INVESTIGATION OF CHARGE TRANSFER KINETICS IN NON–AQUEOUS ELECTROLYTES USING VOLTAMMETRIC TECHNIQUES AND MATHEMATICAL MODELING

by

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LIST OF SYMBOLS

С	Concentration, mol/cm ³
D	Diffusion coefficient, cm ² /s
Е	Electrode potential, V
E^0	Standard reduction potential, V
Ei	Initial potential, V
E _{eq}	Equilibrium potential, V
E _{peak}	Peak potential, V
F	Faraday's constant, (96485 C/mol)
i	Current density, mA/cm ²
i ₀	Exchange current density (mA/cm ²)
$i_{ m L}$	Limiting current density (mA/cm ²)
i _{peak}	Peak current density (mA/cm ²)
Ι	Current, A
k_0	Reaction rate constant, cm/s
k _B	Boltzmann constant, $(1.38 \times 10^{-16} \text{ cm}^2 \text{ g/s K})$
K	Equilibrium constant
т	Number of Cl ⁻ needed to complex Cu ¹⁺
n	Number of Cl ⁻ needed to complex Cu ²⁺
n	Number of electrons transferred during electrochemical reaction
[0]	Concentration of species O ([Cu ²⁺], [Nd ³⁺], etc.), mol/cm ³
r	Radius of electrode, cm
$r_{\rm sphere}$	Radius of spherical object, cm

R	Ideal gas constant, (8.314 J/mol K)
R_{Ω}	Ohmic resistance, Ω
t	Time, s
Т	Temperature, K
v	Scan rate, V/s
V	Applied potential, V
Wa	Wagner number, dimensionless
х	Number of free Cl^- involved in Cu^{2+} complexation reaction
x	Distance away from electrode surface, cm
У	Number of free Cl ⁻ involved in Cu ¹⁺ complexation reaction

Greek

α_c	Cathodic charge transfer coefficient
β	Charge transfer symmetry factor
δ	Diffusion boundary layer thickness, cm
η_s	Surface overpotential, V
κ	Electrolyte conductivity, S/cm
μ	Electrolyte viscosity (g/cm s)
ρ	Electrolyte density (g/cm ³)
ψ	Irreversibility parameter, dimensionless
ω	Angular rotation rate of RDE, rad/s

Subscripts/Superscripts

1+	Value related to Cu ¹⁺
2+	Value related to Cu^{2+} (chapters 2, 3) or Nd^{2+} (chapter 4)
3+	Value related to Nd ³⁺
а	Value related to the anodic reaction
b	Bulk value
c	Value related to the cathodic reaction
n+	Oxidation state of species
0	Oxidized species
total	Total concentration, mol/cm ³

Investigation of Charge Transfer Kinetics in Non– aqueous Electrolytes Using Voltammetric Techniques and Mathematical Modeling

Abstract

by

DAI SHEN

Understanding the reaction mechanisms underlying charge-transfer kinetics in non-aqueous electrochemical systems is central to developing efficient processes for industrial applications. In the present work, non-aqueous electrochemistry in two classes of electrolytes (deep eutectic solvents and high-temperature eutectic molten salts) is investigated. Specifically, the charge transfer kinetics of associated electrochemical reactions are determined using voltammetric techniques and mathematical modeling, which then sheds light onto the mechanistic processes that limit electron-transfer rates.

Deep eutectic solvents (DES), on account of their low–cost, non–flammability and electrochemical stability, are attracting attention for their potential use in energy storage applications such as redox flow battery. In such application, knowledge of the transport and electrochemical kinetics properties of DES is critically important. To date, attempts to measure the kinetics parameters of the $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$ reaction in ethaline DES have yielded unreliable kinetic results. In this work, detailed recommendations are developed and verified for avoiding pitfalls in kinetics analysis of highly resistive DES electrolytes. These recommendations include the application of accurate IR_{Ω} correction and the use of electrode configurations where the secondary current distribution is relatively uniform. Incorporating these recommendations, a comprehensive study of the kinetics and transport properties of the aforementioned redox reaction was carried out. Using steady-state and transient polarization measurements on RDE and microelectrodes combined with diffusion–reaction modeling, we demonstrate that the Cu^{2+}/Cu^{1+} transition exhibits a charge transfer coefficient in the range of 0.49 - 0.54 and a reaction rate constant in the range $(1.78 - 1.95) \times 10^{-4}$ cm/s. The result indicates that the Cu^{2+}/Cu^{1+} redox reaction in chloride–containing DES media suffers from sluggish charge transfer kinetics. The effects of DES composition and temperature on kinetics provide important insights into the origins of rate–limiting factors. Specifically, the role of Cl⁻ in complexing the cations and thereby hindering charge-transfer is demonstrated. To explain how charge transfer kinetics depend on the various system parameters, a model incorporating complexation phenomena was developed and its predictions were compared to experiments.

For potential application in rare-earth metal recovery from spent waste, the electrodeposition of neodymium (Nd) metal from NdCl₃-containing molten LiCl-KCl eutectic melts was investigated using voltammetry and diffusion-reaction modeling. Voltammetry studies confirmed that Nd electrodeposition is a two-step reduction process involving first a reversible one-electron transfer reduction of Nd³⁺ to Nd²⁺, followed by quasi-reversible reduction of Nd²⁺ to Nd metal. In the electrode potential range where Nd³⁺ is reduced to Nd²⁺, the peak current density measured in a voltammetry scan showed good agreement with the classical Randles–Sevcik model for reversible soluble–

soluble redox transitions. However, in the potential range where Nd²⁺ is reduced to Nd metal, the experimentally measured peak currents in the voltammogram were substantially lower than those predicted by applying the Berzins–Delahay model for reversible soluble–insoluble redox transitions. This discrepancy was addressed using transient diffusion–reaction modeling, which accounted for the multivalent (Nd²⁺ and Nd³⁺) species transport and their multi–step reduction to Nd metal. The diffusion–reaction model accurately predicts the voltammetric response during Nd electrodeposition in a broad range of operating conditions (species concentrations and voltammetry scan rates), while providing access to the kinetic parameters governing Nd electrodeposition from halide melts.

1.1 Motivation: To Enable Grid-scale Energy Storage and Rare Earth Metal Recycling

The applications explored by this work span two areas – grid–scale energy storage using redox flow batteries, and recycling of spent rare earth metal waste. Though different, they both rely on electrochemical reactions in non–aqueous eutectic electrolytes. This work develops voltammetric techniques and associated mathematical methods to accurately determine charge transfer kinetics of electrochemical reactions in these eutectic systems thereby unraveling the mechanistic processes that limit charge-transfer rates.

1.1.1 Grid-scale Energy Storage Devices Using Deep Eutectic Solvents as Electrolytes

Grid–scale energy storage devices, such as redox flow batteries (RFBs), are critical to the renewable energy revolution. Because renewable energy sources such as solar and wind are intermittent, RFBs can store excess harnessed energy during peak production hours and release it during times of peak demand, thereby achieving load leveling.^{1–3} Unlike conventional batteries, in a RFB, redox actives species are dissolved in the electrolyte, which are stored externally in tanks and circulated through the system.⁴ Such configuration enables the decoupling of power and energy thereby offering benefits of flexible design and scalability. Currently, most redox flow batteries utilize an aqueous media, which limits the electrochemical operating range to the electrochemical stability window of water. The use of non–aqueous electrolyte can lead to higher voltages and

greater energy densities.⁵ One such class of non–aqueous electrolytes that has been gaining attention is deep eutectic solvents (DES).⁶

DES are a class of liquids comprised of a hydrogen bond donor and a hydrogen bond acceptor.⁷ When mixed together, the DES constituents form an eutectic mixture with a lower melting point that either of the parent compounds (Fig. 1.1).⁸ In addition to its wide electrochemical stability window^{9–11}, other advantages of DES over conventional aqueous media include low cost^{12,13}, biodegradability, environmental benignity⁸, ease of preparation⁷, non–flammability, and non–volatility. Thus, DES–based redox- and hybrid-flow batteries holds great potential for next–generation grid–scale energy storage.



