Ln^{0} can be affected by the reactions in Equations 22, and 23. And all oxidation states can be affected by Equation 24. The variations in peak heights on the second sweep versus

the first sweep and between fast and slow scan rates support this.

4.4 Conclusions

A relatively inexpensive, readily assessable benchtop method to analyze lanthanides electrochemically has been developed. Mercury electrodes, ionic liquids, and molten salts are avoided. Nafion solubilizes the lanthanide compounds, possibly by replacement or equilibrium of a triffate ligand with a sulfonate group. Acetonitrile widens the accessible potential window and shifts the standard potential of the lanthanides through solvation effects. Ligand complexation by the triffate also shifts the standard potential. Lanthanides can be detected in this system in two steps: complexation with triffates and electrochemical analysis. Instrumental limitations of the XPS prevented analysis of the film electrolyzed at -1.4 V vs Ag/AgO. If analysis can be performed, it may be possible to discriminate between a one electron reaction $Yb^{2+} + e \rightleftharpoons Yb^{1+}$ and a two electron reaction $Yb^{2+} + 2e \rightleftharpoons Yb^0$ by whether the binding energy shifts by another 4 eV or 8 eV.

CHAPTER 5

MAGNETIC EFFECTS ON LANTHANIDE ELECTROCHEMISTRY

Prior studies in the Leddy lab have shown significant impacts of magnetic fields on heterogeneous and homogeneous electron transfer rates. The observed effects scale with the magnetic properties of the electroactive species. Because lanthanides have access to f electrons, lanthanides have a more extreme range of paramagnetic properties than transition metals limited to d electrons. Lanthanides have up to seven unpaired electrons as compared to five for transition metals. Thus, magnetic field effects on lanthanide electrochemistry are explored.

5.1 Background

The lanthanides are difficult to separate from each other in solution because lanthanides have few distinct properties. For lanthanides, the ionic radii, oxidation states, standard potentials, and ligand binding constants are largely invariant [20]. Lanthanides do have different numbers of unpaired 4f electrons that manifest as distinct magnetic properties.

Magnetic exploitation of the different number of 4f electrons between lanthanides will allow electrochemists to differentiate lanthanides with nearly indistinguishable standard potentials. Use of magnetic fields to differentiate lanthanides based on their magnetic properties is a significant advance in electroanalytical chemistry and separations. Use of magnetic fields coupled to benchtop voltammetry of lanthanide complexes in common electrochemical solvents opens lanthanides to electrochemical inspection as not previously possible. Present lanthanide separation methods are costly, tedious, and time-consuming. The separations are based on minute differences in complexation affinities that require subsequent chemical separations such as fractional crystallization, ion-exchange methods, and solvent extraction [20,21,35,36]. These chemical methods require an additional technique to identify the lanthanides once they are separated; electrochemistry provides both simultaneously. A separation method made more efficient in a magnetic electrochemical matrix would be a faster, less expensive method to separate and analyze lanthanides produced by nuclear reactions for reuse, thus reducing radioactive waste [36].

5.1.1 4f Orbitals

4f orbitals dictate the magnetic properties of lanthanides but are without significant influence on the chemical properties of lanthanides. Different numbers of unpaired 4f electrons give lanthanides different magnetic properties, but due to the lanthanide contraction, 4f orbitals do not contribute to bonding. As the atomic number of lanthanides increases and more protons are added to the nucleus, the 4f orbitals contract and become more stable than the 5d orbitals. Pr has the electronic configuration [Xe]6s²4f³ and Nd through Eu follow the same pattern where each successive electron adds to the 4f orbital. At Eu, [Xe]6s²4f⁷, the 4f subshell is half filled and highly stable. After Eu, the stability of the half filled f subshell is preserved as the next electron is added to 5d. The electronic configuration of Gd is therefore [Xe]6s²5d¹4f⁷. Tb through Yb resume the same pattern as Pr [20]. Tb is [Xe]6s²4f⁹ and each successive electron is added to 4f so that Yb is [Xe]6s²4f¹⁴, which is a filled f orbital. The last lanthanide, Lu, adds the electron to the 5d orbital to form [Xe]6s²5d¹4f¹⁴. See Table 17 for electronic configurations of lanthanides in various oxidation states. The 4f orbitals penetrate the Xe core considerably, so 4f orbitals cannot overlap with ligand orbitals to participate significantly in bonding. The spectroscopic and magnetic properties of lanthanides are largely unaffected by ligands. The ability to form π bonds is also difficult, so Ln=O and Ln=N compounds are rare [20].

5.1.2 Magnetic Properties of Lanthanides

Lanthanides have magnetically ordered structures associated with unpaired 4f electrons. There are potentially seven 4f orbitals that can contain unpaired electrons as well as some of the 5d orbitals. All trivalent lanthanides except lutetium have unpaired f electrons. However, their magnetic moments deviate considerably from spin only values ($\mu_{eff} = \sqrt{n(n+2)}$ where n is the number of unpaired electrons) because of strong spin-orbit coupling. Gd³⁺ has the maximum number of unpaired electrons (7), but Dy³⁺ and Ho³⁺ have the largest magnetic moments. Lanthanide magnetic moments are better calculated considering spin-orbit coupling with the equation

$$\mu_{eff} = g_J \sqrt{J(J+1)} \tag{25}$$

where μ_{eff} is the effective magnetic moment, J is the total angular momentum, and g_J is calculated from J, the orbital angular momentum L, and the spin angular momentum S [20]. L is calculated from the orbital quantum number ℓ , which sets the shape of atomic orbitals and has allowed values of 0, 1, 2, and 3 for elements

with s, p, d, and f orbitals, respectively. S is calculated from the spin quantum number s, which sets the magnitude of the spin angular momentum of an electron and has a value of $\frac{1}{2}$.

$$L = \left[\sqrt{\ell(\ell+1)}\right] \frac{h}{2\pi} \tag{26}$$

$$S = \left[\sqrt{s(s+1)}\right] \frac{h}{2\pi} \tag{27}$$

$$J = L \pm S \tag{28}$$

$$g_J = \left[S(S+1) - L(L+1) + 3J(J+1)\right]/2J(J+1)$$
(29)

Table 17 lists the number of unpaired electrons (assuming seven orbitals of equivalent energy), calculated magnetic moments for trivalent and divalent lanthanide ions, and experimentally measured magnetic moment values [20]. Except for Sm³⁺ and Eu³⁺ where contributions from low-lying paramagnetic excited states add to the magnetic moment, the spin-orbit μ_{eff} equation predicts the magnetic moment for trivalent lanthanides better than $\mu_{eff} = \sqrt{n(n+2)}$. Most lanthanide species are paramagnetic. Exceptions occur when 4f is empty (0) or full (14). In Gd³⁺, 4f⁷, all electrons have parallel spin. Gd does not form an antiferromagnetic structure [20,22]. Some antiferromagnetic lanthanides are subject to metamagnetism, where they switch from an antiferromagnetic state to a ferromagnetic state in a suitably high external magnetic field [20,22].

5.2 Methods and Materials

Platinum electrodes are modified with Nafion[®] films and magnetized composites of chemically inert, magnetic microparticles suspended in a Nafion film. Lanthanide

State	Lanthanide	Pr	Sm	Gd	Dy	Yb
3+	Electronic Configuration [Xe]	$4f^2$	$4f^5$	$4f^7$	$4f^9$	$4f^{13}$
	# Unpaired Electrons	2	5	7	5	1
	$\mu_{eff} \ (\mu \mathbf{B}) = \sqrt{n(n+2)}$	2.83	5.92	7.94	5.92	2.45
	Spin-Orbit μ_{eff} (µB)	3.58	0.85^{*}	7.94	10.63	4.53
	Measured μ_{eff} (µB)	3.48	1.64^{*}	7.97	10.60	4.47
2+	Electronic Configuration [Xe]	$4f^3$	$4f^6$	$4f^8$	$4f^{10}$	$4f^{14}$
	# Unpaired Electrons	3	6	6	4	0
	$\mu_{eff} \ (\mu \mathbf{B}) = \sqrt{n(n+2)}$	3.87	6.93	6.93	4.90	0.00
	Spin-Orbit μ_{eff} (µB)	3.68	0.00*	9.72	10.60	0.00
	Measured μ_{eff} (µB)	3.44	3.36^{*}	9.81	10.70	0.00
0	Electronic Configuration [Xe]	$4f^36s^2$	$4f^66s^2$	$4f^75d^16s^2$	$4f^{10}6s^2$	$4f^{14}6s^2$
	# Unpaired Electrons	3	6	8	4	0

Table 17. Electronic configurations and calculated magnetic moments for various lanthanides with different oxidation states

*Experimentally, Sm³⁺ has higher magnetic moments than calculated from spin-orbit.

trifluoromethanesulfonate compounds are electrochemically evaluated in an acetonitrile system. Analysis is done by cyclic voltammetry in a three electrode setup. The film preparation, magnetization, and electrochemical analysis are described below. Many of the protocols are as described in Chapter 4.

5.2.1 Electrode and Solution Preparation

Platinum electrodes (Pine Instruments, $A = 0.452 \text{ cm}^2$) are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 MΩ water and dried in air before film modification. Electrodes are modified with either a Nafion only film or a composite of methyl-siloxane coated maghemite microparticles (SiMag-C1, volume magnetic susceptibility 16.1 ± 0.8 μ cgs) in Nafion. Nafion only films are made by casting 5.0 μ L of Nafion solution (5 % w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface. The casting solvents evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the plane of the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 5.0 μ L, the density of Nafion in acetonitrile solution, and the electrode area, the film will be $\sim 7 \mu$ m thick when immersed in the acetonitrile solution [52].

To prepare magnetized composites of Nafion and SiMag-C1 particles, an aqueous suspension of particles is mixed in a microcentrifuge tube with the Nafion suspension in a 1:20 volumetric ratio to yield a 6 % w/w loading of particles in the dry composite film. Immediately before casting the film, the solution is briefly vortexed (5 seconds) to ensure complete and even suspension of the particles and Nafion. 5 μ L of the Nafion + SiMag-C1 solution is cast onto the electrode surface. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. The film air dries for ≥ 24 hours. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. As shown in the diagram in Figure 7, a NdFeB ring magnet (o.d. = 7.6 cm, i.d. = 3.8 cm, 1.3 cm height) is placed around the electrode such that the electrode is in the center of the ring and the electrode surface is in the same plane as the magnet. A Teflon cylinder is still placed around the electrode to protect it from dust but still allow air flow, and the film air dries for \geq 24 hours. The ring magnet is removed after the first hour. A photograph of the Teflon cylinder with ring magnet drying setup is provided in Figure 8. On visual inspection, the Nafion only and Nafion + SiMag-C1 films look the same.

Redox probes are all lanthanide trifluoromethanesulfonate compounds

(Sigma), referred to generally as LnOTf. Solutions of LnOTf and electrolyte tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma) are prepared in acetonitrile (Fisher, dried over 4A molecular sieves). Trifluoromethanesulfonate (short name triflate) is a ligand that closely resembles the side chains of Nafion as shown in Figure 19. Three triflate ligands chelate one lanthanide ion in the 3+ oxidation state. For most experiments, solutions are 1.00 mM LnOTf and 0.10 M TBABF₄. If other concentrations are used, the ratio of electrolyte to redox probe remains 100:1. Lanthanides investigated are ytterbium (Yb), samarium (Sm), dysprosium (Dy), praseodymium (Pr), and gadolinium (Gd). Background/blank measurements are made with 0.10 M TBABF₄ only in acetonitrile.

5.2.2 Electrochemical Measurements

A three electrode setup is used for all electrochemical measurements. All measurements are made in the LnOTF and TBABF₄ acetonitrile solutions except as noted. Films equilibrate for ≥ 5 hours before applying a potential, and reequilibrate for 30 minutes between each scan. The redox probe takes less time to equilibrate into Nafion in acetonitrile than in water. This is confirmed by measurements taken at intervals after the Nafion modified electrode is placed in the probe solution until a reproducible maximum current is achieved. Nitrogen is bubbled into the solution between scans and a nitrogen blanket is maintained during scans. A three neck flask is modified with an additional inlet. Each electrode is inserted through one of the joints. A gas line is fed through the fourth joint. All openings are parafilmed to maintain an inert atmosphere under nitrogen sparge. See Figure 20 for a diagram of the cell. Triplicate measurements are completed for each lanthanide triflate and at each scan rate. The working electrode is a platinum disk (Pine Instruments, $A = 0.452 \text{ cm}^2$), the counter electrode is platinum mesh, and the reference electrode is a Ag/AgO quasireference electrode (QRE). Ferrocene (+0.64 V vs NHE) is used as an internal reference.

Cyclic voltammetry is performed (CH Instruments 760B potentiostat) at scan rates 20, 50, 75, 150, and 200 mV/s in a randomized order. The potential is swept from +1.5 V to -2.0 V to +2.0 V vs. Ag/AgO QRE; the forward sweep is then immediately repeated from +2.0 V to -2.0 V.

5.3 Results and Discussion

Voltammetric results for electrodes modified with Nafion films and Nafion + SiMag-C1 composites are discussed. Then, a method of lanthanide separation utilizing shifts in formal potential is investigated theoretically.

5.3.1 Electrochemical Measurements

When possible, the same solution is used for the Nafion films and Nafion + SiMag-C1 composites. Otherwise, currents are normalized by concentration of the redox probe. Data for electrodes modified with Nafion only films are labelled N and data for electrodes modified with Nafion + SiMag-C1 composites are labelled C1. Analysis focuses on how the introduction of magnetic microparticles changes the cyclic voltammetric response with specific focus on changes in the difference the peak potentials between waves A and B $\Delta\Delta E_{AB}$ (where $\Delta E_{AB} = |E_B - E_A|$ and $\Delta \Delta E_{AB} = \Delta E_{AB,C1} - \Delta E_{AB,N}$ and changes in peak currents at A and B.

Ytterbium: Figure 41 is an overlay of 20 mV/s cyclic voltammograms for ytterbium triflate at electrodes modified with a Nafion film and a Nafion + SiMag-C1 composite. The voltammetry for the composite is better resolved and more chemically reversible than for Nafion only. The current is higher when magnets are present, particularly for peak B. Peak A (Yb^{3+/2+}) currents increase 24 ± 6 % and peak B (Yb^{2+/0}) currents increase 34 ± 14 %. For n electrons in the electron transfer step, this corresponds to a current increase for both waves of 24 (n^{1/2}) %. ΔE_{AB} increases by 70 mV as E_A shifts more positive than E_B . Yb^{3+/2+} goes from [Xe]4f¹³ to [Xe]4f¹⁴ (1 unpaired electron to zero unpaired electrons) and 4.53 μ B to 0.00 μ B. Yb^{2+/0} goes from [Xe]4f¹⁴ to [Xe]4f¹⁴6s². There is no change in the number of unpaired electrons. The larger shift in wave A than B is consistent with either a faster heterogeneous electron transfer or faster following reaction or both.

Samarium: Figure 42 is an overlay of 20 mV/s cyclic voltammograms for samarium triflate at electrodes modified with a Nafion film and a Nafion + SiMag-C1 composite. The voltammetry for the composite is better resolved and more chemically reversible than for Nafion only. The current is higher when magnets are present for peak B. Peak A (Sm^{3+/2+}) currents decrease 1 ± 6 % and peak B (Sm^{2+/0}) currents increase 40 ± 3 %. ΔE_{AB} increases by 40 mV as E_A shifts more positive than E_B . Sm^{3+/2+} goes from [Xe]4f⁵ to [Xe]4f⁶ (3 unpaired electrons to 4 unpaired electrons) and 0.85 µB to 0.00 µB, where 0.00 µB results from no unpaired spins in the Sm²⁺ complex. Experimentally, Sm³⁺ has a magnetic moment of 1.64



Figure 41. Overlay of 20 mV/s cyclic voltammograms for ytterbium triflate at electrodes modified with a Nafion film (black solid line) and a Nafion + SiMag-C1 composite (red dashed line). Current is normalized by solution concentration.



Figure 42. Overlay of 20 mV/s cyclic voltammograms for samarium triflate at electrodes modified with a Nafion film (black solid line) and a Nafion + SiMag-C1 composite (red dashed line). Current is normalized by solution concentration.

 μ B because contributions from low-lying paramagnetic excited states add to the magnetic moment. Sm^{2+/0} goes from [Xe]4f⁶ to [Xe]4f⁶6s². There is no change in the number of unpaired electrons.