Figure 1.1. Schematic of deep eutectic phase diagram illustrating the melting point depression. Example of 'A' is choline chloride and that of 'B' is ethylene glycol which when mixed in a 1:2 molar ratio provides ethaline DES.

An all–copper (Cu) hybrid RFB using DES has been proposed by Lloyd, *et al.*⁶ In such a system, Cu electrodeposition (during battery charging) and Cu dissolution (during battery discharging) occur at the metallic Cu anode, according to the following reaction:

$$\mathrm{Cu}^{1+} + \mathrm{e}^{-} \rightleftarrows \mathrm{Cu}^{0} \tag{1.1}$$

At the cathode, Cu^{1+} oxidation (during battery charging) and Cu^{2+} reduction (during battery discharging) occur on an inert cathode substrate:

$$\mathrm{Cu}^{2+} + \mathrm{e}^{-} \rightleftarrows \mathrm{Cu}^{1+}$$
 [1.2]

The work described in this dissertation focuses on reaction 1.2 occurring on the cathode.

A promising electrolyte for such all–copper hybrid RFB is ethaline, a DES prepared by mixing choline chloride (ChCl) and ethylene glycol (EG) at 1:2 molar ratio (Fig. 1.2). However, despite its recent emergence as a promising electrolyte candidate, fundamental knowledge about the electron transfer reactions involving redox active species in ethaline is still lacking. The relationship between chemical structure of the DES and electrochemical properties of dissolved ions is also not well understood. Finally, DES possess high viscosity which lowers diffusional transport and increases solution resistance¹⁴ – undesirable attributes that require further mechanistic studies and greater attention.



Figure 1.2. The chemical structures of choline chloride (ChCl) and ethylene glycol (EG). Ethaline is the eutectic mixture of ChCl and EG at 1:2 molar ratio.

The electrochemical investigation of charge transfer kinetics has to contend with the low conductivity of the DES solution. The conductivity of ethaline (~10 mS/cm) is about 10 times lower than typical aqueous media. Due to such low conductivity, significant portion of the applied potential during experimentation is lost to overcoming ohmic resistance of the solution. In applying certain voltammetric techniques such as cyclic voltammetry (CV) to probe electrochemical reactions in DES, the high resistivity of the solution results in incorrect characterization of the system kinetics parameters. The ramifications of this IR effect will be explained in detail in chapter 2 and a potential resolution is provided together with some general guidelines as to how to perform voltammetry in DES media. The general guidelines allow a thorough investigation of how kinetics are modulated by system variables, *e.g.*, DES composition and temperature. This helps unravel the relationship between solution-phase complexation phenomena and electron transfer kinetics as explored in chapter 3.

In this work, reaction 1.2 in ethaline serves as a model system to study the charge transfer kinetics in DES. The technique presented in chapters 2 and 3 to study kinetics can

be extended to other metal redox couples in other DES electrolyte. The kinetics information gleaned here serves as foundation in developing RFBs utilizing DES as electrolyte.

1.1.2 Neodymium Recycling Using High Temperature Molten Salt

Rare earth metals (REMs), or rare earth elements (REEs), enable important functions in numerous processes. They are used in permanent magnets in electric motors and electronic memory storage, in catalysts for automobile catalytic converters and for petroleum refining, and in phosphors for energy–efficient lighting and color displays.¹⁵ Despite their prolific usage, due to their geographical location and the complexity associated with extracting and refining them, REMs are very expensive and face potential supply risks. In fact, nearly 90% of the world's useful REM ores are mined in China.^{16,17} In the last decade, China has frequently imposed export restrictions on REMs, causing major concerns in countries that heavily use this metal for electronics and defense applications.¹⁸ For future sustainable use of REMs, the recovery and recycling of these materials from product waste is of great practical importance.¹⁹ For energy–efficient recovery of rare earth elements, one promising technique is the electrolytic refining of these metals from waste streams such as electronic waste.²⁰

Electrochemical processing, *i.e.*, electrowinning or electrorefining, using high temperature molten salt electrolytes is particularly attractive, because molten salts offer high ionic conductivity,²¹ good electrochemical stability,^{22,23} and low interfacial charge transfer resistance.^{24,25} For example, the high temperature (400 – 500 °C) halide melt used in this work – an eutectic mixture of lithium chloride and potassium chloride (LiCl–KCl)

at 55–45 mol% ratio – has excellent ionic conductivity approaching 2 S/cm, which is an order of magnitude higher than typical aqueous electrolytes. It allows for low ohmic loss, low cell voltage, and thus reduced operating costs. Also, this eutectic halide melt has a wide electrochemical stability window (above ~3.5 V), which is crucial for energy– efficient processing of active REMs. Furthermore, the low interfacial charge transfer resistance offers industrially relevant rates of processing (high current densities) and ease of scalability to large–volume manufacturing at low cost.^{26–29} These are desirable attributes for industrial scale process implementation. Because of the numerous advantages listed above, electrochemical refining in molten salts is deemed as an excellent method to recycle rare earth metals. This work focuses on neodymium (Nd) – a rare earth metal – as a model system.

Nd is a multivalent metal that is indispensable for fabricating neodymium–iron– born (Nd₂Fe₁₄B) magnets.^{19,30,31} These magnets, referred to commonly as Nd–Fe–B magnets, are the strongest of all known permanent magnets and are naturally used in applications requiring strong magnetic fields, such as hardware memory storage and electric motors.

FOCUS OF PROPOSED PROJECT



Figure 1.3. Schematic of a Nd recycling process. Nd–containing waste is placed in an molten salt electrochemical cell. By applying a voltage, Nd is selectively dissolved into Nd^{3+} ions at the anode, while on the cathode, the dissolved Nd^{3+} ions are electrodeposited as metallic Nd.

Fig. 1.3 depicts the overall concept of electrochemical recovery of Nd from electronic waste. In this concept, Nd–Fe–B magnets are first physically isolated from devices that reach end of life. Then, these magnets are inserted into an electrolytic cell containing aforementioned LiCl–KCl eutectic mixture at 400 – 500 °C, where they are anodically polarized. Application of current to cell leads to selective dissolution of the Nd metal at the anode in the form of Nd³⁺ ions. These ions migrate through the electrolyte to the cathode, where they are electrodeposited as pure Nd metal. The process leads to electrolytic separation (extraction) and purification (refining) of the Nd from Nd–Fe–B and thus is commonly referred to as 'electrorefining'.

Given the importance of Nd electrorefining, however, the fundamental electrochemical knowledge regarding Nd has not reached a mature level as compared to

other metal electrorefining processes. The key challenges with electrochemically studying Nd and developing an electrorefining process are:

- (i) Nd is multivalent, *i.e.*, it exists in multiple oxidation states. During the electrodeposition process, Nd³⁺ is first reduced to Nd²⁺ before deposited as Nd⁰ at the electrode surface. Because Nd²⁺ is only generated and consumed *in situ* near the electrode surface during reaction, its precise concentration is difficult to determine. As such, systematic analysis of the Nd system, such as measurement of the exchange currents of the Nd²⁺/Nd⁰ reaction, is difficult. In this work, the concentration of the intermediate species is numerically simulated based on a reaction–diffusion model, so that useful kinetic parameters can be extracted.
- (ii) The electrodeposition reaction displays irreversible kinetics. Due to the sluggish reaction rate, the intermediate Nd^{2+} species generated near the electrode surface is not immediately consumed. As a result, Nd^{2+} can diffuse away from the electrode surface, thus diminishing the current efficiency to 30 60%. This irreversibility is confirmed using mathematical modeling in chapter 4.