Dysprosium: Figure 43 is an overlay of 20 mV/s cyclic voltammograms for dysprosium triflate at electrodes modified with a Nafion film and a Nafion + SiMag-C1 composite. The voltammetry for the composite is better resolved than for the film. The current is higher when magnets are present for both peak A and peak B. Peak A (Dy^{3+/2+}) currents increase 24 ± 6 % while peak B (Dy^{2+/0}) currents increase 30 ± 11 %. For n electrons in the electron transfer step, this corresponds to a current increase for both waves of ~24 (n^{1/2}) %, a value similar to YbOTf. ΔE_{AB} increases by 60 mV as E_A shifts more positive than E_B . Dy^{3+/2+} goes from [Xe]4f⁹ to [Xe]4f¹⁰ (5 unpaired electrons to 4 unpaired electrons) and 10.63 µB to 10.60 µB. Dy^{2+/0} goes from [Xe]4f¹⁰ to [Xe]4f¹⁰6s². There is no change in the number of unpaired electrons as they are added to the 6s orbital.

Gadolinium: Figure 44 is an overlay of 20 mV/s cyclic voltammograms for gadolinium triflate at electrodes modified with a Nafion film and a Nafion + SiMag-C1 composite. The voltammetry for the composite is somewhat better resolved than for the film. The current is higher when magnets are present, particularly for peak B. Peak A (Gd^{3+/2+}) currents increase 2 ± 2 % and peak B (Gd^{2+/0}) currents increase 28 ± 9 %. ΔE_{AB} increases by 30 mV as E_A shifts more positive than E_B . Gd^{3+/2+} goes from [Xe]4f⁷ to [Xe]4f⁸ (7 unpaired electrons to 6 unpaired electrons) and 7.94 µB to 9.72 µB. Gd^{2+/0} goes from [Xe]4f⁸ to [Xe]4f⁷5d¹6s² (6 unpaired electrons to 8 unpaired electrons).



Figure 43. Overlay of 20 mV/s cyclic voltammograms for dysprosium triflate at electrodes modified with a Nafion film (black solid line) and a Nafion + SiMag-C1 composite (red dashed line). Current is normalized by solution concentration.



Figure 44. Overlay of 20 mV/s cyclic voltammograms for gadolinium triflate at electrodes modified with a Nafion film (black solid line) and a Nafion + SiMag-C1 composite (red dashed line). Current is normalized by solution concentration.

Praseodymium: Figure 45 is an overlay of 20 mV/s cyclic voltammograms for praseodymium triflate at electrodes modified with a Nafion film and a Nafion + SiMag-C1 composite. The voltammetry for the composite is better resolved than for the film. The current is higher when magnets are present. Peak A ($Pr^{3+/2+}$) currents increase 12 ± 4 % and peak B ($Pr^{2+/0}$) currents increase 16 ± 10 %. The current is again increased in proportion to the number of electrons, $12 (n^{1/2})$ %, but the overall increase is about half of YbOTf. ΔE_{AB} decreases by 270 mV as E_B shifts more positive than E_A . $Pr^{3+/2+}$ goes from [Xe]4f² to [Xe]4f³ (2 unpaired electrons to 3 unpaired electrons) and 3.58 µB to 3.68 µB. $Pr^{2+/0}$ goes from [Xe]4f³ to [Xe]4f³6s². There is no change in the number of unpaired electrons.

Table 18 lists peak potentials for the reductive wave peaks A and B, E_A and E_B , and their corresponding peak currents for the first and second sweeps, i_{pA1} , i_{pB1} , i_{pA2} , and i_{pB2} , for the 20 mV/s scans of the first and second redox reactions for all LnOTfs for Nafion modified electrodes and Nafion + SiMag-C1 modified electrodes. Currents are normalized to 1 mM concentrations of LnOTf. Table 19 lists ΔE_{AB} s for all LnOTfs for Nafion modified electrodes and Nafion + SiMag-C1 modified electrodes as well as peak current ratios of i_p for C1 divided by i_p for N. Table 20 lists the difference in ΔE_{AB} s, $\Delta \Delta E_{AB}$, between Nafion modified electrodes and Nafion + SiMag-C1 modified electrodes for each LnOTf and percent current increases for peaks A and B as the ratio of C1 to Nafion electrodes averaged across all scan rates. Tables 21 and 22 give peak currents for the first and second sweeps, i_{pA1} , i_{pB1} , i_{pA2} , and i_{pB2} and corresponding peak potentials E_A and E_B for 20, 50, and 200 mV/s scan rates for each LnOTf for electrodes modified with Nafion and



Figure 45. Overlay of 20 mV/s cyclic voltammograms for praseodymium triflate at electrodes modified with a Nafion film (black solid line) and a Nafion + SiMag-C1 composite (red dashed line). Current is normalized by solution concentration.

Table 18. Potentials and peak currents for 20 mV/s scans of reductive peaks A and B for various lanthanide triflates at electrodes modified with Nafion films (N) and Nafion + SiMag-C1 composites (C1) (n = 3)

				Peak Forward Currents (μ A/mM)				
Film	Ln	E_A (V)	E_B (V)	i _{pA1}	i_{pB1}	i _{pA2}	i_{pB2}	
N	Yb	$-0.38_2 \pm 0.01$	-1.11 ± 0.01	74.7 ± 1.5	78.0 ± 1.6	72.1 ± 1.3	76.5 ± 1.5	
	Sm	$-0.38_2 \pm 0.02$	-1.10 ± 0.02	89.8 ± 1.8	87.5 ± 1.8	85.5 ± 2.0	80.8 ± 1.5	
	Dy	$-0.33_2 \pm 0.01$	-1.06 ± 0.01	88.1 ± 1.7	94.0 ± 2.1	977 ± 30	97.4 ± 1.6	
	Gd	$-0.41_0 \pm 0.05$	-1.12 ± 0.02	92.4 ± 2.0	106 ± 3	89.5 ± 1.6	94.2 ± 2.1	
	Pr	$-0.36_1 \pm 0.01$	-1.42 ± 0.10	91.7 ± 2.3	130 ± 5	95.1 ± 2.1	98.6 ± 2.8	
C1	Yb	$-0.30_4 \pm 0.01$	-1.10 ± 0.01	89.4 ± 3.0	100 ± 4	92.9 ± 2.0	96.2 ± 1.5	
	Sm	$-0.31_7 \pm 0.01$	-1.07 ± 0.08	92.4 ± 1.1	116 ± 2	86.5 ± 0.8	115 ± 2	
	Dy	$-0.24_6 \pm 0.01$	-1.01 ± 0.01	126 ± 3	132 ± 5	116 ± 2	125 ± 3	
	Gd	-0.304 ± 0.001	-1.05 ± 0.05	86.0 ± 1.5	128 ± 4	81.8 ± 1.2	92.6 ± 1.7	
	Pr	$-0.33_2 \pm 0.03$	-1.12 ± 0.01	103 ± 2	119 ± 3	93.1 ± 1.8	114 ± 2	

Table 19. Potential differences and peak current ratios between peaks A and B for various lanthanide triflates at electrodes modified with Nafion films (N) and Nafion + SiMag-C1 composites (C1) averaged across all scan rates (n = 3)

			Peak Current Ratios $(i_p C1/i_p N)$					
Ln	$\Delta E_{AB} \ N \ (mV)$	$\Delta E_{AB} \operatorname{C1} (\mathrm{mV})$	i _{pA1}	i_{pB1}	i _{pA2}	i_{pB2}		
Yb	730 ± 50	800 ± 20	1.19 ± 0.06	1.40 ± 0.10	1.28 ± 0.01	1.27 ± 0.18		
Sm	720 ± 50	760 ± 20	0.95 ± 0.07	1.35 ± 0.03	1.03 ± 0.05	1.44 ± 0.03		
Dy	700 ± 50	760 ± 20	1.24 ± 0.07	1.31 ± 0.07	1.23 ± 0.04	1.29 ± 0.16		
Gd	710 ± 50	740 ± 20	1.08 ± 0.02	1.18 ± 0.05	0.95 ± 0.02	1.37 ± 0.14		
\Pr	1060 ± 70	790 ± 20	1.15 ± 0.03	1.10 ± 0.04	1.09 ± 0.06	1.22 ± 0.15		

Nafion + SiMag-C1 composites.

An example of evidence for variation with magnetic properties is shown in Figure 47 where peak currents vary with the magnetic moment of the Ln^{3+} . This is not a full description of correlation of magnetic impacts on currents, but highlights some of the patterns and the magnitude of the effects observed upon magnetic modification. Figure 46 shows 20 mV/s scans of all lanthanide triflates at electrodes modified with Nafion films and Nafion + SiMag-C1 composites on the same plot.

Table 20. Change in potential difference between peaks A and B and percent increase in current for various lanthanide triflates at electrodes modified with Nafion films (N) and Nafion + SiMag-C1 composites (C1) (n = 3)

Ln	$\Delta \Delta E_{AB} (\mathrm{mV})$	% Current Increase, Peak A	% Current Increase, Peak B
Yb	70 ± 30	24 ± 6	34 ± 14
Sm	40 ± 20	-1 ± 6	40 ± 3
Dy	60 ± 30	24 ± 6	30 ± 11
Gd	30 ± 10	2 ± 2	28 ± 9
\Pr	-270 ± 60	12 ± 4	16 ± 10

Table 21. Potentials and peak currents for 20, 50, and 200 mV/s scans of reductive peaks A and B for ytterbium, samarium, and dysprosium triflates at electrodes modified with Nafion films (N) and Nafion + SiMag-C1 composites (C1) (n = 3)

						Peak Forward Currents (μ A/mM)			
Ln	Film	v (mV/s)	E_A (V)	E_B (V)	i _{pA1}	i_{pB1}	i _{pA2}	i_{pB2}	
Yb	N	200	$-0.55_3 \pm 0.01$	-1.37 ± 0.01	254 ± 5	252 ± 5	182 ± 4	219 ± 9	
		50	$-0.40_3 \pm 0.01$	-1.15 ± 0.02	121 ± 5	127 ± 5	111 ± 4	131 ± 3	
		20	$-0.38_2 \pm 0.01$	-1.11 ± 0.01	747 ± 2	78.0 ± 2	72.1 ± 1	76.4 ± 1	
	C1	200	$-0.37_4 \pm 0.01$	-1.28 ± 0.01	279 ± 5	324 ± 9	229 ± 5	270 ± 8	
		50	$-0.33_9 \pm 0.01$	-1.17 ± 0.01	148 ± 3	180 ± 3	142 ± 5	144 ± 5	
		20	$-0.30_4 \pm 0.01$	-1.10 ± 0.01	89.4 ± 3	100 ± 4	92.9 ± 2	96.2 ± 2	
Sm	N	200	$-0.61_8 \pm 0.02$	-1.25 ± 0.02	345 ± 9	205 ± 5	214 ± 6	190 ± 7	
		50	$-0.37_4 \pm 0.02$	-1.17 ± 0.02	167 ± 5	156 ± 5	151 ± 5	138 ± 5	
		20	$-0.38_2 \pm 0.02$	-1.10 ± 0.02	89.8 ± 2	87.5 ± 2	85.5 ± 2	80.8 ± 1	
	C1	200	$-0.38_2 \pm 0.01$	-1.07 ± 0.05	306 ± 5	284 ± 8	235 ± 5	280 ± 9	
		50	$-0.36_8 \pm 0.01$	-1.14 ± 0.06	156 ± 5	209 ± 7	150 ± 5	197 ± 4	
		20	$-0.31_7 \pm 0.01$	-1.07 ± 0.08	92.4 ± 1	116 ± 2	86.5 ± 1	115 ± 2	
Dy	N	200	$-0.39_6 \pm 0.02$	-1.14 ± 0.01	320 ± 10	264 ± 5	208 ± 5	216 ± 6	
		50	$-0.33_9 \pm 0.01$	-1.08 ± 0.03	170 ± 5	183 ± 5	144 ± 5	174 ± 5	
		20	$-0.33_2 \pm 0.01$	-1.06 ± 0.01	88.1 ± 2	94.0 ± 2	977 ± 3	974 ± 2	
	C1	200	$-0.40_3 \pm 0.01$	-1.20 ± 0.01	355 ± 8	295 ± 5	263 ± 9	315 ± 9	
		50	$-0.32_5 \pm 0.01$	-1.07 ± 0.02	202 ± 6	259 ± 3	178 ± 5	196 ± 7	
		20	$-0.24_6 \pm 0.01$	-1.01 ± 0.01	126 ± 3	132 ± 5	116 ± 2	125 ± 3	



Figure 46. 20 mV/s cyclic voltammograms of full potential window first sweeps for Nafion film (solid lines) and Nafion + SiMag-C1 composite (dashed lines) modified platinum electrodes in praesodymium triflate (purple), gadolinium triflate (yellow), dysprosium triflate (red), samarium triflate (green), and ytterbium triflate (blue). Electrolyte is TBABF₄ in acetonitrile for all. Voltammograms are plotted at a vertical offset for clarity, so a 100 μ A current scale is shown at left.



Figure 47. Plot of peak current ratios $i_p C1/i_p N$ for peak A (blue diamonds) and peak B (red squares) versus the Ln³⁺ magnetic moments (μ B).

Table 22. Potentials and peak currents for 20, 50, and 200 mV/s scans of reductive peaks A and B for gadolinium and praseodymium triflates at electrodes modified with Nafion films (N) and Nafion + SiMag-C1 composites (C1) (n = 3)

					Peak Forward Currents (μ A/mM)			
Ln	Film	v (mV/s)	E_A (V)	E_B (V)	i _{pA1}	i_{pB1}	i _{pA2}	i_{pB2}
Gd	Ν	200	$-0.50_3 \pm 0.04$	-1.27 ± 0.01	320 ± 9	273 ± 5	195 ± 5	192 ± 7
		50	$-0.37_4 \pm 0.01$	-1.19 ± 0.03	158 ± 5	175 ± 2	131 ± 3	159 ± 5
		20	$-0.41_0 \pm 0.05$	-1.12 ± 0.02	92.4 ± 2	106 ± 3	89.5 ± 2	94.2 ± 2
	C1	200	$-0.41_0 \pm 0.02$	-1.11 ± 0.01	344 ± 4	291 ± 5	184 ± 9	257 ± 6
		50	$-0.32_5 \pm 0.01$	-1.11 ± 0.01	127 ± 4	158 ± 4	120 ± 4	131 ± 6
		20	-0.304 ± 0.001	-1.05 ± 0.05	86.0 ± 2	128 ± 4	81.8 ± 1	92.6 ± 2
Pr	Ν	200	$-0.43_2 \pm 0.01$	-1.35 ± 0.01	307 ± 7	397 ± 6	221 ± 8	246 ± 8
		50	$-0.37_4\pm0.01$	-1.25 ± 0.01	161 ± 3	173 ± 3	115 ± 5	148 ± 2
		20	$-0.36_1 \pm 0.01$	-1.42 ± 0.10	$91{7} \pm 2$	130 ± 5	95.1 ± 2	98.6 ± 3
	C1	200	$-0.44_6 \pm 0.03$	-1.20 ± 0.03	301 ± 8	253 ± 6	170 ± 4	235 ± 5
		50	$-0.39_{6} \pm 0.01$	-1.23 ± 0.02	201 ± 2	224 ± 3	139 ± 5	191 ± 5
		20	$-0.33_2 \pm 0.03$	-1.12 ± 0.01	103 ± 2	119 ± 3	93.1 ± 2	114 ± 2

5.3.2 Separation Model

Lanthanide potentials are shifted in the magnetic field for the A and B waves and different magnitudes of shifts are observed for A and B. For these weak magnetic microparticles, the shifts are on average less than 100 mV but each lanthanide shifts differently with its magnetic properties. With stronger magnets and fields that can be turned on and off, effective separations are possible.

Consider two one electron reduction processes $O_1 + e \rightleftharpoons R_1$ and $O_2 + e \rightleftharpoons R_2$ with apparent formal potentials $E_1^{0'}$ and $E_2^{0'}$. Allow the initial concentrations of O_1 and O_2 to be c_1^* and c_2^* and that there are no chemical losses so that $c_1^* = [O_1] + [R_1]$ and $c_2^* = [O_2] + [R_2]$. For sufficient time to undertake bulk electrolysis, the Nernst equation governs the concentrations as

$$\frac{c_1^* - [O_1]}{[O_1]} = \exp\left[\frac{-F\left(E - E_1^{0'}\right)}{RT}\right]$$
(30)

$$\frac{O_1}{c_1^*} = f_{O_1} = \frac{1}{1 + \exp\left[-F\left(E - E_1^{0'}\right)/RT\right]}$$
(31)

$$\frac{[R_1]}{c_1^*} = f_{R_1} = 1 - f_{O_1} = \frac{\exp\left[-F\left(E - E_1^{0'}\right)/RT\right]}{1 + \exp\left[-F\left(E - E_1^{0'}\right)/RT\right]}$$
(32)

$$\overline{1 + \exp\left[F\left(E - E_1^{0'}\right)/RT\right]}$$

$$\frac{c_2^* - [O_2]}{[O_2]} = \exp\left[\frac{-F\left(E - E_2^{0'}\right)}{RT}\right]$$
(33)

$$\frac{[O_2]}{c_2^*} = f_{O_2} = \frac{1}{1 + \exp\left[-F\left(E - E_2^{0'}\right)/RT\right]}$$
(34)

$$\frac{[R_2]}{c_2^*} = f_{R_2} = 1 - f_{O_2} = \frac{\exp\left[-F\left(E - E_2^{0'}\right)/RT\right]}{1 + \exp\left[-F\left(E - E_2^{0'}\right)/RT\right]}$$
(35)
$$= \frac{1}{1 + \exp\left[F\left(E - E_2^{0'}\right)/RT\right]}$$

For a potential applied to the electrode E, the fractional concentrations of R_1 and R_2 , f_{R_1} and f_{R_2} , respectively, will vary dependent on c_1^* , c_2^* , $E_1^{0'}$, and $E_2^{0'}$ as

$$\frac{f_{R_1}}{f_{R_2}} = \frac{1 + \exp\left[F\left(E - E_2^{0'}\right)/RT\right]}{1 + \exp\left[F\left(E - E_1^{0'}\right)/RT\right]} = \frac{1 + \exp\left[F\left(E - \left(E_1^{0'} + \Delta E\right)\right)/RT\right]}{1 + \exp\left[F\left(E - E_1^{0'}\right)/RT\right]}$$
(36)

 f_{R_1} and f_{R_2} measure the extent of electrolysis and $\Delta E = E_2^{0'} - E_1^{0'}$.

$$\frac{f_{R_1}}{f_{R_2}} = \frac{1 + \exp\left[F\left(\left(E - E_1^{0'}\right) - \Delta E\right)/RT\right]}{1 + \exp\left[F\left(E - E_1^{0'}\right)/RT\right]}$$
(37)

In Figure 48 and Table 20, f_{R_1}/f_{R_2} is shown for various separations of $E_1^{0'}$ and $E_2^{0'}$ (ΔE) as a function of applied potential E relative to $E_1^{0'}$ ($E - E_1^{0'}$). $E_2^{0'}$ is negative of $E_1^{0'}$. At 200 mV before $E_1^{0'}$, the relative conversion to R_1 and R_2 decreases as | ΔE | decreases. For the formal potentials separated by 100 mV ($\Delta E = -100$ mV),



Figure 48. The ratio f_{R_1}/f_{R_2} is shown for various separations of $E_1^{0'}$ and $E_2^{0'}$ (ΔE) as a function of applied potential relative to $E_1^{0'}$ ($E - E_1^{0'}$).
$E_1^{0'}$ (V)	0	0	0	0	0	0	0
$E_2^{0'}$ (V)	-0.100	-0.075	-0.050	-0.025	-0.010	-0.005	-0.001
$\Delta E \ (V) = E_2^{0'} - E_1^{0'}$	-0.100	-0.075	-0.050	-0.025	-0.010	-0.005	-0.001
$E - E_1^{0'}$ (V)				f_{R_1}/f_{R_2}			
0.200	48.989	18.515	6.998	2.645	1.476	1.215	1.040
0.100	48.049	18.172	6.881	2.613	1.466	1.211	1.039
0.050	43.008	16.333	6.251	2.440	1.416	1.188	1.035
0.025	35.841	13.717	5.355	2.194	1.345	1.156	1.029
0.010	29.618	11.445	4.577	1.981	1.284	1.128	1.024
0.000	25.004	9.761	4.000	1.823	1.238	1.107	1.020
-0.010	20.391	8.078	3.424	1.665	1.192	1.087	1.016
-0.025	14.168	5.806	2.646	1.451	1.131	1.059	1.011
-0.050	7.001	3.190	1.750	1.206	1.059	1.027	1.005
-0.100	1.960	1.350	1.120	1.033	1.010	1.004	1.001
-0.200	1.020	1.007	1.002	1.001	1.000	1.000	1.000

Table 23. Ratio of fractional concentrations of species R1 and R2 when O1 and O2 have been electrolyzed at potential E

the fraction of R_1 to R_2 is almost 50 to 1. For lesser separations of the E⁰'s of -0.075, -0.050, -0.025,-0.010, -0.005, and -0.001 V, f_{R_1}/f_{R_2} decreases as 18.5, 7, 2.6, 1.5, 1.2, and 1.0. The ability to electrolyze R_1 while limiting electrolysis of R_2 is diminished as ΔE approaches 0. The value of f_{R_1}/f_{R_2} is little changed as $E - E_1^{0'} > 0.050$ V. As $E - E_1^{0'}$ decreases below 0.050 V, the discrimination between R_1 and R_2 decreases but the rate of electrolysis for both O_1 and O_2 increases. In any effective separation there is a tradeoff between good separation and efficient separation.

Consider the efficiency in terms of the amount of R_1 and R_2 generated by electrolysis at different values of $E - E_1^{0'}$ as $|\Delta E|$ decreases. In Figure 49, the fraction converted to R_1 is shown by the black line. This follows a simple Nernstian trajectory. The colored lines show the fraction of R_2 generated at $E - E_1^{0'}$ for different values of $|\Delta E|$. As $|\Delta E|$ decreases, the separation efficiency at a given electrode potential decreases. For example, when $E - E_1^{0'}$ and $\Delta E = -0.100$ V,



Figure 49. Fraction of species O_1 or O_2 reduced to R_1 or R_2 at potential $E - E_1^{0'}$ (V) for various $|\Delta E| = E_2^{0'} - E_1^{0'}$. The colored lines show the fraction of R_2 generated at $E - E_1^{0'}$ for different values of $|\Delta E|$. The fraction converted to R_1 is shown by the black line.

 $f_{R_1} = 0.5$ and $f_{R_2} = 0.02$ and the separation efficiency is good. But, when $E = E_1^{0'}$ and $\Delta E = -0.050$ V and -0.010 V, $f_{R_2} = 0.125$ and 0.4, which are substantial fractions of $f_{R_1} = 0.5$.

For a system where $E - E_1^{0'} = +0.025$ V, $f_{R_1} = 0.274$. If $\Delta E = -0.010$ V, $f_{R_2} = 0.204$ and R_1 and R_2 are poorly separated. If the apparent formal potential difference is shifted by 20 mV to $\Delta E = -0.030$ V, then $f_{R_2} = 0.105$. The discrimination for R_1 over R_2 is doubled.

From Table 18, the peak potentials for the waves A and B are closely grouped for each Nafion films and magnetic composites. But the relative positions of the peaks are spaced differently for Nafion compared to composites. By selective use of magnetic modification and Nafion films, the lanthanides can be separated because application of the field shifts potentials. For this discussion, the peak A and B potentials are used to crudely approximate the formal potentials. The experimental peak potentials may include substantial kinetic effects that can also be altered by magnetic fields. Kinetics provide an alternative means to separate the lanthanide species. The separations based on kinetics differ by mechanism but the general qualitative trends in the behavior are anticipated to be similar to the above Nernstian model. Further, the magnetic microparticles used in these studies sustain small fields. With microparticles able to sustain stronger fields, larger potential shifts are anticipated.

5.4 Conclusions

Magnets enhance the differences in the voltammetric responses for these several

lanthanide complexes. The peak A and peak B currents change differently for different LnOTfs and the potential differences between peaks A and B also change differently for different LnOTfs. This demonstrates that magnets can improve identification and separation of lanthanides. The use of magnetic materials, ligated lanthanides, and organic solvents on the benchtop can at least reduce the number of steps to identify and separate lanthanide species. The effect is not yet well described fundamentally, but for the lanthanides there are correlations (albeit complicated) with the magnetic properties. A model suggests even peak potential shifts as small as 50 to 100 mV would be effective for separation. One lanthanide triflate could be electrolyzed to a 2+ state while the other remained 3+. Then, the 2+ lanthanide could be complexed and removed from solution, leaving behind the 3+.

CHAPTER 6

MAGNETIC EFFECTS ON OXYGEN REDUCTION REACTION (ORR)

Many common electrochemical energy systems exploit the oxygen reduction reaction (ORR) as an air fed cathode reaction. Many low temperature proton exchange membrane (PEM) fuel cells (e.g., hydrogen, alcohol fuels with direct and indirect reformation, formic acid, ammonia) exploit the air available oxygen so as to not increase system weight by carrying an alternative oxidant. Other examples include primary zinc air (hearing aid) and aluminum air batteries and secondary lithium air batteries. In metal air batteries, stability is often enhanced by use of nonaqueous electrolytes. The ORR is attractive for energy systems because oxygen is ubiquitously available and the thermodynamic potential for the ORR is high. However, the kinetics of the ORR are slow and energy is lost to ORR kinetics on discharge of all oxygen fed electrochemical energy systems. Improved ORR kinetics improves the efficiency, energy, and power density of many electrochemical energy systems. Here, magnetic field effects on the ORR in nonaqueous electrolyte are evaluated. The solvent is acetonitrile and the electrolyte is tetrabutylammonium tetrafluoroborate ($TBABF_4$).

6.1 Introduction

In nonaqueous, a protic solvents, a quasireversible one electron reduction of O_2 is observed, which produces the paramagnetic superoxide radical $O_2^{\cdot-}$ [2, 12, 13].

$$O_2 + e \rightleftharpoons O_2^{\cdot -} \tag{38}$$

Nonaqueous ORR is important for metal air batteries [12-16]. Lithium air batteries involve the oxidation of lithium at the anode and the reduction of oxygen at the cathode. Lithium air batteries have extremely high theoretical specific energy $(5-15\times$ lithium ion batteries) and energy density (theoretically, 12 kWh/kg excluding the oxygen mass) comparable to gasoline (13 kWh/kg). However, lithium air batteries are not yet used commercially because research has not sufficiently overcome the slow oxygen kinetics. Most limitations in Li air battery development are engendered at the cathode by high overpotential of ORR and slow oxygen kinetics [17–19]. Usually, the cathode is a carbon electrode with incorporated metal (manganese and cobalt oxides) catalysts to decrease the overpotential. A methyl viologen redox catalyst $(MV^{2+}/MV^{+} \text{ couple})$ in acidic DMSO has also been investigated [2]. Lithium triflate is a commonly used electrolyte in lithium air batteries. Abraham, et al. showed that ORR in TBA⁺ electrolyte is analogous to ORR in Li⁺ electrolyte in acetonitrile [54]. What is shown here should be applicable to Li air batteries.

Here, fundamental studies of the catalytic effect of localized magnetic fields on the oxygen reduction reaction (ORR) in organic solvent acetonitrile and electrolyte tetrabutylammonium tetrafluoroborate (TBABF₄) are conducted. Electrodes are modified with magnetic particles suspended in Nafion. Platinum electrodes are modified with Nafion^(R) films and magnetized composites of chemically inert, magnetic microparticles suspended in a Nafion film. ORR is electrochemically evaluated in a TBABF₄ only acetonitrile system and an ytterbium triflate plus TBABF₄ in acetonitrile system. Analysis is done by cyclic voltammetry in a three electrode setup. The film preparation, magnetization, and electrochemical analysis are described below.

6.2.1 Electrode and Solution Preparation

Platinum electrodes (Pine Instruments, $A = 0.452 \text{ cm}^2$) are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. Electrodes are modified with either a Nafion only film or a composite of methyl-siloxane coated maghemite microparticles (SiMag-C1, volume magnetic susceptibility $16.1 \pm 0.8 \ \mu \text{cgs}$) in Nafion. Nafion only films are made by casting 5.0 μ L of Nafion solution (5 % w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface, then allowing the casting solvents to evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 5.0 μ L, the density of Nafion in acetonitrile solution, and the electrode area, the film will be $\sim 7 \ \mu$ m thick when immersed in the acetonitrile solution [52].

Magnetized films of Nafion + SiMag-C1, Nafion + SiMag-C3, and Nafion +SiMag-C8 are evaluated. SiMag-C8 particles have volumetric magnetic susceptibility of $8.7_8 \pm 0.1_2 \ \mu \text{cgs}$, SiMag-C3 particles have volumetric magnetic susceptibility of $1.02 \pm 0.08 \ \mu \text{cgs}$, and SiMag-C1 particles have volumetric magnetic susceptibility of $1.61 \pm 0.08 \ \mu \text{cgs}$. To prepare magnetized composites of Nafion + SiMag-Cx particles, an aqueous suspension of particles is mixed in a microcentrifuge tube with the Nation solution in a 1:20 volumetric ratio to yield a 6 % w/w loading of particles in the dry film. Immediately before casting the film, the solution is briefly vortexed (5) seconds) to ensure complete and even suspension of the particles and Nafion. 5.0 μ L of the Nafion + SiMag-Cx solution is cast onto the electrode surface. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. The film air dries for ≥ 24 hours. A Teflon cylinder is placed around the electrode to protect it from dust but still allow air flow. As shown in the diagram in Figure 7, a NdFeB ring magnet (o.d. = 7.6 cm, i.d. = 3.8 cm, 1.3 cm height) is placed around the electrode such that the electrode is in the center of the ring and the electrode surface is in the same plane. A Teffon cylinder is still placed around the electrode to protect it from dust but still allow air flow, and the film air dries for ≥ 24 hours. The ring magnet is removed after the first hour. A photograph of the Teflon cylinder with ring magnet drying setup is provided in Figure 8. On visual inspection, the Nafion only and Nafion + SiMag-Cx composite films look the same.

Solutions of 0.10 M tetrabutylammonium tetrafluoroborate (TBABF₄, Sigma) electrolyte only and solutions of 1.00 mM ytterbium trifluoromethanesulfonate (YbOTf, Sigma) and 0.10 M TBABF₄ are prepared in acetonitrile (Fisher, dried

with molecular sieve).

6.2.2 Electrochemical Measurements

A three electrode setup is used for all electrochemical measurements. All measurements are made in the YbOTF and TBABF₄ acetonitrile solutions except as noted. Films equilibrate for ≥ 5 hours before applying a potential, and reequilibrate for 30 minutes between each scan. The redox probe takes less time to equilibrate into Nafion in acetonitrile than in water. This is confirmed by measurements taken at intervals after the Nafion modified electrode is placed in the probe solution until a reproducible maximum current is achieved. Nitrogen is bubbled into the solution between scans and a nitrogen blanket is maintained during scans. A three neck flask is modified with an additional inlet. Each electrode is inserted through one of the joints. A gas line is fed through the fourth joint. All openings are parafilmed to maintain an inert atmosphere under nitrogen sparge. See Figure 20 for a diagram of the cell.

When ORR is investigated, solutions are saturated with oxygen. O_2 (g) is bubbled into the solution between scans and an oxygen blanket is maintained during each scan. The concentration of saturated O_2 (g) in acetonitrile is calculated to be 8 mM based on the value for O_2 (g) concentration in acetonitrile in air [53] and experimentally measured currents for a solution equilibrated in air and one saturated with O_2 (g). This saturated O_2 (g) concentration agrees with the value reported by Abraham et al. [54]. Triplicate measurements are completed for each solution at each scan rate. The working electrode is a platinum disk (Pine Instruments, $A = 0.452 \text{ cm}^2$), the counter electrode is platinum mesh, and the reference electrode is a Ag/AgO quasireference electrode (QRE). Ferrocene (+0.64 V vs NHE) is used as an internal reference. Cyclic voltammetry is performed (CH Instruments 760B potentiostat) where the potential is swept from +1.5 V to -2.0 V to +2.0 V vs. Ag/AgO QRE at 200 mV/s.

6.3 Results and Discussion

 $E_{p/2}$ is an experimental estimate of the standard potential E^0 calculated as halfway between E_f and E_r . Peak height ratios of i_{pf} and i_{pr} are an indication of chemical reversibility where $i_{pf}/i_{pr} = 1$ is anticipated for complete chemical reversibility. Peak splitting ΔE_p is an indication of electron transfer reversibility where 58 mV/n is defined as reversible. For ΔE_p larger than 58 mV/n, the electron transfer is quasireversible or irreversible, chemical steps excluded. When modification decreases a less than reversible ΔE_p , the system has been made more reversible. The more rapidly the current increase with potential sweep (i.e. the rise), the faster the electron transfer rate.

Figure 50 is an overlay of 200 mV/s cyclic voltammograms for a nitrogen sparged solution of 0.10 M TBABF₄ and oxygen saturated solutions of 0.10 M TBABF₄ at electrodes modified with a Nafion film and a magnetized Nafion + SiMag-C1 composite. There is no ORR signal when the solution is N₂ (g) sparged. The forward current increases by 19 ± 4 %, the peak splitting decreases by 436 ± 35 mV, and the E_{p/2} shifts positive by 130 ± 9 mV when magnets are present. The



Figure 50. Overlay of 200 mV/s cyclic voltammograms for a nitrogen sparged solution of 0.10 M TBABF₄ at a platinum electrode modified with a Nafion only film (N N2, black solid line) and oxygen saturated solutions of 0.10 M TBABF₄ in acetonitrile at platinum electrodes modified with a Nafion film (N O2, blue long dashed line) and a magnetized Nafion + SiMag-C1 composite (C1 O2, red short dashed line).

potential at half maximum forward current (E at $i_{pf}/2$) shifts by 90 ± 20 mV for the composite compared to the film. This corresponds to a decrease in the kinetic tax (overpotential) for the ORR.