Despite the challenges of multivalency and irreversibility, the mass transport and kinetic parameters associated with Nd electrodeposition are carefully measured in this work. The understanding obtained herein can help guide the development of an electrorefining process for Nd recycling. Though focused on Nd as a model system, the techniques developed in this work can be extended to determining the charge transfer kinetics of other multivalent metals in molten-salt media.

1.2 Electrochemical Analytical Technique: Cyclic Voltammetry

In studying both Cu^{2+}/Cu^{1+} redox transition in DES and multivalent Nd³⁺/Nd²⁺/Nd⁰ electrodeposition in high temperature molten salt, cyclic voltammetry was employed to understand the reaction kinetics. Cyclic voltammetry (CV) is an electrochemical technique in which the electrode potential (V – IR) is scanned linearly as a function of time.^{32,33} The potential is swept from the initial potential to a switching potential, at which point the potential scan reverses direction and the electrode potential continues to be scanned at the same linear rate with respect to time (Fig. 1.4).



Figure 1.4. During cyclic voltammetry, the electrode potential is scanned linearly with respect to time, where the slope is the scan rate *v*.

During the potential scan, the concentrations of both oxidized and reduced species near the electrode surface change with time, thus developing concentration gradients near the electrode. Such behavior is described by Fick's second law of diffusion,

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2}$$
[1.3]

where the concentration C is a function of both time t and distance x away from the electrode surface, and D is the diffusion coefficient. The measured current density response during CV is directly proportional to the concentration gradient near the electrode surface $(I \propto \partial C/\partial x)$. Fig. 1.5 shows a typical current density response during a CV at several different scan rates.



Figure 1.5. The current density response during CV at different scan rates. The peak current density (i_{peak}) is proportional to the square root of the scan rate ($v^{1/2}$).

The current density response during CV exhibits characteristic peaks, where the magnitude of the current density reaches a maximum. When the CV is conducted at different scan rates, the peak current density (i_{peak}) increases linearly with the square root of the scan rate $(v^{1/2})$ (Fig. 1.5). Several classical models have been developed in the last century to explain this dependence of i_{peak} on the scan rate. The various analytical models are briefly discussed in the section below.

1.2.1 Analytical Solutions to CV Response

Classical models analyzing the CV response can be summarized into two categories depending on the reaction kinetics: reversible and irreversible. Assume a generic redox reaction occurring during CV:

$$0 + e^- \leftrightarrow \mathbb{R}$$
 [1.4]

When the reaction (Eq. 1.4) is reversible, the kinetics of the reaction is extremely fast. In such case, the reaction at the electrode surface is assumed to be limited by the mass transport of the reactant to the surface. For such 'reversible' systems involving two dissolved redox species (O and R), mathematical analysis of the diffusional transport (Eq. 1.3) coupled with instantaneous surface reaction yields the Randles–Sevcik equation.^{34,35}

$$i_{\text{peak}} = 0.4463 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D_0^{\frac{1}{2}} [0]_b \nu^{\frac{1}{2}}$$
 [1.5]

The Randles–Sevcik equation (Eq. 1.5) correlates the measured peak current density to number of electrons transferred (n), diffusion coefficient of the reactant (D_0), concentration of the reactant in the bulk electrolyte ([O]_b) and the square root of scan rate ($v^{1/2}$). The coefficient 0.4463 comes from the dimensionless peak current, which Randles and Sevcik solved via Laplace transformation of the Fick's second law of diffusion (Eq. 1.3). The details of the mathematical derivation can be found in standard textbooks.³⁶

For reversible systems that involve deposition of a solid phase, the peak current density is correlated to the scan rate through the Berzins–Delahay equation (Eq. 1.6). Its form is similar to the Randles–Sevcik equation, except that it has a different coefficient.

$$i_{\text{peak}} = 0.6105 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D_0^{\frac{1}{2}} [0]_b \nu^{\frac{1}{2}}$$
 [1.6]

When the reaction (Eq. 1.4) possesses sluggish kinetics, *i.e.*, it is 'irreversible', transport as well as surface reaction resistances need to be incorporated in tandem. In such cases, the Fick's second law of diffusion (Eq. 1.3) can be solved via Laplace transformation, incorporating irreversible charge transfer kinetics (Tafel equation) as the boundary condition. Because the system is kinetically limited, the peak current density depends on the charge transfer coefficient (α_c), as derived by Nicholson and Shain.³⁷

$$i_{\text{peak}} = 0.4958 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} \alpha_c^{\frac{1}{2}} D_0^{\frac{1}{2}} [0]_b \nu^{\frac{1}{2}}$$
[1.7]

The above classical models, while useful and convenient, are limited to only when the reaction (Eq. 1.4) is either reversible or irreversible. For reactions that are in between, *i.e.*, quasi-reversible, the classical models fail to capture the current response during CV. Furthermore, these CV models assume a linear change in the surface potential with time – a condition not easy satisfied in resistive electrolytes. The Cu and Nd systems explored in this work (chapters 2 and 4) will demonstrate the limitations of existing models. Also, these classical theories apply only to single–step reactions. In the case of multi–step reaction, such as the reduction of multivalent Nd, the model is insufficient in explaining the dependence of i_{peak} on $v^{1/2}$.

1.3 Objectives and Outline of Present Work

The specific objectives of the present research are:

- Develop reliable voltammetric methods (and associated mathematical models) in order to gain quantitative insights into the charge transfer kinetics in DES and molten salts. Application of these methods will lead to insights into variables that control sluggish charge transfer kinetics in DES and multivalent Nd electrodeposition kinetics from halide melts;
- 2) Develop guidelines to obtain reliable cyclic voltammetry data when the solution is resistive, *i.e.*, ohmic resistance is large such as in DES (chapter 2);
- Unravel the mechanistic underpinnings (complexation) of the sluggish kinetics associated with metal redox transition in ethaline DES (1:2 molar ratio ChCl:EG) (chapters 2 & 3);

 Using CV studies combined with diffusion–reaction modeling, characterize the electrodeposition kinetics of multivalent Nd in high temperature molten salts (chapter 4).

The above objectives are addressed in chapters 2–4 and key conclusions are summarized in chapter 5.

In chapter 2, common pitfalls when taking measurements in highly resistive electrolytes are discussed. The importance of real-time IR_{Ω} compensation during CV and the use of electrode configurations, such as microelectrodes, that provide uniform secondary current distribution, are highlighted. With these precautions in place, fast scan CV is first performed on Pt RDE to investigate the Cu²⁺/Cu¹⁺ redox reaction. The results are first analyzed in the context of classical reversible and irreversible models and then coupled with diffusion-reaction modeling to yield accurate kinetics parameters. Slow scan linear sweep voltammetry (LSV) is then conducted on Pt RDE to verify the kinetics findings from fast scan CV. To further avoid possible non-uniform secondary current distribution, slow scan LSV is also performed on a Pt microelectrode. These three independent techniques are employed to accurately measure the kinetics parameters (exchange current density, charge transfer coefficients) associated with the Cu²⁺ + $e^- \Rightarrow$ Cu¹⁺ redox reaction.

In chapter 3, slow scan LSV on Pt RDE is used to monitor the dependence of charge transfer kinetics on system parameters, such as copper species concentration, chloride concentration, and operating temperature. A simple mathematical model is developed to explain the dependence of exchange current density on these system parameters, and the role of species complexation with Cl⁻ in DES is highlighted.