Figure 51 is an overlay of cyclic voltammograms at electrodes modified with composites of three different SiMag-Cx particles. Behaviors are consistent with faster rates for higher magnetic susceptibility and the data in Figure 50. There is a linear correlation between the magnetic susceptibilities of the particles and the peak forward currents as shown in Figure 52. Figure 53 demonstrates there is also a linear correlation between the magnetic susceptibilities of the particles and peak splittings. Regression data are provided in the Figures.

Figure 54a is an overlay of 200 mV/s cyclic voltammograms for oxygen saturated solutions of 0.10 M TBABF₄ and 1.0 mM ytterbium triflate plus 0.10 M TBABF₄ at electrodes modified with a Nafion film. The forward current increases by 13 ± 5 %, the peak splitting decreases by 306 ± 28 mV, and the $E_{p/2}$ shifts negative by 240 ± 20 mV when YbOTf is present. The potential at $i_{pf}/2$ shifts by -170 ± 20 mV for the composite compared to the film. YbOTf is known to be a catalyst for Diels Alder reaction, but not for ORR.

Figure 54b is an overlay of 200 mV/s cyclic voltammograms for oxygen saturated solutions of 1.0 mM YbOTf + 0.10 M TBABF₄ at electrodes modified with a Nafion film and a magnetized Nafion + SiMag-C1 composite. The current increases by 33 ± 7 %, the peak splitting decreases by 750 ± 70 , and the $E_{p/2}$ shifts negative by 100 ± 6 mV when magnets are present. The potential at $i_{pf}/2$ shifts by 40 ± 20 mV for the composite compared to the Nafion. Even though $E_{p/2}$ shifts negative, the



Figure 51. Overlay of 200 mV/s cyclic voltammograms for oxygen saturated solutions of 0.10 M TBABF₄ in acetonitrile at platinum electrodes modified with composites of Nafion + SiMag-C1 (C1, red short dashed line), Nafion + SiMag-C3 (C3, blue long dashed line), and Nafion + SiMag-C8 (C8, green solid line).



Figure 52. Plot of peak forward currents (mA) versus volumetric magnetic susceptibility χ_v (µcgs) of the SiMag-Cx particles from ORR at platinum electrodes modified with composites of Nafion + SiMag-C1 (C1), Nafion + SiMag-C3 (C3), and Nafion + SiMag-C8 (C8) in 0.10 M TBABF₄ in acetonitrile. Regression analysis yields slope $(7.5_4 \pm 0.4_8) \times 10^4 \text{ mA}/\mu \text{cgs}$, intercept $1.07 \pm 0.06 \text{ mA}$, and R^2 0.9959. Error bars are standard deviation.



Figure 53. Plot of peak splittings (V) versus volumetric magnetic susceptibility χ_v (μ cgs) of the SiMag-Cx particles from ORR at platinum electrodes modified with Nafion films (N) and composites of Nafion + SiMag-C1 (C1), Nafion + SiMag-C3 (C3), and Nafion + SiMag-C8 (C8) in 0.10 M TBABF₄ in acetonitrile. Regression analysis yields slope $-(3.1_0\pm0.3_4)\times10^4$ V/ μ cgs, intercept 1.82 ± 0.04 V, and R² 0.9771. Error bars are standard deviation.



Figure 54. a) Overlay of 200 mV/s cyclic voltammograms for oxygen saturated solutions of 1.00 mM ytterbium triflate + 0.10 M TBABF₄ in acetonitrile (N YbOTF + O2, blue long dashed line) and 0.10 M TBABF₄ in acetonitrile (N O2, black solid line) at platinum electrodes modified with a Nafion film. b) Overlay of 200 mV/s cyclic voltammograms for oxygen saturated solutions of 1.00 mM ytterbium triflate + 0.10 M TBABF₄ at electrodes modified with a Nafion film (N YbOTF + O2, blue long dashed line) and a magnetized Nafion + SiMag-C1 composite (C1 YbOTF + O2, red short dashed line).

Table 24. Peak forward and reverse potentials, half potentials, and peak splitting data for electrodes modified with Nafion films and Nafion + SiMag-Cx composites in electrolyte only solution and ytterbium triflate + electrolyte solution, all saturated with oxygen, scan rate 200 mV/s (n = 3)

Film	Solution	E_{pf} (V)	E_{pr} (V)	$E_{p/2}$ (V)	$\Delta E_p (V)$	$E_{i_{pf}/2}$ (V)
N	O2	-1.91 ± 0.02	$-0.10_4 \pm 0.02$	-1.01 ± 0.01	1.81 ± 0.04	-1.40 ± 0.01
C1	O2	-1.57 ± 0.05	$-0.19_6 \pm 0.05$	$-0.88_0 \pm 0.02$	1.37 ± 0.10	-1.31 ± 0.01
C3	O2	-1.81 ± 0.03	$-0.10_5 \pm 0.04$	$-0.90_0 \pm 0.03$	1.50 ± 0.07	-1.33 ± 0.02
C8	O2	-1.69 ± 0.02	$-0.11_8 \pm 0.02$	$-0.90_3 \pm 0.03$	1.60 ± 0.04	-1.35 ± 0.02
N	YbOTf+O2	-2.00 ± 0.01	$-0.48_6 \pm 0.02$	-1.25 ± 0.01	1.50 ± 0.03	-1.57 ± 0.01
C1	YbOTf+O2	-1.67 ± 0.02	$-0.61_0 \pm 0.03$	-1.14 ± 0.03	1.06 ± 0.05	-1.36 ± 0.01

Table 25. Peak forward and reverse currents and peak current ratios for electrodes modified with Nafion films and Nafion + SiMag-C1 composites in electrolyte only solution and ytterbium triflate + electrolyte solution, all saturated with oxygen, scan rate 200 mV/s (n = 3)

Film	Solution	i_{pf} (mA)	i_{pr} (mA)
N	O2	1.70 ± 0.02	$-0.78_6 \pm 0.01$
C1	O2	2.28 ± 0.03	$-0.88_9 \pm 0.02$
C3	O2	1.86 ± 0.01	$-0.89_4 \pm 0.01$
C8	O2	1.72 ± 0.02	$-0.76_2 \pm 0.02$
N	YbOTf+O2	1.95 ± 0.02	$-0.59_6 \pm 0.01$
C1	YbOTf+O2	2.28 ± 0.02	$-0.59_5 \pm 0.02$

positive shift in E at $i_{pf}/2$ indicates a decrease in the kinetic tax (overpotential) for the ORR.

Tables 24 and 25 list peak forward and reverse currents i_{pf} and i_{pr} , peak current ratios i_{pf}/i_{pr} , peak forward and reverse potentials E_{pf} and E_{pr} , $E_{p/2}$ s, and peak splitting values for the four variations investigated: O₂ in TBABF₄ only at electrodes modified with Nafion only, Nafion + SiMag-C1, Nafion + SiMag-C3, and Nafion + SiMag-C8; and O₂ in YbOTf and TBABF₄ at electrodes modified with Nafion only and Nafion + SiMag-C1. Table 26 compares these variations to each other

Table 26. Comparative peak current ratios and differences in half potentials and peak splittings for electrodes modified with Nafion films and Nafion + SiMag-C1 composites in electrolyte only solution and ytterbium triflate + electrolyte solution, all saturated with oxygen, scan rate 200 mV/s (n = 3)

F or S	Solution(s)	Film(s)	i_{pf} ratio	i _{pr} ratio	$\Delta E_{p/2}$	$\Delta \Delta E_p$	$\Delta E_{i_{pf}/2}$
				-	$(m\dot{V})$	(mV)	(mV)
F	O_2	N & C1	1.19 ± 0.04	1.13 ± 0.06	130 ± 9	436 ± 35	90 ± 20
F	$YbOTf+O_2$	N & C1	1.17 ± 0.04	1.00 ± 0.03	110 ± 8	443 ± 35	210 ± 20
S	O_2 & YbOTf+ O_2	N	1.13 ± 0.05	0.76 ± 0.06	-240 ± 20	306 ± 28	-170 ± 20
S	O_2 & YbOTf+ O_2	C1	1.11 ± 0.02	0.67 ± 0.05	-260 ± 20	310 ± 29	-50 ± 20
F & S	$O_2 \& YbOTf+O_2$	N & C1	1.33 ± 0.07	0.76 ± 0.02	-100 ± 6	750 ± 70	40 ± 20

with peak forward current ratios, changes in $E_{p/2}$, and changes in peak splitting. To read the table, an F in the comparison column means two solutions are compared for the same film. An S in the comparison column means two films are compared for the same solution. The last row of Table 26 compares O₂ in TBABF₄ only at a Nafion modified electrode with O₂ in YbOTf and TBABF₄ at a Nafion + SiMag-C1 composite modified electrode. Ratios are always calculated for the Nafion only film in the denominator or O2 only in the denominator. $\Delta E_{p/2}$ and $\Delta \Delta E_p$ are always calculated for C1 minus N value or YbOTf+O2 minus O2.

6.4 Conclusions

Evidence of enhanced electron transfer kinetics is observed. When magnets are present in the O₂ (g) saturated electrolyte only solution, currents increase by almost 20 %, the peak splitting is reduced by more than 400 mV, and the overpotential is reduced ($E_{p/2}$ and E at $i_{pf}/2$ shift positive) by ~100 mV, indicating the reaction is more reversible when catalyzed by magnetic fields. When ytterbium triflate is present, currents are increased by a net 33 % change and peak splitting is reduced by a net 750 mV change. $E_{p/2}$ shifts negative by a net 100 mV, but the overpotential E at $i_{pf}/2$ decreases by a net 40 mV change.

These preliminary results have significant implications for nonaqueous metal air batteries, as $M + O_2 \rightleftharpoons M^+ + O_2^{--}$ is analogous to $O_2 + e \rightleftharpoons O_2^{--}$. Improved performance is anticipated either when cathodes are formed by adding magnets or YbOTf is added to the battery electrolyte or both. Here, a novel means to catalyzed the ORR in a nonaqueous solvent is reported, but the mechanism remains unknown.

CHAPTER 7

DIFFUSION IN A GRADED DENSITY FILM

The full version of Fick's second law includes a spatially varying diffusion coefficient. As a consequence, if variation in viscosity is established, the diffusion coefficient will vary spatially, and near steady state transport will result without mechanical stirring. Here, a graded viscosity film is established at the electrode surface with the graded density polymer Ficoll^(R). Flux of redox probes through the graded density film is mapped as cyclic voltammograms with the sigmoidal morphologies characteristic of steady state transport. Graded densities are mapped spectroscopically and simulations vet the observed response.

7.1 Introduction and Background

The ability to design steady state transport into a film at a surface has applications in fields such as microfluidics, coatings, pharmaceutics, and fuel cells. To date, steady state diffusion has only been achievable by mechanical stirring such as achieved at rotating disks and flow cells and at small electrodes such as microdisks and microbands. Here, through exploitation of the full expression of Fick's second law, it is demonstrated that a density graded film on an electrode passively induces near steady state transport of the electroactive species through the film to the electrode. See Appendix A for a derivation of steady state flux from Fick's second law. Experimentally, the density gradient is established by an adsorbed, highly branched polymer that forms a brush structure [57] as illustrated in Figure 55.



Figure 55. Representation of a brush structure polymer film (orange squiggles), which results in a higher density of polymer at the surface of the electrode (diagonally striped rectangle) and a lower density far from the electrode into the solution.

Adsorbed polymers affect the kinetics, equilibria, and mass transport of electrochemical processes by changing how the electroactive species approaches the electrode. Cyclic voltammetry is used to characterize mass transport through modified electrodes, including electrochemically inactive polymer films. The flux of an electroactive species at the electrode surface controls the rate of the reaction and, thus, the faradaic current measured. Under transient conditions and semi-infinite linear diffusion to a large planar electrode, the current decays to zero. Steady state diffusion occurs under conditions such as rotating a disk electrode in which a boundary layer is established and with microelectrodes in which radial diffusion dominates [58]. Modification of a large, planar electrode with a graded density film achieves similar effects for transient methods. This is explained by the expanded version of Fick's second law (Equation 39) that allows for a spatially varying diffusion coefficient D(x).

The common version of Fick's second law assumes a constant diffusion coefficient. The full version includes a diffusion coefficient D that varies in space. In one dimension, the change in concentration c of the diffusing species with respect to time t and space x is [59–61]

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[D(x) \frac{\partial c(x,t)}{\partial x} \right] = D(x) \frac{\partial^2 c(x,t)}{\partial x^2} + \frac{\partial D(x)}{\partial x} \frac{\partial c(x,t)}{\partial x}$$
(39)

The diffusion coefficient through a particular density of polymer is related to the viscosity of the polymer by the Einstein Stokes relationship (Equation 40).

$$D = \frac{k_B T}{6\pi\eta r} \tag{40}$$

The Einstein Smoluchowski relation states that the mobility of a species is proportional to the charge of the species z, its diffusion coefficient D, Faraday constant F, gas constant R, and temperature T [62]. Stokes' Law states that the mobility of a species is inversely equal to the drag coefficient, which can be expressed in terms of the viscosity of the medium through which the species is traveling. The Einstein Stokes relation relates the diffusion coefficient D to the Boltzmann constant k_B , temperature T, inverse viscosity η , and Stokes' radius r of the polymer film [63, 64]. Ficoll is a synthetic copolymer of epichlorohydrin and sucrose. It is commonly used for cell and blood component separation because Ficoll is a neutral, highly-branched, hydrophilic polymer that forms a density gradient in solution [65–67]. The viscosity of Ficoll is a direct function of its density in solution (See Figure 56). Ficoll establishes a density and viscosity gradient on the electrode surface. Voltammograms and current transients for redox probes at Ficoll modified electrodes reflect steady state and near steady state diffusion. The response scales with the steepness of the gradient. The diffusion of probes through a variety of polymer films with uniform density has been studied extensively [58, 68–70]. However, diffusion through films with a graded density has not previously been characterized. This focuses on its mass transport properties. A computer simulation for cyclic voltammetry is developed for redox probes that diffuse through a graded density film on the electrode where the density is highest at the electrode and decreases toward the film solution interface. The computer simulated voltammetric responses map the steady state and near steady state transport and scale with the steepness of the gradient. The following report describes the cyclic voltammetric and



Figure 56. Plot of the relative viscosity of Ficoll with respect to concentration (% w/v) in water. Product data provided by GE Health Sciences. 50 % w/v is the limit of solubility in water. The molecular structure of Ficoll, a copolymer of sucrose and epichlorohydrin, is shown at top.

microscopic characterization of a Ficoll (GE Health Sciences) film and its impact on transport properties.

7.2 Methods and Materials

Platinum electrodes are modified with various concentrations of Ficoll to establish different viscosity gradients. Analysis is by confocal microscopy and cyclic voltammetry in a nonaqueous electrolyte. The film preparation, microscopy, and electrochemical analysis are described below.

7.2.1 Confocal Microscopy

An aqueous solution of a 50.0 % w/v Ficoll PM 400 (Sigma, 400,000 MW) and 0.20 M 7-Hydroxy-8-phenylazo-1,3-naphthalenedisulfonic acid (Orange G, Sigma) is prepared. Serial dilutions of 35.0, 25.0, and 12.5 % w/v Ficoll/ 0.14, 0.10, and 0.050 M Orange G are prepared from the initial solution. The Orange G functions as a dye for the Ficoll. Orange G is a common gel electrophoresis loading dye for DNA studies. Commercial gel loading preparations of the dye (New England BioLabs Inc) often include Ficoll to anchor the Orange G and prevent flotation out of the gel.

See Figure 57a for a visual representation of how the film is cast on the edge of the glass slide. A 75.0 mm × 25.0 mm × 1.0 mm glass slide is set in clamps so that the 75.0 mm × 1.0 mm edge is parallel to the table and the 25.0 mm edge stands perpendicular to the benchtop. 12.0 μ L of a Ficoll + Orange G solution is cast along 30.0 mm of the top edge to cover a 30.0 mm × 1.0 mm surface area and dried in air for \geq 24 hours. A glass beaker is propped above the slide to protect it from dust but still allow air flow. 30.0 % w/w Polyvinyl alcohol (PVA; Sigma, 70-100,000 MW) + 0.20 M Orange G films are prepared the same way. Three films of each polymer solution are cast, imaged, and analyzed.

The film modified slide is then placed in a petri dish with the 75.0 mm \times 25.0 mm side down so that the edge with the film is now normal to the table (see Figure 57b). The petri dish is placed on the microscope (AmScope MT Series) stage and images of the dry film are recorded at 10× magnification (Field of View 700 μ m \times 560 μ m). 5.0 mL of acetonitrile (Aldrich) are then gently added to the petri dish so that the film is immersed and images are recorded every 5 minutes until the acetonitrile has evaporated and the film is once again dry. Films cast from the 12.5 % w/v Ficoll solution are hereafter referred to as 12.5%F; similar nomenclature is used for the other Ficoll solutions. Films cast from the 30.0 % w/w Polyvinyl alcohol solution are hereafter referred to as PVA.

ImageJ (NIH) is used to measure the film thicknesses and grayscale intensity profiles. A straight line is drawn normal to the glass slide, and a gray value versus distance profile is generated.

7.2.2 Cyclic Voltammetry

An organic electrolyte is used to prevent dissolution of the Ficoll film: 1.00 mM N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD, Aldrich) and 0.10 M tetrabutylammonium tetrafluoroborate (TBABF₄, Aldrich) in acetonitrile (Aldrich). A platinum disk working electrode with large surface area (Pine Instruments, $A = 0.452 \text{ cm}^2$), platinum mesh counter electrode, and Ag/AgO quasireference



Figure 57. Diagram of film preparation for microscopy. a) The film is cast on the thin edge of a glass microscope slide and dried. b) The slide is placed wide edge down in a petri dish on the microscope stand.

electrode are used in a three electrode cell in a 250 mL beaker.

Electrodes are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. 5.0 μ L of an aqueous Ficoll solution is cast onto the surface of a platinum working electrode held in a stand so that the planar electrode surface faces up, parallel to the table. The film air dries for ≥ 24 hours. A glass cylinder is placed around the electrode to protect it from dust but still allow air flow. Films cast from aqueous solutions of 12.5, 25.0, 35.0, and 50.0 % w/v Ficoll are investigated. Data are also collected for unmodified electrodes.

Cyclic voltammetry is performed (CH Instruments 760B potentiostat) at scan rates 2, 5, 10, 20, 50, 100 and 200 mV/s in a randomized order. A potential window of -0.1 V to 0.5 V vs Ag/AgO is scanned. Films equilibrate in electrolyte for \geq 5 hours before applying a potential, and reequilibrate for one hour between each subsequent scan. Three films of each Ficoll solution are cast and analyzed, and triplicate measurements are completed for each scan rate.

7.3 Results and Discussion

Microscopy is used to investigate the density profile of the Ficoll polymer films and cyclic voltammetry probes the mass transport properties of the films. Uniform density films of PVA serve for comparison.

7.3.1 Confocal Microscopy

Figures 58a and b are microscope images $(10 \times \text{magnification})$ of a dry Orange

G dyed 50%F film and an Orange G dyed 50%F film immersed in acetonitrile, respectively. The Orange G remains bound to the Ficoll and PVA. (This is not true for Nafion, in which the dye is clearly observed leaching into the solvent over time.) For Ficoll, a clear difference between the dry and wet films is observed. The film expands in the acetonitrile and a density gradient can be seen similar to that predicted in Figure 55. The Ficoll is most dense at the slide surface and becomes less dense further away from the slide. When the acetonitrile has evaporated, the film returns to the thickness and uniform density profile seen in Figure 58a. Imperfections along the rough edge of the glass slide are also observed. While not ideal, these imperfections do demonstrate that addition of the acetonitrile does not affect the magnification of the film; the same imperfections (with the same size) can be seen in each dry and wet image pair. Figures 59a and b plot the gray value intensity versus distance normal to the glass slide of a dry 50%F film and a 50%F film immersed in acetonitrile, respectively. When dry, the 50%F films have an average slope near zero of $-0.08_3 \pm 0.03_9$. When wet, they have an average slope of 0.600 ± 0.003 . Average slopes for the 12.5%F, 25%F, and 35%F films are given in Table 27.

As a control, images of orange G dyed polyvinyl alcohol are taken. Figures 58c and d are microscope images (10x magnification) of a dry PVA film and a PVA film immersed in acetonitrile, respectively. The PVA expands slightly when immersed in acetonitrile, but retains a uniform density. Figures 59c and d plot the gray value intensity versus distance from the glass slide of a dry PVA film and a PVA film immersed in acetonitrile, respectively. When dry, the PVA films have an average slope of 0.160 ± 0.166 gray value/ μ m from slide edge, effectively zero. When



Figure 58. Microscope images (10× magnification) of a) dry 50.0 % w/v Ficoll film, $\ell = 51 \pm 1 \ \mu m$, b) 50.0 % w/v Ficoll film in acetonitrile, $\ell = 218 \pm 8 \ \mu m$, c) dry 30.0 % w/w polyvinyl alcohol film, $\ell = 11 \pm 3 \ \mu m$, and d) 30.0 % w/w polyvinyl alcohol film in acetonitrile, $\ell = 19 \pm 2 \ \mu m$. In each image, the orange is the orange G dyed film. Below the orange films, the rough edges of the glass slide can be observed. Scale bar is 100 $\ \mu m$ in each image.



Figure 59. Profiles of gray scale intensity versus distance (μ m) from the glass slide are shown for a) dry 50.0 % w/v Ficoll film, b) 50.0 % w/v Ficoll film in acetonitrile, c) dry 30.0 % w/w PVA film, d) 30.0 % w/w PVA film in acetonitrile. Profiles taken in a straight line normal to the glass slide with ImageJ. Each profile is for a single line. 10 lines for each film are measured and vary by only 5 %. Note the thinner films and different scale for PVA.

wet, they have an average slope of 0.115 ± 0.155 gray value/ μ m from slide edge, also effectively zero. A swelling coefficient for PVA in acetonitrile is estimated as thickness wet/thickness dry = 1.7 ± 3 .

Lines drawn with ImageJ from the glass slide edge to the film edge measure film thickness. Three films of each FicoII solution are cast and analyzed, and ten lines are measured for each film. Averages \pm standard deviation are reported and regression analysis is done from these averages. 50%F film thicknesses are measured to be $51 \pm 1 \ \mu m$ dry and $218 \pm 8 \ \mu m$ in acetonitrile. Given an area of 0.30 cm² and cast volume of 12.0 μ L, a conversion value of 0.545 cm³/mL is found.

$$\frac{film \ thickness \times casting \ area}{cast \ aliquot \ volume} = conversion \ value \ (cm^3/mL) \tag{41}$$

This conversion value allows the film volume (cm³) in acetonitrile to be calculated from the cast volume of solution (mL); given the casting area (cm²), the swollen film thickness is found. The 50%F films described for the cyclic voltammetry procedure have an estimated wet thickness of $60 \pm 2 \ \mu$ m. PVA film thicknesses are measured to be $11 \pm 3 \ \mu$ m dry and $19 \pm 2 \ \mu$ m in acetonitrile. Conversion values and film thicknesses for the 12.5%F, 25%F, and 35%F films on electrodes are given in Table 27 below. A linear correlation between Ficoll concentration (% w/v) and wet film thickness is found with slope $4.74 \pm 0.08 \ \mu$ m/% w/v, intercept $-19.4 \pm 2.6 \ \mu$ m, and R² 0.9995. The linear correlation between Ficoll concentration (% w/v) and dry film thickness has slope $0.012 \pm 0.002 \ \mu$ m/% w/v, intercept $0.01_7 \pm 0.07 \ \mu$ m, and R² 0.9441.

Table 27 .	Wet and	dry film	thicknesses,	slopes ((density	gradients),	and co	onversion	values
for Ficoll	and PVA	films (n	$= 3 \ge 10$						

Film	Film Thickness ℓ (μ m)			Conversion	Slope (Gray Value/ μ m from Ed		
Type	Slide Dry	Slide Wet	Electrode Wet	$(\mathrm{cm}^3/\mathrm{mL})$	Dry	Wet	
$12.5\%\mathrm{F}$	8 ± 1	40 ± 3	13 ± 1	0.100	-0.119 ± 0.127	0.183 ± 0.002	
$25\%\mathrm{F}$	17 ± 1	101 ± 10	28 ± 3	0.253	-0.163 ± 0.154	0.258 ± 0.003	
$35\%\mathrm{F}$	24 ± 1	144 ± 7	40 ± 2	0.360	0.0433 ± 0.0465	0.489 ± 0.005	
$50\%\mathrm{F}$	51 ± 1	218 ± 8	60 ± 2	0.545	-0.0825 ± 0.0394	0.600 ± 0.003	
PVA	11 ± 3	19 ± 2			0.160 ± 0.166	0.115 ± 0.155	

7.3.2 Cyclic Voltammetry

Representative cyclic voltammograms for scan rates 2, 20, and 200 mV/s at an unmodified electrode and a polyvinyl alcohol modified electrode are shown in Figure 60. Magnifications of the 2 mV/s cyclic voltammograms are shown in the lower right corners of Figure 60a and b. At all scan rates, the cyclic voltammograms have the avian morphology of a system with reversible electron transfer and transient mass transport.

Figures 61a, b, c and d are cyclic voltammograms at electrodes modified with 12.5%F, 25%F, 35%F, and 50%F films, respectively. All scan rates (2, 5, 10, 20, 50, 100, and 200 mV/s) are shown for 50%F, and only scan rates 2, 20, and 200 mV/s are shown for 12.5%F, 25%F, and 35%F for the sake of visual clarity. The sigmoidal morphology of the cyclic voltammograms at Ficoll modified electrodes reflect mass transport that approaches steady state diffusion. To confirm that voltammetric morphology arises from steady state transport generated by the density gradient in the film, data are analyzed with uniform density film models and checked for pinholes and data are analyzed with respect to a graded density film model.



Figure 60. Cyclic voltammograms of a) scan rates 2 (blue short dashed lines), 20 (green long dashed lines), and 200 mV/s (red solid lines) at an unmodified electrode and b) scan rates 10 (blue short dashed lines), 50 (green long dashed lines), and 200 mV/s (red solid lines) at a 30.0 % w/w polyvinyl alcohol film modified electrode. Insets are current magnified views of the a) 2 mV/s unmodified electrode voltammogram and b) 10 mV/s PVA voltammogram. Voltammograms are plotted at an offset for clarity, so potential scales (mV) are shown. All voltammograms scan the range -0.1 V to 0.5 V versus Ag/AgO quasireference electrode.



Figure 61. Cyclic voltammograms of scan rates 2 mV/s (blue short dashed lines), 20 mV/s (green long dashed lines), and 200 mV/s (red solid lines) at electrodes modified with a) 12.5 % w/v Ficoll, b) 25.0 % w/v Ficoll, c) 35.0 % w/v Ficoll, and d) 50.0 % w/v Ficoll. Additional scan rates of 5 mV/s (dark red solid line), 10 mV/s (orange long dashed line), 50 mV/s (dotted purple line), and 100 mV/s (cerulean dashed line) are shown for 50.0 % w/v Ficoll. Voltammograms are plotted at an offset for clarity, so a potential scale (mV) is shown at lower right. All voltammograms scan the range -0.1 V to 0.5 V versus Ag/AgO quasireference electrode.

Data are evaluated with the traditional Randles Sevcik equation [58] and a uniform film model developed by the Leddy group [68] to confirm that results are not consistent with a uniformly dense film.

From the Randles Sevcik equation for cyclic voltammetry in a semi-infinite uniform density matrix of a probe with reversible (fast) electron transfer, the peak forward current i_{pf} (A) should be linearly related to the square root of the scan rate v(V/s) by $i_{pf} = (2.69 \times 10^5) n^{3/2} A D^{1/2} c^* v^{1/2}$ (at room temperature) so that the probe has a uniform diffusion coefficient throughout. n is the number of electrons, A (cm²) is the area of the electrode, D (cm²/s) is the diffusion coefficient, and c^* (mol/cm³) is the probe concentration. The Randles Sevcik equation applies to modified electrodes for scan rates in which the diffusion length remains inside a film of uniform density, as well as for unmodified electrode systems. Randles Sevcik plots of an unmodified electrode and a polyvinyl alcohol film modified electrode (for scan rates 2, 5, 10, 20, 50, 100, and 200 mV/s) have lines $y = -(960 \pm 15)x - (10 \pm 4)$, $R^2 = 0.9987$, and $y = -(9.2 \pm 0.2)x - (0.73 \pm 0.06)$, $R^2 = 0.9984$, respectively. Thus, for PVA over the entire range of scan rates, the diffusion length is confined to a uniform film and linear diffusion is established.

Figure 62a plots the peak forward currents versus the square root of the scan rates for an electrode modified with a 25%F film. The 25%F film is representative of all the Ficoll films. None of the Ficoll films yield linear plots of i_{pf} versus $v^{1/2}$ and, therefore, do not qualify for Randles Sevcik analysis. Diffusion is not linear.


Figure 62. Plots shown for an electrode modified with a 25.0 % w/v Ficoll film. a) Peak forward current (μ A) versus square root of scan rate (V/s)^{1/2} for analysis by Randles Sevick equation (error bars are relative standard deviation). b) Log peak forward current versus negative log scan rate for analysis of same data by uniform film model.

In the uniform film model, the probe has two distinct diffusion coefficients, a uniform diffusion coefficient in the film D_f and a uniform (if different from the film) diffusion coefficient in the solution D_s . Sigmoidal cyclic voltammogram morphologies can be observed when solution flux is much greater than film flux and the scan rates dictate diffusion lengths near the film solution interface. In this case, a linear relationship between the log of the peak forward currents and the negative log of the scan rate $\ln \frac{i_{pf}}{nFAc^*\sqrt{D_s}} = -\ln \left[\frac{\ell^2}{D_f t_k}\right]^{m/2} + c$ is characteristic. D_f and D_s are the diffusion coefficients (cm²/s) in the film and solution, respectively, ℓ (cm) is the film thickness, t_k (s) is the scan time, and m and c are constants determined by the relative flux in the film and solution. tk = RT/nFv is the total time of the scan. Figure 62b plots log of the peak forward currents $\ln(i_{pf})$ versus the negative log of the scan rates $-\ln(v)$ for an electrode modified with a 25%F film. None of the Ficoll films have linear plots and, therefore, do not qualify for analysis by the uniform film model.

7.3.2.2 Evaluation for Pinholes

As shown by Amatore, Saveant, and Tessier [71,72], pinholes can cause sigmoidal voltammogram morphology. Thus, the data are analyzed for the existence of pinholes. In terms of the qualitative morphology of the cyclic voltammograms, the data for the Ficoll modified electrodes does not follow the pattern expected for pinholes. For diffusion lengths longer than the film thickness (low scan rates), planar diffusion would occur and result in cyclic voltammograms with avian morphology characteristic of semi-infinite linear diffusion. For diffusion lengths near the film

N	$R_a (\rm cm)$	$R_0 (\mathrm{cm})$	$1-\theta$	$A_{R_a} (cm^2)$	$A_{R_0} (cm^2)$	$A_{Total} (cm^2)$	Fits?
1	10.6	0.564	353	705	2.00	707	No
2	5.30	0.399	176	176	1.00	355	No
5	2.12	0.252	70.5	28.2	0.400	143	No
10	1.06	0.178	35.3	7.05	0.200	72.5	No
10^{2}	0.106	$5.64 imes 10^{-2}$	0.353	$7.05 imes 10^{-2}$	0.0200	9.05	No
10^{3}	$1.06 imes 10^{-2}$	1.78×10^{-2}	$3.53 imes 10^{-2}$	$7.05 imes 10^{-4}$	$2.00 imes 10^{-4}$	2.71	No
10^{6}	$1.06 imes 10^{-5}$	5.64×10^{-4}	$3.53 imes 10^{-4}$	7.05×10^{-10}	2.00×10^{-6}	2.00	No

Table 28. Pinhole model parameters calculated from limiting current of 2 mV/s 50F cyclic voltammogram

solution interface, radial diffusion around the pinholes would result in sigmoidal cyclic voltammograms. For diffusion lengths shorter than the film thickness (high scan rates), planar diffusion would occur within the pinholes and result in avian morphology characteristic of a non-steady state system. This morphology pattern of avian, sigmoid, avian is not observed for the Ficoll film modified electrodes as scan rate varies from fast to slow.

Data are also considered in terms of equations provided by Tessier, et al., for disc-type pinhole sites and fast electron transfer kinetics. The radius of the pinhole site R_a , the degree of coverage of the electrode by the pinholes $1 - \theta$ (see Equation 42), N the number of pinholes, and the distance between pinhole sites, $2R_0$, are the parameters considered.

$$1 - \theta = N\pi R_a^2 \tag{42}$$

These parameters are related to each other by

$$R_a = R_0 \sqrt{1 - \theta} \tag{43}$$

The limiting current, i_{lim} , of a sigmoidal cyclic voltammogram is evaluated by

$$\frac{FAc^*D}{i_{\rm lim}} = 2R_0F(1-\theta) \tag{44}$$

where

$$F(1-\theta) = \frac{0.3}{\sqrt{1-\theta}} \tag{45}$$

 $c^* = 1.00 \text{ mol/cm}^3$ is the solution concentration, $A = 0.452 \text{ cm}^2$ is the area of the electrode, and $D = 6.20 \times 10^{-6} \text{ cm}^2/\text{s}$ is the diffusion coefficient in solution. Scenarios for values of N between 1 and 1×10^6 are generated based on the limiting current of 9.00 μ A for the 50%F 2 mV/s voltammogram. For each N value, the area of the pinhole, distance between pinholes, and coverage are calculated and used to determine what is the total area required for such a film with N pinholes. In all scenarios, the theoretical total area exceeded the actual electrode area. Therefore, it is unlikely in both a qualitative and quantitative sense that pinholes are the cause of the sigmoidal voltammograms observed for Ficoll modified electrodes. Table 28 lists calculated parameters and disproves the pinhole model.