In chapter 4, Nd electrodeposition is studied. A three–electrode setup is used to conduct fast scan CV at different scan rates in a NdCl₃-containing LiCl-KCl halide melt at 475 °C. The resulting peak currents are first compared to classical Randles–Sevcik and Berzins–Delahay models. Deviations from theory are used to indicate system irreversibility. A diffusion–reaction model is developed and compared with experiments to precisely determine the reaction kinetics of the multistage reduction process associated with Nd electrolysis.

CHAPTER 2. Guidelines on Voltammetric Techniques to Analyze Kinetic Parameters of Metal Redox Couple in Deep Eutectic Solvents

As discussed in the introduction, grid–scale energy storage devices, *i.e.*, redox flow batteries, are critical to the renewable energy revolution. Deep eutectic solvents (DES) are drawing attention as a suitable electrolytes because of their numerous advantages over conventional organic or ionic liquid electrolytes. These advantages include low–cost,^{12,13} ease of preparation,⁷ biodegradability and environmentally benignity,⁸ electrochemical stability,^{9–11} and non–flammability.

A popular DES system incorporates ethaline which is a mixture of choline chloride (ChCl) and ethylene glycol (EG) in a 1:2 molar ratio.⁶ Electroactive species, such as cupric (Cu²⁺) and cuprous (Cu¹⁺) ions are added to ethaline in the form of their respective chloride salts. The density, conductivity and viscosity of CuCl₂–containing ethaline at various concentrations and temperatures were reported by Ghosh *et al.*³⁸ Similar work was also done by Popescu *et al.*³⁹

Abbott *et al.* first investigated the transport properties of such a DES system by performing cyclic voltammetry (CV) studies.⁴⁰ Since then, Lloyd *et al.* proposed an all– copper hybrid RFB.⁶ In the context of electrodeposition, which occurs on the anode during charging of the RFB, Abbott's group demonstrated high current efficiencies (>99%) for Cu electrodeposition from dilute (10–20 mM) electrolytes and the possibility to obtain bright Cu deposits via electronucleation in a progressive mode.⁴⁰ Ghosh *et al.* also obtained smooth deposits with high current efficiencies (>90%) when using more concentrated (200 mM) electrolytes.⁴¹
In terms of the reaction occurring on the cathode, Lloyd *et al.* first reported the kinetics of $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$ in ethaline medium.⁴² These investigators reported a cathodic charge transfer coefficient $\alpha_c \approx 0.2$ –0.3 and a reaction rate constant $k_0 \approx (8$ –11) $\times 10^{-4}$ cm/s associated with the Cu²⁺/Cu¹⁺ redox reaction. The value of the charge transfer coefficient α_c well below 0.5 suggested an asymmetric polarization behavior of Cu²⁺/Cu¹⁺ redox transition. Such low values of α_c stand in contrast to accepted symmetric behavior ($\alpha_c \approx 0.5$) of this redox reaction in aqueous media. For example, Kiekens *et al.*⁴³ reported $\alpha_c = 0.49$ and $k_0 = 4.6 \times 10^{-3}$ cm/s for the Cu²⁺/Cu¹⁺ redox reaction. This apparent discrepancy in the kinetics parameters motivated this work outlined in chapter 2 and 3 to investigate more carefully the kinetics behavior for Cu²⁺/Cu¹⁺ in ethaline with the goal of understanding the source of this inconsistency.

Accurate kinetics measurements in DES electrolytes are particularly difficult to conduct. This is because of the fact that, near ambient temperature, DES systems such as ethaline are highly resistive with ionic conductivities only in the 1–10 mS/cm range.^{44,45} Other DES systems with higher viscosities may be even more resistive.^{46,47} The resistive nature of the electrolyte, as shown below, necessitates precise IR_{Ω} correction during kinetics measurements as also emphasized by Lloyd *et al.*⁴² Furthermore, care must be taken to avoid conditions under which the resistive DES renders the current distribution on a macro–electrode such as RDE to be highly non–uniform. This may be accomplished by operating at low current densities; however, background currents often interfere with such low reaction rates and this further adds uncertainty to the kinetics analysis. In this chapter, the common pitfalls associated with kinetics measurements in resistive DES electrolytes is discussed. While ethaline is used as a model system, the best practices presented herein

can be extended to other DES systems. Here, we present a comprehensive study of the transient (CV) and steady–state polarization measurements on RDE and microelectrodes coupled with diffusion–reaction modeling. This study results in the identification of reliable kinetics parameters for the Cu^{2+}/Cu^{1+} redox transition in ethaline.

2.1 Experimental Procedure

In this chapter, electrochemical reduction of Cu^{2+} to Cu^{1+} in ethaline DES was investigated. The electrochemical cell consisted of a cylindrical Pyrex container with a flat bottom. A Teflon[®] lid with appropriate opening for electrodes was used to slow down the absorption of moisture and oxygen during cell operation. The ethaline electrolyte was prepared by mixing choline chloride (ChCl, 99% purity, Acros Organics) and ethylene glycol (EG, anhydrous, 99.8% purity, Sigma–Aldrich) in 1:2 molar ratio at 80 °C until a homogeneous phase was obtained. All experiments were carried out at room temperature $(20 \pm 1 \text{ °C})$. Cupric chloride dihydrate (CuCl₂·2H₂O, 99% purity, Acros Organics) and cuprous chloride (CuCl, anhydrous, 99% purity, Acros Organics) were added to ethaline to provide Cu²⁺ and Cu¹⁺ concentrations of 10 mM or 100 mM. The ethaline containing CuCl₂·2H₂O was dried at 100 °C for 12–14 hours to remove moisture content. The electrolytes were then purged with Ar to remove dissolved O₂ before CuCl was added. The removal of O_2 is critical in order to prevent bulk oxidation of Cu^{1+} to Cu^{2+} . The electrolytes were stored under Ar atmosphere until experimentation and were used as soon as possible to avoid further moisture and oxygen uptake. For careful analysis, both Cu²⁺ and Cu¹⁺ were added to the ethaline electrolyte, so that the equilibrium potential of

the working electrode was well-defined, stable and reproducible. During electrochemical experiments, a three-electrode configuration was employed, in which the working electrode was a 0.5 cm diameter platinum RDE (mirror polished, Pine Research Instrumentation, Inc) with electrode area of 0.196 cm^2 . Experiments were also carried out on a 10 μ m diameter platinum microelectrode (BASi MF-2005, surface area = 78.5 μ m²) working electrode. For all experiments, the counter electrode was a 0.32 cm diameter graphite rod (Graphite store). The reference electrode was a silver (Ag) wire (99.9% purity, Rio Grande) anodized in ethaline. By holding the Ag wire at a positive potential (1 V vs. graphite counter electrode), a thin, white AgCl layer formed, which provided a pseudo Ag/AgCl reference electrode for experiments. Such reference electrodes have been employed in previous studies of ethaline.^{40,48} All potentials reported below are with respect to the Ag/AgCl reference. A Princeton Applied Research PARSTAT-4000 potentiostat with automated data acquisition and IR_{Ω} compensation was used for all electrochemical measurements. For cyclic voltammetry studies, scan rate was varied between 10–1500 mV/s. RDE rotation speed was varied between 100–1500 RPM. Steady-state polarization studies were carried out at a slow scan rate of 1 mV/s to minimize transient effects. Viscosity measurements were done using an automated viscometer (RheoSense *micro*VISCTM). Electrolyte conductivity was measured using an Oakton PC 2700 multi-purpose meter.

2.2 Cyclic Voltammetry Studies of Cu²⁺/Cu¹⁺ Redox Transition – Avoiding Pitfalls and Obtaining Reliable Voltammograms

In this section, sub–optimal experimental conditions during CV, *i.e.*, large background currents and incorrect IR_{Ω} compensation, are shown to introduce errors in CV analysis. Selection of experimental conditions to enable reliable CV data is first discussed, and then the actual CV results are analyzed in greater detail.

2.2.1 Contribution of Background Current during Voltammetry

Cyclic voltammetry (CV) was employed to study the redox reaction $Cu^{2+} + e^- \Rightarrow Cu^{1+}$ in deep eutectic solvent ethaline. Fig. 2.1 shows the cyclic voltammograms (at 1.5 V/s) measured on a Pt RDE immersed in blank ethaline (*black*) and in ethaline containing Cu^{2+} at 10 mM (*green*) and 100 mM (*blue*) concentrations. In the absence of Cu^{2+} ions, the background current was low in the potential range from -0.2 to 1.0 V indicating reasonable electrochemical stability of ethaline. With the addition of Cu^{2+} , CV showed a prominent reduction peak (0.3 V) in the cathodic scan direction, corresponding to $Cu^{2+} + e^- \rightarrow Cu^{1+}$ reduction reaction, and an oxidation peak (0.6 V) in the anodic scan direction, corresponding to $Cu^{1+} \rightarrow Cu^{2+} + e^-$ oxidation reaction. At the low Cu^{2+} concentration (10 mM), the background current (*black*) constituted as much as 20% of the measured reduction current (*green*). On the other hand, at bulk Cu^{2+} concentration of 100 mM, the background current became just ~2% of the reduction current (*blue*). To avoid cumbersome background subtraction and to simplify the data analysis, we

performed subsequent CV experiments at Cu²⁺ and Cu¹⁺ concentrations of 100 mM each, so that the measured current can be assumed to be predominantly due to the Cu²⁺ + $e^- \rightleftharpoons$ Cu¹⁺ redox reaction.



Figure 2.1. Cyclic voltammograms (1500 mV/s) measured on a Pt RDE immersed in ethaline in the presence of Cu^{2+} (10 mM – *green*; 100 mM – *blue*) and in the absence of Cu^{2+} (*black*). Data at the higher Cu^{2+} concentration is less convoluted by the background current which constitutes less than 2% of the total measured current.

2.2.2 Importance of Real-Time IR Compensation

During a linear sweep of the electrode potential, the applied potential V is related to the electrode potential E via:

$$V - IR_{\Omega} = E$$
 [2.1]

Since the current I varies as V is swept, the ohmic drop IR_{Ω} too varies over time. In situations where the electrolyte resistance R_{Ω} is large, such as in viscous DES including ethaline, the ohmic drop may shift the electrode potential E substantially depending on the magnitude of the current. Moreover, as I varies non–linearly with V, a linear scan of V implies a non–linear drift in the actual electrode potential E over time. Such interference from uncompensated or incorrectly compensated ohmic resistance could be mistaken as heterogeneous kinetics limitations.³² For analysis of CV data, it is essential to ensure a linear change in E over time. This can be accomplished using real–time IR_{Ω} compensation in which a non–linear variation in V over time is intentionally introduced (Fig. 2.2, in *red*) so as to ensure that V – IR_{Ω} (Fig. 2.2, in *black*) varies linearly with time. The slope of the IR_{Ω} –corrected potential profile is the scan rate, which was set at 1.5 V/s for the data presented in Fig. 2.2.



Figure 2.2. During real-time IR_{Ω} compensation during CV, a non-linear potential (V) profile is applied to the electrode surface, which provides a linear surface potential (E = V - IR_{Ω}) variation with time. Data is shown for scan rate of 1.5 V/s.

For live IR_{Ω} compensation, the ohmic resistance R_{Ω} must be known. For a disc electrode with radius *r*, R_{Ω} is given by:⁴⁹

$$R_{\Omega} = \frac{1}{4\kappa r}$$
[2.2]

where κ is the conductivity of the electrolyte. For ethaline containing $[Cu^{2+}] = 100 \text{ mM}$ and $[Cu^{1+}] = 100 \text{ mM}$, the conductivity was measured to be $\kappa = 9.4 \text{ mS/cm}$. Thus, for a disc of radius r = 0.25 cm, R_{Ω} is 110 Ω . This electrolyte resistance was also confirmed using electrochemical impedance spectroscopy (EIS) measurements, which yielded a value of 110 Ω . Knowing R_{Ω} , live IR_{Ω} compensation could be implemented in CV.

2.2.3 Analysis of Current Response during Potential Scan

After selection of the Cu²⁺ and Cu¹⁺ concentrations (100 mM) and after applying real-time IR_Ω compensation, CVs were collected on a Pt RDE at various scan rates (10– 1500 mV/s). The presence of Cu²⁺ and Cu¹⁺ in equimolar concentrations establishes a stable equilibrium potential of 0.415 V vs. Ag/AgCl on a Pt electrode. During CV, the potential was first scanned from 0.415 V to -0.2 V and then back to 1.0 V. Fig. 2.3(a) shows the first cycle of the CV collected at three representative scan rates (100, 300 and 500 mV/s). As the scan rate increased, the maximum (peak) cathodic current density (i_{peak}) increased. The peak potential (E_{peak}, at which the current density is i_{peak}) was observed to shift slightly with scan rates too, which suggests irreversibility and sluggish kinetics analogous to the observations reported by Abbott and co–workers.⁴⁰ The equilibrium potential (0.415 V) matched the average of the cathodic and anodic peak potentials further confirming that the CV represents the redox reaction Cu²⁺ + $e^- \Rightarrow$ Cu¹⁺.



Figure 2.3. (a) Voltammograms collected on a Pt RDE immersed in ethaline containing 100 mM Cu²⁺ and 100 mM Cu¹⁺ at scan rates: 100 mV/s (*black*), 300 mV/s (*green*) and 500 mV/s (*blue*). During the cathodic scan direction, Cu²⁺ is reduced into Cu¹⁺. (b) The cathodic peak current density (i_{peak}) exhibits a linear dependence on the square root of the scan rate. Also, i_{peak} is fairly independent of the RDE rotation speed.

The cathodic peak current density (i_{peak}) measured at different scan rates (v) and RDE rotation speeds (ω) is plotted as a function of the square root of the scan rate (\sqrt{v}) in Fig. 2.3(b). Two observations can be made: (*i*) A linear relationship between i_{peak} and \sqrt{v} is noted; and (*ii*) i_{peak} is relatively independent of the ω . These observations suggest either a diffusion–limited reversible or irreversible behavior of the Cu²⁺ + $e^- \rightleftharpoons$ Cu¹⁺ reaction as will be analyzed quantitatively in the subsequent section.

2.3 Application of Classical Theory to Experimental CV Data

2.3.1 Treatment of Diffusion–Limited Reversible Redox Transitions

If $Cu^{2+} + e^- \rightarrow Cu^{1+}$ were a diffusion-limited reversible electrochemical reaction, i_{peak} during a linear potential (E) scan would be given by the Randles-Sevcik equation (Eq. 1.5).^{34,35} In this context, Eq. 1.5 could be written as

$$i_{\text{peak}} = -0.4463 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D_{2+}^{\frac{1}{2}} \left[Cu^{2+}\right]_{b} \nu^{\frac{1}{2}}$$
[2.3]

where F is the Faraday's constant, R is the ideal gas constant, T is the temperature, n is the number of electrons transferred, D_{2+} is the Cu²⁺ diffusion coefficient, $[Cu^{2+}]_b$ is the Cu²⁺ bulk concentration, and ν is the scan rate. Taking n = 1, $D_{2+} = 1.56 \times 10^{-7}$ cm²/s, the basis for which is discussed in the section below, and $[Cu^{2+}]_b = 100$ mM, the peak current density predicted by Eq. 2.3 is plotted in Fig. 2.4 (reversible theory, *dashed* line). While reasonable agreement with experimentally measured i_{peak} data is noted only at low scan rates (<30 mV/s), i_{peak} predicted by Eq. 2.3 deviates considerably from experiments at higher scan rates (>50 mV/s). The suppression in the peak cathodic current density suggests kinetics limitations. Previous studies too have reported the $Cu^{2+} + e^- \rightarrow Cu^{1+}$ redox transition to be 'quasi-reversible'.⁴² To assess irreversibility, this work performs below analytical and numerical simulations of the diffusion-reaction processes involved in the $Cu^{2+} + e^- \rightarrow Cu^{1+}$ redox transition. However, before such analysis can be performed, the diffusion coefficients of the Cu^{2+} and Cu^{1+} species must be precisely measured.