7.3.2.3 Graded Density Film Analysis

Data are analyzed based on a system with a graded density film, in which the density of the film (and, therefore, the diffusion coefficient) changes with x distance normal from the electrode. Figure 63 plots $1/i_{pf}$ versus $1/\sqrt{v}$. At small scan rates, diffusion length samples the entire film gradient, and peak currents become independent of the scan rate as shown by the rollover at high $1/\sqrt{v}$ (slow scan rate). For the unmodified electrode, the plot is linear as anticipated by the Randles Sevcik equation, but for



Figure 63. Plot of $1/i_{pf}$ (μA^{-1}), versus $1/\sqrt{v} (V/s)^{-1/2}$. Each series is $1/i_{pf}$ vs $1/\sqrt{v}$ of each scan rate at an unmodified electrode (purple circles, abbreviated U) and electrodes modified with films of concentration: 12.5 % w/v Ficoll (red squares), 25.0 % w/v Ficoll (blue diamonds), and 50.0 % w/v Ficoll (green triangles). Error bars are relative standard deviations.

Table 29. Peak forward currents for unmodified electrodes and Ficoll film modified electrodes at various scan rates $(n = 3 \times 3)$

			Peak Forward Currents i_{pf} (μA)						
			at Scan Rates $v (mV/s)$						
F	ìlm	2	5	10	20	50	100	200	
	U	-53.9 ± 1.9	-74.5 ± 1.7	-102 ± 6	-143 ± 5	$-23_3 \pm 1_1$	$-31_7 \pm 1_4$	$-43_2 \pm 1_9$	
12	$.5\%\mathrm{F}$	-12.0 ± 0.2	-12.5 ± 0.4	-13.4 ± 0.4	-14.2 ± 0.1	-14.9 ± 0.5	-16.0 ± 0.5	-17.2 ± 0.5	
25.	$.0\%\mathrm{F}$	-11.1 ± 0.2	-12.1 ± 0.2	-12.9 ± 0.3	-13.4 ± 0.4	-14.4 ± 0.5	-14.9 ± 0.4	-15.4 ± 0.5	
35.	$.0\%\mathrm{F}$	-10.2 ± 0.3	-11.1 ± 0.1	-11.2 ± 0.3	-12.5 ± 0.9	-13.5 ± 1.0	-14.7 ± 0.5	-16.7 ± 0.3	
50.	$.0\%\mathrm{F}$	$-6.7_5\pm0.8$	-6.99 ± 0.5	$-7.5_{1} \pm 0.4$	$-8.3_{7} \pm 0.7$	-10.0 ± 0.3	-11.4 ± 0.8	-13.1 ± 0.6	

Table 30. Regression analysis values for a linear fit of i_p^{-1} vs $v^{-0.5}$

Film	Slope $(\mu A^{-1} V^{1/2} s^{-1/2})$	Intercept (μA^{-1})	\mathbb{R}^2
U	$(8.88 \pm 0.28) \times 10^{-4}$	$(0.00 \pm 0.04) \times 10^{-2}$	0.9942
$12.5\%\mathrm{F}$	$(1.31 \pm 0.08) \times 10^{-3}$	$(6.15 \pm 0.08) \times 10^{-2}$	0.9966
$25\%\mathrm{F}$	$(1.19 \pm 0.02) \times 10^{-3}$	$(6.59 \pm 0.03) \times 10^{-2}$	0.9996
$50\%\mathrm{F}$	$(3.26 \pm 0.63) \times 10^{-3}$	$(9.80 \pm 0.68) \times 10^{-2}$	0.9644

Ficoll films, the plots roll over. For the Ficoll modified electrodes, data plotted in Figure 63 are shown in Table 29; regression data are given for the three slowest scan rates in Table 30. The intercepts are nonzero, indicative of steady state. Regression data for all scan rates for an unmodified electrode have intercept of zero.

Figure 64 plots i_{pf} /film thickness (ℓ) versus 1/relative viscosity (η) of the casting solution. Because the same volume is cast of the different FicoII concentrations, upon drying the films have a different thickness. However, analysis also indicates they may have different gradient steepnesses. The peak currents are normalized by the film thickness in an attempt to remove any effects of diffusion length relative to film thickness and focus on effects from the viscosity. Film thicknesses and relative viscosity are listed in Table 31. The data are plotted in series by



Figure 64. Plot of i_{pf}/ℓ ($\mu A/\mu m$) vs $1/\eta$ where η is the relative viscosity of the Ficoll film casting solutions and ℓ is film thickness. Each series is i_{pf}/ℓ vs $1/\eta$ of each film concentration for a single scan rate. 2 mV/s (blue diamonds), 10 mV/s (green triangles), 50 mV/s (purple circles), 200 mV/s (red squares). Error bars are relative standard deviation. Data are provided in Tables 29 and 31. Slope, intercept, and R² values are listed in Table 32. Error bars are relative standard deviation.

Film	Cast Aliquot	Electrode Wet	Relative
Type	Volume (μ L)	Film Thickness ℓ (μ m)	Viscosity η
12.5%F	5.0	13 ± 1	9 ± 1
$25\%\mathrm{F}$	5.0	28 ± 3	35 ± 4
$25\%\mathrm{F}$	10.0	56 ± 6	35 ± 4
$35\%\mathrm{F}$	5.0	40 ± 2	110 ± 10
50%F	5.0	60 ± 2	590 ± 60

Table 31. Film thicknesses and relative viscosities for Ficoll modified electrodes

scan rate, so that for the 2 mV/s series, data are the peak forward currents at 2 mV/s for 12.5%F, 25%F, 35%F, and 50%F. Only the 2, 10, 50, and 200 mV/s series are plotted for ease of view. All regression data are available in Table 32. The slopes and intercepts of the $i_{pf}/\ell \text{ vs } 1/\eta$ regression analysis are linear versus $\ln v$ with lines $y = -(0.21 \pm 0.02)x - (3.7 \pm 0.1)$, R² 0.9736 and $y = -(0.0046 \pm 0.0004)x - (0.066 \pm 0.002)$, R² 0.9821, respectively.

Figure 65 compares the cyclic voltammograms at scan rate 2 mV/s for 12.5%F, 25%F, and 50%F, and a 10.0 μ L 25%F film was cast and analyzed for comparison with the 5.0 μ L 50%F film. Film thicknesses can be calculated from the conversion values in Table 27 to be 56 ± 6 μ m and 60 ± 2 μ m, respectively. Although the film thicknesses are statistically the same, there is still a difference in the current that indicates a different gradient steepness in spite of the same initial mass of cast Ficoll. The 2 mV/s cyclic voltammogram for 50%F appears more sigmoidal than those for the 12.5% and 25%F, while the 200 mV/s 50%F cyclic voltammogram seems less sigmoidal than the 12.5% and 25%F cyclic voltammograms (see Figure 61). This



Figure 65. Cyclic voltammograms of scan rate 2 mV/s for electrodes modified with 5 μ L 12.5 % w/v Ficoll film (dark red solid line), 5 μ L 25.0 % w/v Ficoll film (orange long dashed line), 10 μ L 25.0 % w/v Ficoll film (purple short dashed line), and 5 μ L 50.0 % w/v Ficoll film (light blue dotted line). The 10 μ L 25%F and 5 μ L 50%F films are the same thickness. Voltammograms are plotted at an offset for clarity, so a potential scale (mV) is shown at lower right. All voltammograms scan the range -0.1 V to 0.5 V versus Ag/AgO quasireference electrode.

Scan Rate (mV/s)	Slope $(\eta \cdot \mu A/\mu m)$	Intercept $(\mu A/\mu m)$	\mathbf{R}^2
2	$-2.4_0 \pm 0.1_3$	$-0.038_4 \pm 0.007_3$	0.9945
5	$-2.6_0 \pm 0.1_5$	$-0.041_1 \pm 0.008_4$	0.9938
10	$-2.7_2 \pm 0.1_6$	$-0.044_3 \pm 0.009_0$	0.9935
20	$-2.8_0 \pm 0.1_5$	$-0.048_0 \pm 0.008_9$	0.9939
50	$-2.9_7 \pm 0.1_5$	$-0.054_4 \pm 0.008_5$	0.9951
100	$-3.1_9 \pm 0.1_4$	$-0.058_0 \pm 0.007_9$	0.9963
200	-3.43 ± 0.08	$-0.058_4 \pm 0.004_5$	0.9990

Table 32. Regression analysis values for plot of ipf normalized by film thickness versus inverse relative viscosity

may be explained by consideration of the film thicknesses and scan rate diffusion lengths. The 50%F film is thick enough that for the diffusion length of a 200 mV/s scan, a relatively uniform density is sampled.

A linear viscosity profile $\eta(x)$ as depicted in Figure 66 can be described by

$$\eta(x) = \frac{(\eta_s - \eta_0)}{\ell} x + \eta_0 \tag{46}$$

$$D \propto 1/\eta$$
 (47)

$$D(x) = \frac{1}{\eta(x)} = \frac{1}{\frac{(\eta_s - \eta_0)}{\ell}x + \eta_0} = \frac{\ell}{(\eta_s - \eta_0)x + \ell\eta_0}$$
(48)

Given that D is inversely proportional to η , the diffusion coefficient profile D(x) (Equation 48) can be found.

$$\frac{i(t)}{nFA} = \left[D(x)\frac{\partial c}{\partial x} \right] \Big|_{x=0} = -J(x=0,t)$$
(49)

$$= \left[\frac{\ell}{(\eta_s - \eta_0) x + \ell \eta_0} \frac{\partial c}{\partial x} \right] \Big|_{x=0}$$

$$(50)$$

$$\frac{i(t)}{\ell n F A} = \frac{1}{\ell \eta_0} \frac{\partial c}{\partial x} \Big|_{x=0}$$
(51)

A current expression in terms of viscosity and film thickness is derived from Fick's first law in Equation 51, explaining Figure 64 where the slope can be thought of as



Figure 66. Theoretical profiles for the viscosity of the film $\eta(x)$ and diffusion coefficient D(x) in acetonitrile with respect to x normal to the electrode surface. ℓ is the edge of the film in solution.



7.3.3 Proposed Model and Computer Simulation Fit

The full version of Fick's second law, which takes into account spatial variation, elucidates the changes in current as related to the diffusion coefficient gradient. Derivation of the steady state current from Fick's second law is provided in the appendix. An explicit finite difference computer simulation is developed for a macroscopic, planar electrode modified with a graded density film placed in a solution of redox probe with reversible electron transfer. Under cyclic voltammetric perturbation, the redox probe is electrolyzed at the electrode surface and diffuses from the solution toward the electrode on the resulting concentration gradient. Space and time are discretized into increments of Δx "boxes" and Δt steps. To simulate the variation in δ with scan rate, the number of space boxes that constitute the film are varied in relation to the total number, where

$$rL = \frac{\ell}{x_{\max}} \tag{52}$$

Figure 66 illustrates the theoretical viscosity and diffusion coefficient profiles used in the simulation. The viscosity varies linearly within the film as

$$\eta(x) = \eta_f(0) \pm \frac{\eta_s - \eta_f(0)}{\ell} x \tag{53}$$

The diffusion coefficient at each box in the film is then set by

$$D(x) = \frac{D_s}{\eta(x)} \tag{54}$$

The ratio of the diffusion coefficient at the electrode surface (in the film) to the

diffusion coefficient in solution is an important parameter

$$rD = \frac{D_f(0)}{D_s} = \frac{\eta_s}{\eta_f(0)}$$
(55)

rD sets the gradient steepness. The simulation mathematical specification and C++ code are available in Appendix B. The simulation is vetted by testing its resolution limits and confirming that results are consistent with semi-infinite linear diffusion when parameter inputs match those for a spatially invariant diffusion coefficient (rD = 1).

Figure 67 is a group of simulated cyclic voltammograms for different gradient steepnesses. A pattern emerges. As the gradient increases, voltammograms approach sigmoid-like morphology and a limiting current, as demonstrated by the levelling off of the peak dimensionless current Zpf. Table 33 lists simulation values for three different gradient steepnesses. The experimental cyclic voltammograms with Ficoll modified electrodes follow the same pattern as the computer simulation.

Experimental cyclic voltammograms for 2, 20, and 200 mV/s at an unmodified electrode are fit with the simulation to find basic parameters, such as the dimensionless electron transfer coefficient X0 = 5.5. Then, an experimental cyclic voltammogram for 2 mV/s at a 50%F modified electrode is fit to the simulation for $rD = 10^{-3}$ and rL = 1. Figure 68 shows the experimental 2 mV/s voltammogram at a 50%F modified electrode and the simulated voltammogram for $rD = 10^{-3}$ and rL = 1. The experimental and simulated voltammograms are shown both side by side and overlaid.

Interestingly, simulations in which the gradient is reversed so that the film is most



Figure 67. Simulated cyclic voltammograms, in order from left to right of rD = 1, 10^{-2} , 10^{-3} , 10^{-4} , and 10^{-5} . Current Z is dimensionless and voltammograms are magnified for visual clarity. Zpf values in order from left to right are -0.446, -0.295, -0.131, -0.0438, and -0.0438. Voltammograms are plotted at an offset for clarity, so a potential scale (mV) is shown at lower right. All voltammograms scan the range -0.5 V to 0.5 V.



Figure 68. Simulated (orange dashed lines) and experimental (black solid lines) cyclic voltammograms of scan rate 2 mV/s for an electrode modified with a 50.0 % w/v Ficoll film. Voltammograms are plotted at an offset for clarity, so a potential scale (mV) is shown at lower right. All voltammograms scan the range -0.1 V to 0.5 V vs Ag/AgO QRE. Simulation parameters are X0 = 5.5, $rD = 10^{-3}$, and rL = 1.



Figure 69. Simulated cyclic voltammograms, in order from left to right of $rD = 1, 10^2$, $10^3, 10^4$, and 10^5 . Current Z is dimensionless. Zpf values in order from left to right are 0.446, 0.526, 0.719, 0.921, and 0.955. Voltammograms are plotted at an offset for clarity, so a potential scale (mV) is shown at lower right. All voltammograms scan the range 0.5 V to -0.5 V.

Gradient Steepness rD	$rL = \ell/x_{\max}$	Dimensionless Current Zpf
1×10^{-2}	0.01	0.29541
	0.05	0.29487
	0.10	0.29473
	0.20	0.29465
	0.50	0.29455
	1.00	0.29451
1×10^{-3}	0.01	0.130788
	0.05	0.130784
	0.10	0.130783
	0.20	0.130782
	0.50	0.130782
	1.00	0.130782
1×10^{-4}	0.01	0.0438485
	0.05	0.0438457
	0.10	0.0438457
	0.20	0.0438457
	0.50	0.0438457
	1.00	0.0438457

Table 33. Simulation data for peak dimensionless current, Zpf, film thickness relative to diffusion length, rL, and gradient steepness, rD

dense at the solution interface and least dense at the electrode surface show that the currents increase with increased gradient steepness. Figure 69 illustrates this pattern.

7.4 Conclusions

Ficoll does form a graded density film similar to the brush model when wet. Conversion values can be used to calculate wet and dry film thicknesses. Gradient steepness is varied by the use of different casting solution concentrations. From microscopy images, the viscosity of the film varies linearly with x normal to the electrode surface. The density and, therefore, the diffusion coefficient varies in a one over viscosity form. Cyclic voltammogram morphology suggests the graded films lead to diffusion approaching steady state. At slow scan rates, currents become scan rate independent with a nonzero intercept. Computer simulation suggests the same morphological and quantitative pattern. This could have many applications in industries such as pharmaceutics and fuel cells.

CHAPTER 8

FICOLL NAFION COMPOSITE FILMS

In Chapter 7, the full version of Fick's second law

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[D(x) \frac{\partial c}{\partial x} \right]$$
(56)

was exploited to build a density gradient layer normal to a planar electrode surface and establish near steady state transport of redox probes to the electrode without mechanical stirring. The density gradient was established with the sucrose epichlorohydrin copolymer Ficoll^(R). Nafion, a perfluorosulfonic acid polymer, is the most commonly employed separator in electrochemical energy systems and sensors. To tailor the transport properties of Nafion so as to control transport of probes to the electrode surface at near steady state has advantages in control of reaction rates and transport. Here, composites of Nafion and Ficoll are described.

8.1 Introduction

Graded density films in Chapter 7 demonstrate near steady state mass transport at electrodes modified with Ficoll. However, because Ficoll dissolves in water, Ficoll may have limited use in many practical applications. Therefore, a method for templating other polymers into a graded density film could be useful. Computer simulations indicate that a reversed gradient where the film is most dense on the solution side and least dense at the electrode surface could yield higher currents and flux. Platinum electrodes are modified with composite films of Ficoll and Nafion. Various casting methods are investigated. Analysis is done by cyclic voltammetry in a nonaqueous system. The film preparation and electrochemical analysis are described below.

8.2.1 Film Preparation

Platinum electrodes (Pine Instruments, $A = 0.452 \text{ cm}^2$) are polished successively with 1.0, 0.3, and 0.05 μ m alumina, rinsed in nitric acid, then rinsed with 18 M Ω water and dried in air before film modification. Electrodes are modified with either a Nafion film or a composite of Nafion and Ficoll. Nafion films are made by casting 10.0 μ L of Nafion solution (5% w/v suspension of Nafion in aliphatic alcohols and water, 1100 eqwt, Aldrich) on the electrode surface, then allowing the casting solvents to evaporate in air for ≥ 24 hours. The electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A glass cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 10.0 μ L, the density of Nafion in acetonitrile, and the electrode area, the film will be ~14 μ m thick when immersed in acetonitrile [52].

Three different methods are used to cast the Nafion Ficoll composite films. An aqueous solution of a 50.0 % w/v Ficoll PM 400 (Sigma, 400,000 MW) is prepared. In the first method, a 1:1 mixture of the 50.0 % w/v Ficoll and 5% w/v suspension of Nafion is prepared. 10.0 μ L of the mixture are cast and dried in air \geq 24 hours. In the second method, 5.0 μ L of the 50.0 % w/v Ficoll is cast and dried for 10 minutes. Then, 5.0 μ L of the 5% w/v suspension of Nafion is cast on top of the Ficoll film and the composite is dried in air ≥ 24 hours. In the third method, 5.0 μ L of the 50.0 % w/v Ficoll is cast and dried ≥ 24 hours. Then, 5.0 μ L of the 5% w/v suspension of Nafion is cast on top of the Ficoll film and the composite is dried in air ≥ 24 hours. In all cases, during drying the electrode is held in a stand so that the planar electrode surface faces up, parallel to the table. A glass cylinder is placed around the electrode to protect it from dust but still allow air flow. Based on the casting volume of 5.0 μ L, the density of Nafion in acetonitrile, and the electrode area, the Nafion will contribute $\sim 7 \mu$ m to the film thickness when immersed in acetonitrile [52]. The conversion value found in Chapter 7 for 5.0 μ L of a 50.0 w/v % Ficoll solution suggests a contribution of $\sim 30 \mu$ m to film thickness when immersed in acetonitrile.

Hereafter, Nafion only films are labelled N. Films cast from a 1:1 mix of the Nafion and Ficoll solutions (first method) are labelled NFmix. Films prepared by first casting the Ficoll and drying 10 minutes, then casting the Nafion (second method) are labelled NF10m. Films prepared by first casting the Ficoll and drying 24 hours, then casting the Nafion (third method) are labelled NF24h.

8.2.2 Cyclic Voltammetry

An organic electrolyte is chosen to avoid dissolution of Ficoll films in water: 1.0 mM N,N,N',N'-tetramethyl-1,4-phenylenediamine (TMPD, Aldrich) and 0.10 M tetrabutylammonium tetrafluoroborate (TBABF₄, Aldrich) in acetonitrile (Aldrich). A platinum working electrode (Pine Instruments, $A = 0.452 \text{ cm}^2$), platinum mesh counter electrode, and Ag/AgO quasireference electrode are used in a three electrode setup.

Cyclic voltammetry is performed (CH Instruments 760B potentiostat) at scan rates 2, 20, 50, and 200 mV/s in a randomized order. A potential window of -0.1 V to 0.5 V vs. Ag/AgO is scanned. Films equilibrate for \geq 5 hours before applying a potential, and reequilibrate for one hour between each subsequent scan. Three films of each type are cast and analyzed, and triplicate measurements are completed for each scan rate.

8.3 Results and Discussion

Figure 70 shows representative 2, 20, and 200 mV/s cyclic voltammograms for electrodes modified with either a Nafion only film or composites of Nafion and Ficoll prepared by three different methods. Horizontally, 2, 20, and 200 mV/s cyclic voltammograms are shown for electrodes modified with NFmix composite films in the first (red) row, NF24h composite films in the second (green) row, and NF10m composite in the third (blue) row. The fourth (black) row is for electrodes modified with Nafion only films. Vertically, the columns are for 2 (solid lines), 20 (short dashed lines), and 200 (long dashed lines) mV/s sweeps. Faster scan rates correlate with shorter diffusion lengths. Diffusion lengths approximate the distance from the electrode where the concentration of the redox probe has been perturbed from its initial value on the time scale of the experiment.

In Figure 70, a range of morphologies are observed. The avian shape is



Figure 70. Representative cyclic voltammograms for platinum electrodes modified with various Nafion Ficoll composite films and measured in 1.0 mM TMPD 0.10 TBABF₄ in acetonitrile. Horizontally, cyclic voltammograms are shown for electrodes modified with NFmix composite films in the first (red) row, NF24h composite films in the second (green) row, and NF10m composite in the third (blue) row. The fourth (black) row is for electrodes modified with Nafion only films. Vertically, the columns are for 2 (solid lines), 20 (short dashed lines), and 200 (long dashed lines) mV/s sweeps.

	i_{pf} (μA) at v (mV/s)						
Film	2	20	50	200			
Ν	-38.1 ± 0.9	-111 ± 1	-174 ± 5	-332 ± 8			
NFmix	-10.6 ± 0.3	-46.3 ± 0.3	-82.8 ± 1.0	-156 ± 9			
NF24h	$-6.15 \pm 0.2^{*}$	-14.5 ± 0.2	-30.7 ± 1.2	-49.9 ± 2.0			
NF10m	$-4.83 \pm 0.2^{*}$	$-5.24 \pm 0.2^{*}$	-7.39 ± 0.4	-13.8 ± 0.2			

Table 34. Peak forward currents for electrodes modified with Nafion only and Nafion Ficoll composite films at various scan rates (n = 3)

*Sigmoidal morphology - no peak, just limiting steady state current

characteristic of semi-infinite linear diffusion and observed at the two faster scan rates for N and NFmix. At 2 mV/s in solution, the scan rate is sufficiently slow that the probe concentration profiles are disrupted by natural convection and the avian shape is distorted. For NF10m and NF24h at 200 mV/s, the voltammograms have gaussian features characteristic of probe transport in a confined volume or thin layer. For all the modified electrodes at 2 mV/s, the voltammograms have sigmoidal components, but the NF10m and NF24h composites have the clear sigmoidal morphology generated by steady state mass transport. For each of the composites, the morphologies at 20 mV/s reflect transitions between fast and slow scan rates.

Data for peak or limiting forward currents i_{pf} , peak forward and reverse potentials E_{pf} and E_{pr} , and peak splittings ΔE_p are listed in Tables 34, 35, 36, and 37, respectively.

Variations in morphology reflect different density profiles of each composite film on the electrode surface and the effects of probing at short distances (fast scan rates) and long distances (slow scan rates) into the solution. The gaussian or thin layer components are most apparent for the NF10m and NF24h composites at high

Table 35. Peak forward potentials for electrodes modified with Nafion only and Nafion Ficoll composite films at various scan rates (n = 3)

	E_{pf} (V) at v (mV/s)					
Film	2	20	50	200		
N	0.228 ± 0.002	0.231 ± 0.002	0.236 ± 0.002	0.227 ± 0.004		
NFmix	0.236 ± 0.001	0.227 ± 0.002	0.239 ± 0.002	0.249 ± 0.002		
NF24h	$0.279 \pm 0.001^*$	0.216 ± 0.001	0.224 ± 0.003	0.229 ± 0.004		
NF10m	$0.286 \pm 0.001^*$	$0.246 \pm 0.003^*$	0.221 ± 0.001	0.203 ± 0.003		

*Sigmoidal morphology - no peak, just limiting steady state current

Table 36. Peak reverse potentials for electrodes modified with Nafion only and Nafion Ficoll composite films at various scan rates (n = 3)

	E_{pr} (V) at v (mV/s)						
Film	2	20	50	200			
N	0.160 ± 0.002	0.160 ± 0.002	0.154 ± 0.003	0.124 ± 0.001			
NFmix	0.164 ± 0.001	0.166 ± 0.002	0.157 ± 0.001	0.130 ± 0.001			
NF24h	$0.126 \pm 0.001^*$	0.174 ± 0.001	0.166 ± 0.003	0.139 ± 0.004			
NF10m	$0.104 \pm 0.001^*$	$0.154 \pm 0.003^*$	0.171 ± 0.003	0.159 ± 0.002			

*Sigmoidal morphology - no peak, just limiting steady state current

Table 37. Peak splittings for electrodes modified with Nafion only and Nafion Ficoll composite films at various scan rates (n = 3)

	$\Delta E_p \text{ (mV) at } v \text{ (mV/s)}$					
Film	2	20	50	200		
N	68 ± 2	71 ± 3	82 ± 8	103 ± 10		
NFmix	72 ± 3	61 ± 2	82 ± 9	119 ± 11		
NF24h	$153 \pm 10^*$	42 ± 4	58 ± 6	90 ± 10		
NF10m	$182 \pm 12^*$	$92 \pm 10^*$	50 ± 4	44 ± 3		

*Sigmoidal morphology - no peak, just limiting steady state current

scan rates, short diffusion length. At high scan rates, only a short distance from the electrode surface is sampled. Because of the way the NF10m and NF24h composites are formed, Nafion may not have soaked into the most dense region of the Ficoll, so a Nafion/Ficoll interface forms a thin layer at the electrode. As the scan rates slow for NF10m and NF24h, the diffusion length moves into the bulk phase of the Nafion Ficoll composite. At the slowest scan rate, the response is sigmoidal consistent with the redox probe sampling a graded density phase. The composite has not segregated into two polymer phases.

The NFmix voltammograms resemble the Nafion only voltammograms. Currents are smaller as Ficoll is a blocking polymer: Ficoll restricts or hinders access of the probe to the electrode. Because Nafion and Ficoll have different densities, the polymers may settle on the electrode at different rates when cast as NFmix. If the denser Nafion settles faster than Ficoll, no commingled density layer would be established and Nafion with perhaps entrapped Ficoll would be at the electrode surface. Without the density gradient, the voltammetry would reflect characteristics consistent with the uniform density Nafion film (N) with lower currents because the entrapped Ficoll dilutes the Nafion with inert polymer. The NF10m 2 mV/s is most sigmoidal, consistent with near steady state behavior. Thus, 10 minutes is sufficient time for the Ficoll to establish a density gradient that remains sufficiently fluid for Nation to intercalate into the Ficoll effectively. NF24h is less sigmoidal, indicating that after 24 hours, the Ficoll may be too dry for the Nafion to effectively intercalate into the Ficoll; instead, the Nafion forms a layer on top of the Ficoll and compresses the density gradient due to greater density.



Figure 71. Plots of peak forward current (μ A) versus square root of scan rate (V/s)^{1/2} for platinum electrodes modified with composite films of a) NFmix (red squares), b) NF24h (green circles), c) NF10m (blue diamonds), and d) N (black triangles). Error bars are standard deviation.



Figure 72. Plots of one over peak forward current $(\mu A)^{-1}$ versus one over square root of scan rate $(V/s)^{-1/2}$ for platinum electrodes modified with composite films of a) NFmix (red squares), b) NF24h (green circles), c) NF10m (blue diamonds), and d) N (black triangles). Error bars are relative standard deviation.

Figure 71 plots peak forward current (μ A) versus square root of scan rate (V/s)^{1/2} for the electrodes modified with Nafion and composites of Nafion and Ficoll made from the three different methods. Nafion and NFmix are linear for i_{pf} versus \sqrt{v} . Regression analysis yields slope $-730 \pm 9 \ \mu \text{As}^{1/2} \text{V}^{-1/2}$, intercept $-7.2 \pm 2.4 \ \mu\text{A}$, and R² 0.9997 for N and $-360 \pm 15 \ \mu \text{As}^{1/2} \text{V}^{-1/2}$, intercept $3.7 \pm 3.9 \ \mu\text{A}$, and R² 0.9967 for NFmix. NF10m and NF24h may be linear at high scan rates, but reach limiting currents at slower scan rates. Figure 72 plots one over peak forward current $1/i_{pf}$ versus one over square root of scan rate $1/\sqrt{v}$ for the electrodes modified with Nafion and composites of Nafion and Ficoll made from the three different methods. NF10m levels out to a scan rate independent value (limiting steady state current) at slow scan rate similar to the Ficoll modified electrodes in Figure 63 in Chapter 7.

8.4 Conclusions

Voltammetry of the NF10m modified electrodes indicates a density graded ion exchange polymer film has been made with the NF10m method to cast composite Nafion Ficoll films. Near steady state diffusion is achieved with NF10m films. NF24h and NFmix have other academically interesting transport properties but analysis is complicated by the possibility of multiple Nafion/Ficoll interfaces within the films. In the future, NF10m films should be further evaluated for long term stability and retention of ion exchange properties for use in industrial applications.

CHAPTER 9

CONCLUSIONS AND FUTURE WORK

Electroanalytical techniques were used to investigate mass transport through density gradient films; lanthanide triflate reduction and oxidation in a Nafion/acetonitrile matrix; and magnetic field effects on hydrogen evolution reaction (HER), oxygen reduction reaction (ORR), and lanthanide electrochemistry.

Graded density films lead to near steady state mass transport to a planar surface. The expanded version of Fick's second law anticipates the effect. Ficoll forms a graded density film similar to the brush model when wetted in acetonitrile. Cyclic voltammetric analysis of a redox probe moving through a Ficoll film on the electrode establishes near steady state diffusive transport. Steady state transport through a graded density layer has applications in industries and technologies like pharmaceutics and fuel cells. A density graded ion exchange polymer film was made by sequential addition of Ficoll and then the ion exchange polymer Nafion (NF10m) to cast composite Nation Ficoll composites. Near steady state diffusion is achieved with NF10m composites. In future work, NF10m films should be further evaluated for long term stability and retention of ion exchange properties. Ficoll is inert and hinders access of redox probes to the electrode. It would be useful to remove the Ficoll from composites such as NF10m after templating so that Nation retains a graded density structure but Ficoll no longer impedes probe flux to the electrode. It may be possible to achieve Ficoll removal simply by soaking films in water after formation. Other types of density graded composites should be explored. Separate from the brush model, density graded films could be created with photopolymerization by controlling the amount of light or exposure time to different regions of a film.

Addition of magnetic fields greatly impacts electrochemical systems. Currents increase, efficiencies improve, and overpotentials decrease. For composites of micromagnets in Nafion, mass transport effects from magnetic fields are precluded by the nanostructure of Nafion. Apparent diffusion proceeds by self exchange; the redox molecules do not actually move but rather the electrons hop. The observed effects of decreased overpotential and enhanced current are electron transfer driven. Magnetization versus demagnetization of magnetic microparticles greatly influences the magnitude of the effect. The particles are coated so they are chemically inert and loadings do not exceed the 15 % percolation limit. Thus, observed effects are due to the magnetic fields of the particles, not chemical interactions or percolation.

A decrease in the hydrogen evolution overpotential is observed for magnetically modified glassy carbon, gold, and mercury electrodes. Glassy carbon, gold, and mercury are poor electrodes for hydrogen evolution. On modification with magnetic composites, the overpotential for the onset of H_2 evolution decreases at diamagnetic electrodes. The onset of H_2 evolution occurs at more positive potentials (lower overpotentials) as the magnetic susceptibility of the microparticles increases. Control electrodes modified with demagnetized particles have larger overpotentials than electrodes modified only with Nafion. Future work should investigate additional diamagnetic electrodes including boron-doped diamond (BDD), indium tin oxide (ITO), and mercury film electrodes. Evidence of enhanced electron transfer kinetics in the presence of magnets is observed for the ORR in nonaqueous electrolyte. For O_2 as the only electroactive species in the nonaqueous electrolyte, currents increase and overpotential decreases. When ytterbium triflate is added to the electrolyte, O_2 reduction current increases but overpotential may also increase. These preliminary results have significant implications for nonaqueous metal air batteries, as $M + O_2 \rightleftharpoons M^+ + O_2^-$ is analogous to $O_2 + e \rightleftharpoons O_2^-$. Improved performance is anticipated either when cathodes are formed by adding magnets or YbOTf is added to the battery electrolyte or both. Future work should include investigation of additional scan rates for more detailed analysis of the electrocatalysis. Stronger magnetic microparticles and higher loadings of particles in the composites should be evaluated. Magnetic effects on the ORR in a lithium electrolyte should be examined.