Figure 2.4. Comparison between the experimentally measured cathodic peak current densities (from Fig. 2.3) and those computed using classical models for diffusion–limited reversible (Eq. 2.3, *dashed* line) and irreversible reactions (Eq. 2.6, *dotted* line). The experimental peak currents are in closer agreement with the irreversible theory predictions especially at higher scan rates.

2.3.2 Determination of Cu²⁺ and Cu¹⁺ Diffusion Coefficients in Ethaline

Previous literature have reported diffusion coefficient values of the Cu²⁺ and Cu¹⁺ species in ethaline. Using chronoamperometry and EIS, Lloyd *et al.*⁴² determined D_{2+} to be 1.6×10^{-7} cm²/s and D_{1+} to be 2.8×10^{-7} cm²/s. Abbott *et al.*⁴⁰ reported D_{2+} to be 2.4×10^{-7} cm²/s by applying the Randles–Sevcik equation to CV data at small scan rates (<50 mV/s). Similar to Abbott et al., Ghosh *et al.*³⁸ also applied the Randles–Sevcik equation to their CV data at small scan rates (<50 mV/s) and they reported D_{2+} to be 1.22×10^{-7} cm²/s. Given the considerable variability in diffusion coefficients reported in literature, it is necessary to precisely determine the diffusivity values using steady–state limiting current measurements, as the precise values of D_{2+} and D_{1+} are essential for kinetics analysis.



Figure 2.5. Cathodic (a) and anodic (b) limiting current densities were measured on a Pt RDE immersed in ethaline containing 100 mM each of Cu^{2+} and Cu^{1+} . From the dependence of the limiting current densities on the RDE rotation speed, the Cu^{2+} and Cu^{1+} diffusion coefficients (D_{2+} and D_{1+}) were estimated. These values are reported in Table 2.2.

The Cu^{2+} and Cu^{1+} diffusion coefficients were obtained from limiting current measurements on a Pt RDE immersed in ethaline containing equimolar (100 mM) concentration of Cu^{2+} and Cu^{1+} . The diffusion coefficient is related to the limiting current through the Levich equation:⁵⁰

$$i_{\rm L}^{\rm c} = -0.62 {\rm nFD}_{2+}^{\frac{2}{3}} \left[\frac{\mu}{\rho}\right]^{-\frac{1}{6}} [{\rm Cu}^{2+}]_{\rm b} \omega^{\frac{1}{2}}$$
[2.4]

$$i_{\rm L}^{\rm a} = 0.62 {\rm nF} D_{1+}^{\frac{2}{3}} \left[\frac{\mu}{\rho} \right]^{-\frac{1}{6}} [{\rm Cu}^{1+}]_{\rm b} \omega^{\frac{1}{2}}$$
[2.5]

where $i_{\rm L}$ is the limiting current density (superscript 'c' indicates cathodic and 'a' indicated anodic reactions), ω is the RDE rotation speed, μ is the viscosity and ρ is the density of the electrolyte ($\mu/\rho = 0.53 \text{ cm}^2/\text{s}$ at 20 °C). Other parameters have their usual meanings as defined before. Fig. 2.5 shows the dependence of the cathodic and anodic limiting current densities on the RDE rotation speed. A linear relationship between $i_{\rm L}$ and $\sqrt{\omega}$ is observed, with the linear regression line going through origin, hence confirming Levich behavior. The cathodic limiting current density $i_{\rm L}^{\rm c}$ values were taken at -0.1 V vs. Ag/AgCl where the reaction $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^{1+}$ exhibits diffusion–limited behavior (Fig. 2.5(a)). The anodic limiting current density $i_{\rm L}^{\rm a}$ values were taken at 0.8 V vs. Ag/AgCl where the reaction $\text{Cu}^{1+} \rightarrow \text{Cu}^{2+} + e^-$ exhibits diffusion–limited behavior (Fig. 2.5(b)). The best– fit slope of the $i_{\rm L}$ vs. $\sqrt{\omega}$ data provided the Cu²⁺ and Cu¹⁺ diffusion coefficients as: $D_{2+} =$ $1.56 \times 10^{-7} \text{ cm}^2/\text{s}$ and $D_{1+} = 2.57 \times 10^{-7} \text{ cm}^2/\text{s}$. These diffusion coefficients are in good agreement with those found in literature.

2.3.3 Treatment of Diffusion–Limited Irreversible Redox Transitions

In the case where the redox transition between two soluble species (*i.e.*, $Cu^{2+} + e^- \rightarrow Cu^{1+}$) is irreversible, the dependence of i_{peak} on the scan rate is given by the expression derived by Nicholson and Shain (Eq. 1.7).³⁷ For this system, the equation is written as

$$i_{\text{peak}} = -0.4958 \left(\frac{F^3}{\text{RT}}\right)^{\frac{1}{2}} \alpha_c^{\frac{1}{2}} D_{2+}^{\frac{1}{2}} \left[\text{Cu}^{2+}\right]_b \nu^{\frac{1}{2}}$$
[2.6]

where α_c is the charge transfer coefficient of the electrochemical reaction. Eq. 2.6 differs from the aforementioned Randles–Sevcik equation in that it incorporates the charge transfer coefficient α_c . Taking α_c to be 0.49 (the basis for which is explained in the next section on numerical modeling of the linear sweep voltammetry response) and D_{2+} to be 1.56×10^{-7} cm²/s (as discussed above), Eq. 2.6 provided the predicted value of i_{peak} as a function of the scan rate. This result is plotted in Fig. 2.4 (irreversible theory, *dotted* line). It is observed that, particularly at high scan rates (\gg 50 mV/s), the irreversible model (Eq. 2.6) is in better agreement with experimental CV data than the reversible model (Eq. 2.3).

Besides providing i_{peak} , the model assuming irreversible Cu²⁺/Cu¹⁺ redox transition provides an expression for E_{peak} which depends on the reaction rate constant k_0 as:³²

$$E_{\text{peak}} = E^{0} - \frac{RT}{\alpha_{c}F} \left[0.780 + \ln\left(\frac{D_{\text{Cu}^{2+}}^{\frac{1}{2}}}{k_{0}}\right) + \ln\left(\frac{\alpha_{c}F\nu}{RT}\right)^{\frac{1}{2}} \right]$$
[2.7]

Assuming $\alpha_c = 0.49$, and fitting E_{peak} obtained from Fig. 2.3(a) to Eq. 2.7 at high scan rates (500–1500 mV/s), we obtained $k_0 = 1.85 \times 10^{-4}$ cm/s. For equimolar concentrations of Cu^{2+} and Cu^{1+} of 100 mM, the exchange current density (i_0) could be estimated via: $i_0 = 1 F k_0 [Cu^{2+}]^{1-\beta} [Cu^{1+}]^{\beta}$, where β is the symmetry factor and $\beta \times n = \alpha_c$.⁴⁹ This provides $i_0 = 1.78 \text{ mA/cm}^2$ which is a value that is further validated in the diffusion– reaction modeling of linear scan voltammetry discussed below. Nonetheless, $i_0 = 1.78$ mA/cm^2 suggests that the Cu^{2+/}Cu¹⁺ redox transition does not have very fast kinetics. In contrast, in previous studies of the Cu²⁺/Cu¹⁺ redox transition in aqueous media, Kiekens et al.⁴³ reported $\alpha_c = 0.49$ and $k_0 = 4.6 \times 10^{-3}$ cm/s. Independently, Bockris et al.⁵¹ reported $i_0 \approx 100 \text{ mA/cm}^2$. The k_0 and i_0 values for Cu²⁺/Cu¹⁺ in ethaline measured in this work are 1-2 orders of magnitude lower than those known for the same redox reaction in aqueous media. Yet, our values agree reasonably well to those reported by Bahadori *et al.* for electrochemical reduction of metallocene derivatives in ethaline ($k_0 \approx$ 10^{-4} cm/s),¹⁰ suggesting that the medium ethaline plays a role in modulating reaction rates at the electrode surface. The exact mechanism through which ethaline modulates the reaction rate will be explained in chapter 3.