A relatively inexpensive, readily assessable benchtop method to analyze lanthanides electrochemically was developed. Mercury electrodes, ionic liquids, and molten salts can now be avoided. Nafion solubilizes the lanthanide triffate complexes, possibly by replacement or equilibrium of a triffate ligand with a sulfonate group. Acetonitrile widens the accessible potential window and triffate ligands shift the lanthanide formal potentials into the acetonitrile solvent window. Future work should further evaluate the mechanism of the reductive peak B and the oxidative waves. Instrumental limitations of the XPS prevented analysis of the film electrolyzed at -1.4 V vs Ag/AgO. If analysis can be performed, it may be possible to discriminate between a one electron reaction $Yb^{2+} + e \rightleftharpoons Yb^{1+}$ and a two electron reaction $Yb^{2+} + 2e \rightleftharpoons Yb^0$ by whether the binding energy shifts by another 4 eV or $8~{\rm eV}.$

Magnets enhance the differences in the voltammetric responses for these several lanthanides. The effect is not yet well described fundamentally, but for the lanthanides, there are correlations with the magnetic properties albeit complicated. More lanthanides should be studied to delineate patterns in the magnetic effects with properties of the lanthanides. Future work should include investigation of magnetic effects on lanthanide isotopes to see if there is a nuclear effect in addition to the observed electron transfer effect. A model suggests peak potential shifts as small as 50 to 100 mV would be effective for separation of lanthanide mixtures. Results thus far demonstrate that magnets can improve identification and separation of lanthanides. Future work should include actual separation of a mixture of two different lanthanides using magnetic field effects in the triflate system. In addition, the system should be optimized with stronger magnetic microparticles and higher loading of the particles in the composites.

APPENDIX A

DERIVATION OF STEADY STATE FLUX FROM FICK'S SECOND LAW

The form of Fick's second law typically used for diffusion in a solution (where the diffusion coefficient is invariant) is

$$\frac{\partial c\left(x,t\right)}{\partial t} = D \frac{\partial^2 c\left(x,t\right)}{\partial x^2} \tag{A.1}$$

The full form of Fick's second law allows for spatially variant diffusion coefficients.

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[D(x) \frac{\partial c(x,t)}{\partial x} \right]$$
(A.2)

This expands to

$$\frac{\partial c(x,t)}{\partial t} = D(x)\frac{\partial^2 c(x,t)}{\partial x^2} + \frac{\partial D(x)}{\partial x}\frac{\partial c(x,t)}{\partial x}$$
(A.3)

In this expression, the first term on the right hand side (RHS) is similar to the single term on the RHS in Equation A.1. The second term introduces additional terms that can augment or decrement the change in concentration with time.

Steady State or Approach to Steady State

Consider the steady state or at least the approach to steady state. At steady state, $\frac{\partial c(x,t)}{\partial t} \longrightarrow 0$, such that

$$\frac{\partial c(x,t)}{\partial t} \longrightarrow 0 = \frac{\partial}{\partial x} \left[D(x) \frac{\partial c(x)}{\partial x} \right]$$
(A.4)

This means that

$$D(x)\frac{\partial c(x)}{\partial x} = A' \tag{A.5}$$

where A' is a constant independent of x.

Once rearranged and integrated,

$$\frac{\partial c(x)}{\partial x} = \frac{A'}{D(x)}$$
(A.6)

$$\int \partial c(x) = \int \frac{A'}{D(x)} \partial x \qquad (A.7)$$

$$c(x) = A' \int \frac{1}{D(x)} \partial x \qquad (A.8)$$

$$c(x) = A' \ln [D(x)] \frac{\partial D(x)}{\partial x} + B'$$
(A.9)

This yields the time independent concentration profile as a function of D(x).

For a finite concentration c^* and an expression for D(x) such that $\lim_{x \to \infty} \frac{\partial D(x)}{\partial x} \longrightarrow 0$ (which is physically likely especially out in the bulk solution)

$$\lim_{x \to \infty} c(x) = c^* = B' \tag{A.10}$$

Steady State or Near Steady State Current:

The steady state (or approach to steady state) current i_{ss} is defined as

$$\frac{i_{ss}}{nFA} = D(0) \frac{dc(x)}{dx} \bigg|_{x=0}$$
(A.11)

$$= D(0)\frac{\partial}{\partial x}\left[A'\ln\left[D(x)\right]\frac{\partial D(x)}{\partial x} + B'\right]_{x=0}$$
(A.12)

$$= D(0) \left[\frac{A'}{D(x)} \left(\frac{\partial D(x)}{\partial x} \right)^2 + A' \ln \left[D(x) \right] \frac{\partial^2 D(x)}{\partial x^2} \right]_{x=0}$$
(A.13)

$$\frac{i_{ss}}{nFA} = A'D(0) \left[\frac{1}{D(x)} \left(\frac{\partial D(x)}{\partial x} \right)^2 + \ln[D(x)] \frac{\partial^2 D(x)}{\partial x^2} \right]_{x=0}$$
(A.14)

Thus, if D(x) is not a constant, then a steady state current arises.

Note that if $D(x) = D_0$, a constant, then $i_{ss} \longrightarrow 0$, as is normally found for example in solution.

APPENDIX B

GRADED DENSITY FILM COMPUTER SIMULATION

Simulation Development

This work employs an explicit finite difference simulation method that explicitly mimics the physical system. The simulation accounts for the physical phases and phase boundaries which affect electrode kinetics (Butler Volmer) and transport phenomena of the system to build the model for simulation by incorporating the mathematical specifications of the system. An explicit finite difference method expresses partial differential equations as finite difference equations. Hence, the physical system that comprises the film and the solution is considered as discretized space increments rather than a continuum. The film and solution are divided into small uniform spatial segments, or "boxes". Each space increment has an assigned index of j and the total number of such space elements representing the film and solution is j_{max} . Of this j_{max} , the number of elements representing the polymer film phase will be LL and adjacent to the electrode. The size of each box is fixed at Δx . Because all the boxes are the same size, the simulation is a fixed grid simulation. The total time of the experiment is also divided into uniform time increments of Δt . The one dimensional spatial discretization of film and solution is shown in Figure 1. **Dimensionless** Parameters:

Dimensionless parameters reduce the number of simulations needed to map the parameter space. For the graded density film model, dimensionless parameters for

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Figure B1. Discretization of film and solution into uniform one dimensional array elements. The electrode is shown filled with diagonal lines; the spatially varied diffusion profile is $1 \le j \le \mathbb{LL}$; jmax is the total number of elements in the system.

time, space, electron transfer rate constants, diffusion coefficients, concentrations, and currents are utilized.

The specification of the dimensionless parameterization starts with a period of time characteristic of the experiment, t_k . For cyclic voltammetry, this time is defined in relationship to the scan rate, ν as $t_k = RT/Fv = 1/nfv$. The time period t_k is then discretized into k_{max} number of time increments with duration Δt .

$$t_k = k_{\max} \Delta t \tag{B.1}$$

 k_{max} is the maximum number of time steps. Any time between t = 0 and t_k is expressed in terms of the time counter k as

$$t = (k - 0.5)\Delta t \tag{B.2}$$

where $1 \le k \le k_{\text{max}}$. The time is set in the middle of each increment such that k is offset by 0.5. Dividing both sides by t_k yields the dimensionless time.

$$\frac{t}{t_k} = \frac{(k-0.5)\Delta t}{t_k} = \frac{k-0.5}{k_{\max}}$$
(B.3)

The diffusion coefficient, D, has units of cm^2/s and is made dimensionless with

 Δt and Δx to yield the dimensionless diffusion coefficient, \mathbb{D} .

$$\mathbb{D} = \frac{D\Delta t}{\Delta x^2} \tag{B.4}$$

Thus, Δx is related to Δt through \mathbb{D} . The dimensionless diffusion coefficients for the solution and the film are \mathbb{D}_s and \mathbb{D}_f , respectively.

Once the temporal resolution k_{\max} is selected, Δx is set through \mathbb{D} . Whereas k is the time counter, j is the space counter. The distance x_j from the electrode to the middle of box j is

$$x_j = (j - 0.5)\,\Delta x\tag{B.5}$$

The diffusion length grows out normal to the electrode with time as

$$j_{\max} = 1 + 6\sqrt{\mathbb{D}\ k} \tag{B.6}$$

Thus, at time step k, the diffusion length has grown out a distance such that at $j_{\text{max}}\Delta x$ the concentration is not perturbed from the initial value.

 \mathbb{LL} is the number of space elements or boxes in the film where ℓ is the film thickness.

$$\mathbb{LL} = \frac{\ell}{\Delta x} \tag{B.7}$$

Dimensionless fractional concentration in box j is f(j).

$$f(j) = \frac{c(j)}{c^*} \tag{B.8}$$

where c(j) is the concentration in the j^{th} box at a given time and c^* is the bulk concentration.

Definition of Dimensionless Diffusion Coefficients and Scan Rate:

To simulate the variation in diffusion length with scan rate, the number of space

boxes that constitute the film are varied in relation to the total number, where

$$rL = \frac{\ell}{x_{\max}} = \frac{\mathbb{LL}}{j_{\max}} \tag{B.9}$$

When diffusion length and film thickness are equal, the scan rate is such that the full density gradient is sampled and rL = 1.

The viscosity varies linearly within the film as

$$\eta(x) = \eta_f(0) \pm \frac{\eta_s - \eta_f(0)}{\ell} x \tag{B.10}$$

The diffusion coefficient at each box in the film is then set by

$$D(x) = \frac{D_s}{\eta(x)} \tag{B.11}$$

The ratio of the diffusion coefficient at the electrode surface (in the film) to the diffusion coefficient in solution, rD, sets the gradient steepness

$$rD = \frac{D_f(0)}{D_s} = \frac{\eta_f(0)}{\eta_s}$$
 (B.12)

Film Solution Interface:

No partitioning between the film and solution is considered here. Within the film, D_f changes smoothly until it equals D_s .

Grade Density Film C++ Code

//Simulation: Cyclic Voltammetry of an Electrode Modified with a Graded Density Film

#include <io.h>
#include <iostream.h>
#include <fcntl.h>

```
#include <fstream>
#include <math.h>
#include <stdio.h>
int main (void)
{
ofstream outFile1;
outFile1.open("cyclic voltammogram gd.txt");
if (outFile1.fail())
{
cerr << "unable to open file cyclic voltammogram gd.out for output" << endl;
exit(1);
}
ofstream outFile2;
outFile2.open("diffusion_profiles.txt");
if (outFile2.fail())
{
cerr << "unable to open file diffusion profiles.out for output" << endl;
exit(1);
}
//-----
//Inputs
//double gg = 1500; //relates diffusion length, film thickness, and gradient
```

double rD = 0.001; //ratio of D0/Ds

double Dsa = 0.49; //dimensionless diffusion coefficients in solution

double Dsb = 0.49;

double D0 = Dsa * rD; //Df at electrode surface Df[0]

int kmax = 1e5; //total time steps (>1e4)

double kkmax; kkmax = kmax;

 $//int LL = sqrt((Dsa^{*}(1-rD)^{*}kmax)/gg); //number of boxes in film$

//int LL = 20;

double jmaxmax = 6*sqrt(Dsa*kmax) + 10;

int $LL = v^*jmaxmax;$

double eta0 = 1;

double etaS = 1/rD;

//double b = 0.1;

//double om = 0.99; // -1 < om < +1

//CV Specifications

double X0 = 500000.0; //dimensionless rate constant

double Xf; //forward rate constant

double Xb; //backward rate constant

double alpha = 0.5; //transfer coefficient

double Ei = -0.5; //initial potential

double Ef = 0.5; //switching potential

double E0 = 0.0; //formal potential

const double f = 38.92; //F/RT @ 298K

//-----

//Variable Declarations

double potrang = $f^*(Ef - Ei)$; //dimensionless potential range

double potinit = $f^{*}(Ei - E0)$; //dimensionless initial potential corrected for E0

int k; //time counter

int j; //space counter

double jmax; //diffusion length

int intjmax;

double t;

double E = 0; //potential wrt time

double Enorm = 0; //potential normalized by E0 and F/RT

long double Z = 0; //dimensionless current

double Zmax = -5.0;

double Zmin = 5.0;

double Emax = -100.0;

double Emin = 100.0;

//Calculation of Dimensionless Diffusion Coefficients

double etaF[1001];

double Dfa[1001]; //dimensionless diffusion coefficients in film

```
double Dfb[1001];
```

```
for (j=1; j<LL+1; j++)
```

{

etaF[j] = eta0 + ((LL-j+1)*(etaS - eta0)/LL);

```
{fan[j] = 0.0;}
```

fao[j] = 0.0;

fbn[j] = 1.0;

fbo[j] = 1.0;

}

//Begin Time Loop

for (k=1; k<=kmax; k++)

{

jmax = 6*sqrt(Dsa*k) + 10; //number of space boxes

```
intjmax = ceil(jmax);

t = (k - 0.5)/kkmax; //offset forward difference

if ( k<(kmax/2) ) //forward potential sweep

{

E = Ei + 2*(Ef - Ei)*t;

Enorm = potinit + 2*potrang*t;

}

else //backward potential sweep

{

E = Ei + 2*(Ef - Ei)*(1 - t);

Enorm = potinit + 2*potrang*(1 - t);

Enorm = potinit + 2*potrang*(1 - t);

}
```

//Diffusion (j is defined from box 1 to jmax, where 1 is the box immediately next to the electrode and jmax is the diffusion length of each time step.)

```
//In Solution
for( j=LL+1; j<intjmax; j++ )
{
  fan[j] = fao[j] + Dsa*(fao[j+1] - 2*fao[j] + fao[j-1]);
  fbn[j] = fbo[j] + Dsb*(fbo[j+1] - 2*fbo[j] + fbo[j-1]);
}
//In Film
for( j=1; j<LL+1; j++ )
{</pre>
```

$$\begin{aligned} &fan[j] = fao[j] + Dfa[j]^*(fao[j+1] - 2^*fao[j] + fao[j-1]); \\ &fbn[j] = fbo[j] + Dfb[j]^*(fbo[j+1] - 2^*fbo[j] + fbo[j-1]); \\ &//fan[j] = fao[j] + (Dfa[j+1]^*fao[j+1]) - (2^*Dfa[j]^*fao[j]) + (Dfa[j-1]^*fao[j-1]); \\ &//fbn[j] = fbo[j] + (Dfb[j+1]^*fbo[j+1]) - (2^*Dfb[j]^*fbo[j]) + (Dfb[j-1]^*fbo[j-1]); \\ &\} \end{aligned}$$

```
//At Electrode Surface
```

```
fan[1] = fao[1] + Dfa[1]*(fao[2] - fao[1]);
fbn[1] = fbo[1] + Dfb[1]*(fbo[2] - fbo[1]);
//Test for no film
//for ( j=1; j<intjmax; j++ )
//{
//fan[j] = fao[j] + Dsa^{*}(fao[j+1] - 2^{*}fao[j] + fao[j-1]);
//fbn[j] = fbo[j] + Dsb^{*}(fbo[j+1] - 2^{*}fbo[j] + fbo[j-1]);
//}
//fan[1] = fao[1] + Dsa^{*}(fao[2] - fao[1]);
//\text{fbn}[1] = \text{fbo}[1] + \text{Dsb}^*(\text{fbo}[2] - \text{fbo}[1]);
//Dimensionless Rate Constants
Xf = X0^* exp((0 - alpha)^* Enorm);
Xb = X0^* exp((1 - alpha)^* Enorm);
//Dimensionless Current
double norm = 2*sqrt(Dfa[1]*kkmax);
Z = norm^*((Xf^*fao[1] - Xb^*fbo[1])/(norm + Xf + Xb));
```

//Current Normalized by Unmodified Nicholson & Shain Electrode

```
double Zns = (Z/0.4463*sqrt(2*fabs(potrang))))*((1 - om)/(1 + om));
double Zns = Z/(0.4463*sqrt(2*fabs(potrang))); //just ns
double Zu = Z*0.4463*sqrt(Dsa/Dfa);
//Electrolysis at Electrode Surface
fan[1] = fan[1] - (Z^*sqrt(Dfa[1]/kkmax));
fbn[1] = fbn[1] + (Z*sqrt(Dfb[1]/kkmax));
if (k%100==0)
{
}
//Ageing
for (j=1; j \le intjmax; j++)
{
fao[j] = fan[j];
fbo[j] = fbn[j];
}
if (Z>Zmax)
{
Zmax = Z;
Emax = E;
}
if (Z<Zmin)
{
```

```
Zmin = Z;
Emin = E;
}
}
//End Time Loop
//______
outFile1.close();
outFile2.close();
return 0;
```

}

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