The irreversibility of the Cu²⁺/Cu¹⁺ redox transition can also be assessed by a scaling method developed by Nicholson,⁵² in which the peak potential separation ΔE_{peak} , *i.e.*, $|E_{\text{peak}}^c - E_{\text{peak}}^a|$ which is a measure of irreversibility, is related to a dimensionless parameter ψ . For n = 1, and for $0.3 \le \alpha_c \le 0.7$, Nicholson provides:

$$\psi = \frac{\left[\frac{D_{2+}}{D_{1+}}\right]^{\frac{\alpha_c}{2}}}{\left[\frac{\pi D_{2+}F}{RT}\nu\right]^{\frac{1}{2}}}k_0$$
[2.8]

If ψ is low (approaching 0), the reaction is deemed irreversible. In the case of the Cu²⁺/Cu¹⁺ redox transition, we confirmed that $\psi < 0.1$ for $\nu > 300$ mV/s. This confirms irreversible redox transition consistent with the relatively low k_0 determined above by applying Eq. 2.7 and the agreement (at high scan rates) between the irreversible model (Eq. 2.6) and experimental data shown in Fig. 2.4.

2.4 Diffusion-Reaction Modeling for Precise Determination of the Kinetics Parameters

2.4.1 Diffusion–Reaction Model Setup

The multi–component transport and interfacial charge–transfer ($Cu^{2+} + e^- \rightarrow Cu^{1+}$) processes in the proximity of a disc electrode^{28,53} are depicted in Fig. 2.6. Assuming diffusion as the primary mode of transport, the Cu²⁺ and Cu¹⁺ concentrations within the Nernst boundary layer (thickness = δ) obey Fick's second law:

$$\frac{\partial [\operatorname{Cu}^{2+}]}{\partial t} = D_{2+} \frac{\partial^2 [\operatorname{Cu}^{2+}]}{\partial x^2}$$
[2.9]

$$\frac{\partial [\operatorname{Cu}^{1+}]}{\partial t} = D_{1+} \frac{\partial^2 [\operatorname{Cu}^{1+}]}{\partial x^2}$$
[2.10]

where *x* represents position and *t* represents time. During an electrode potential scan, the surface potential $E (= V - IR_{\Omega})$ is varied with the following time–dependence:

$$\mathbf{E} = \mathbf{E}_{\mathbf{i}} - \nu t \tag{2.11}$$

where E_i is the initial potential (taken as 0.415 V vs. Ag/AgCl, *i.e.*, the measured equilibrium potential as discussed above for $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$) and ν is the scan rate.



Figure 2.6. Schematic representation of the diffusion and electrochemical reaction processes during the reduction of Cu^{2+} to Cu^{1+} . This mechanistic picture serves as the basis for the mathematical model presented in this chapter.

Initially (t = 0), the concentrations of Cu²⁺ and Cu¹⁺ are equal to their bulk values. Thus:

$$t = 0$$
; $0 \le x \le \delta$: $[Cu^{2+}] = [Cu^{2+}]_{b}$ [2.12]

$$t = 0$$
; $0 \le x \le \delta$: $[Cu^{1+}] = [Cu^{1+}]_{b}$ [2.13]

At the edge of the boundary layer, the concentrations of Cu^{2+} and Cu^{1+} are fixed at their bulk values:

$$t > 0$$
; $x = \delta$: $[Cu^{2+}] = [Cu^{2+}]_b$ [2.14]

$$t > 0$$
; $x = \delta$: $[Cu^{1+}] = [Cu^{1+}]_b$ [2.15]

At the electrode surface (x = 0), mass balance dictates that the Cu²⁺ diffusional flux towards the electrode must be equal to the Cu¹⁺ diffusional flux away from it:

$$-D_{2+}\frac{\partial[\operatorname{Cu}^{2+}]}{\partial x} = D_{1+}\frac{\partial[\operatorname{Cu}^{1+}]}{\partial x}$$
[2.16]

The rate of electrochemical conversion of Cu^{2+} to Cu^{1+} is assumed to obey classical Butler–Volmer kinetics. Thus:^{32,54}

$$-D_{2+} \frac{\partial [Cu^{2+}]}{\partial x} = k_0 [Cu^{1+}]^{\beta} [Cu^{2+}]^{1-\beta} \left\{ \left(\frac{[Cu^{1+}]}{[Cu^{1+}]_b} \right) e^{\frac{(1-\beta)nF}{RT}\eta_s} - \left(\frac{[Cu^{2+}]}{[Cu^{2+}]_b} \right) e^{\frac{-\beta nF}{RT}\eta_s} \right\}$$

$$[2.17]$$

where k_0 is the reaction rate constant, β is the charge transfer symmetry factor, which can be correlated to the cathodic charge transfer coefficient α_c via $\alpha_c = \beta \times n$, (in this case, $\alpha_c = \beta$), and η_s is the surface overpotential ($\eta_s = E - E_{eq}$, where E_{eq} is the equilibrium potential of 0.415 V). The transient diffusion equations (Eq. 2.9 and 2.10), with the appropriate initial and boundary conditions (Eq. 2.12–2.17), can be solved numerically, *e.g.*, using COMSOL Multiphysics, to compute the time–dependent concentration profiles of Cu²⁺ and Cu¹⁺ in the diffusion boundary layer during the linear potential scan. Also, for a given value of α_c and of k_0 , the transient current density during the potential scan can be computed:

$$i = nFk_0[Cu^{1+}]^{\beta}[Cu^{2+}]^{1-\beta} \left\{ \left(\frac{[Cu^{1+}]}{[Cu^{1+}]_b} \right) e^{\frac{(1-\alpha_c)F}{RT}\eta_s} - \left(\frac{[Cu^{2+}]}{[Cu^{2+}]_b} \right) e^{\frac{-\alpha_cF}{RT}\eta_s} \right\}$$
[2.18]

2.4.2 Model Parameters and Simulation Results

The parameters used in the numerical simulations are listed in Table 2.1. The bulk concentrations of Cu²⁺ and Cu¹⁺ were 100 mM similar to experiments reported above. The diffusion coefficients values were available from limiting current measurements as described above. The diffusion boundary layer thickness was calculated using the Levich equation for a RDE rotation speed of 100 RPM. Since the kinetic parameters, *i.e.*, α_c and k_0 , are not *a priori* known, a multi–parameter optimization was performed to determine their best values. The coefficient α_c was varied in the range 0.1–0.8 and the reaction rate constant k_0 was varied between 6.5×10^{-5} and 2.3×10^{-4} cm/s. Optimal values of α_c and k_0 that provide simulated i_{peak} and E_{peak} both within 3% of the respective experimental values were determined for 300 mV/s scan rate. The result is displayed in the form of a contour plot (Fig. 2.7). The region in black represents a difference between modeled and

experimental i_{peak} and E_{peak} values of 3% or below. Error minimization provided the following best–fit values of the two parameters: $\alpha_c = 0.5$ and $k_0 = 1.95 \times 10^{-4}$ cm/s. Using these optimum kinetics parameters, the simulated current response during a cathodic potential sweep shows reasonable agreement with experiment as seen in Fig. 2.8 for the case of $\nu = 300$ mV/s.

Parameter Value $[Cu^{2+}]_{b}$ 100 mM $[Cu^{1+}]_b$ 100 mM $1.56 \times 10^{-7} \text{ cm}^2/\text{s}$ D_{2+} $2.57 \times 10^{-7} \text{ cm}^2/\text{s}$ D_{1+} 0.415 V vs. Ag/AgCl Ei $10 - 1500 \ mV/s$ ν δ 24 µm 100 RPM ω

Table 2.1. Model parameters for the diffusion–reaction model used in simulating current responses during potential sweep.



Figure 2.7. Contour plot showing percentage difference between numerical model predictions of i_{peak} and E_{peak} and corresponding experimental data for 300 mV/s scan rate. Error minimization provides best–fit kinetics parameters: $\alpha_c = 0.5$ and $k_0 = 1.95 \times 10^{-4}$ cm/s.



Figure 2.8. Comparison between experimental voltammetry data (*green*) and current– potential response predicted by the diffusion–reaction model (*blue*) for a scan rate of 300 mV/s. Model parameters are reported in Table 2.1. Kinetics parameters were: $\alpha_c = 0.5$ and $k_0 = 1.95 \times 10^{-4}$ cm/s. Good agreement between experiments and model predictions is observed.

The numerical model now allows prediction of i_{peak} over a wide range of scan rates (10–1500 mV/s). The simulated i_{peak} is shown by the solid *blue* line in Fig. 2.9. Note the excellent agreement with experimental data. The fact that numerical simulations must incorporate kinetic limitations (Eq. 2.17) to provide good agreement with experimental data especially at high scan rates is once again confirmation that $Cu^{2+} + e^- \rightarrow Cu^{1+}$ is not a fast reaction. Note also that the numerical model provides agreement with experiments over the entire range of scan rates studied. This is a considerable advantage over analytical models (Eq. 2.3 and Eq. 2.6) which, as seen in Fig. 2.9, either agree with experiments at low–scan rates (reversible) or high scan rates (irreversible) but do not provide agreement over both regimes. Additionally, the incorporation of full Butler–Volmer kinetics accurately captures the system behavior.



Figure 2.9. Comparison between the cathodic peak current densities measured experimentally (*red* data points) and the prediction from the diffusion–reaction model (*blue* curve) developed herein. Good agreement is noted. At slow scan rates, the model prediction merges with the reversible theory prediction. At high scan rates, the model prediction merges with the irreversible theory prediction.

The optimized value for k_0 provided a reliable estimate for the exchange current density: $i_0 = 1Fk_0[Cu^{2+}]^{1-\beta}[Cu^{1+}]^{\beta}$. Taking $\beta = \alpha_c = 0.5$, $k_0 = 1.95 \times 10^{-4}$ cm/s, and $[Cu^{2+}] = [Cu^{1+}] = 100$ mM, we get $i_0 = 1.88$ mA/cm². To further confirm that the kinetics parameters obtained via diffusion–reaction modeling are reliable, traditional polarization measurements were performed on a rotating disc electrode as well as a microelectrode.

2.5 RDE and Microelectrode Investigations of Electrochemical Kinetics

2.5.1 Slow–Scan Linear Sweep Voltammetry on RDE

To experimentally determine the kinetics parameters of the Cu^{2+}/Cu^{1+} redox transition, slow scan (1 mV/s) linear sweep voltammetry was performed on a Pt RDE immersed in ethaline containing equimolar (100 mM) concentrations of Cu^{2+} and Cu^{1+} . The slow scan ensured pseudo steady–state conditions at all times during measurement. The electrode potential was scanned from 0.415 V to –0.2 V vs. Ag/AgCl and the current response was recorded. The current varied as a function of the surface overpotential (η_s) which is defined as:

$$\eta_{\rm s} = \mathrm{E} - \mathrm{E}_{\rm eq} = (\mathrm{V} - \mathrm{IR}_{\Omega}) - \mathrm{E}_{\rm eq}$$
[2.19]

Fig. 2.10(a) shows a plot of the current density as a function of η_s . At large surface overpotentials, mass transport limitations are observed ($i_L^c \approx -1.4 \text{ mA/cm}^2$ at 500 RPM). At smaller overpotentials, the polarization data could be fitted to the Tafel equation:³²

$$i = i_0 \left(1 - \frac{i}{i_{\rm L}} \right) \exp\left(-\frac{\alpha_{\rm c} F}{RT} \eta_{\rm s} \right)$$
[2.20]

Fig. 2.10(b) shows the Tafel plot from which the slope and y-intercept were determined. These provided the kinetics constants: $\alpha_c = 0.49$ and $i_0 = 1.72 \text{ mA/cm}^2$ (corresponding to a rate constant $k_0 = 1.78 \times 10^{-4} \text{ cm/s}$). These values are in excellent agreement with those obtained from diffusion-reaction modeling of CV presented above.



Figure 2.10. (a) Linear scan voltammogram measured on a Pt RDE immersed in ethaline containing 100 mM Cu²⁺ and 100 mM Cu¹⁺. The electrode potential is scanned at 1 mV/s. (b) A Tafel plot from which the kinetics parameters were extracted. The *red* portion represents portion of the data fitted using Eq. 2.20, which provided α_c and i_0 .

Due to the high ohmic resistance of the electrolyte, the current distribution to the RDE electrode surface was only moderately uniform. The current distribution uniformity can be estimated via the Wagner number,⁵⁵

$$Wa = \frac{RT}{\alpha_c Fi} \left(\frac{4\kappa}{\pi r}\right)$$
[2.21]

where κ is the conductivity, r is the radius of the RDE and i is the current density. Taking $\kappa = 9.4$ mS/cm as measured, r = 0.25 cm, and i = 1.4 mA/cm² as the current density, Wa = 1.8 at the mass transport limit. The current distribution is uniform only when Wa approaches 5 or higher. Given the moderately uniform current distribution on the RDE (Wa = 1.8), a more precise measurement of the kinetic parameters using microelectrodes was deemed necessary.

2.5.2 Slow–Scan Linear Sweep Voltammetry on a Microelectrode

Microelectrodes, on account of their size (small r), possess negligibly small ohmic resistance.⁵⁶ This provides uniform current distribution and eliminates the IR_{Ω}– correction of polarization data, thereby enabling accurate determination of the kinetics parameters.⁵⁶ This advantage is particularly important in analysis of electrochemical reactions in deep eutectic solvents which often have high viscosities and low ionic conductivities. A Tafel plot (Eq. 2.20) collected on a Pt microelectrode immersed in ethaline containing equimolar (100 mM) concentrations of Cu²⁺ and Cu¹⁺ is shown in Fig. 2.11. For this plot, slow–scan (2 mV/s) linear sweep voltammetry was employed again to preserve near steady–state conditions. The slope and the y–intercept of this plot provided the following kinetics parameters: $\alpha_c = 0.54$ and $i_0 = 1.73$ mA/cm² (corresponding to $k_0 = 1.79 \times 10^{-4}$ cm/s). These measured values on a Pt microelectrode agree well with those reported above for a Pt RDE as well as those determined via diffusion–reaction modeling of the fast–scan voltammetry response. A comparison of the transport and kinetics parameters associated with Cu²⁺/Cu¹⁺ in ethaline and reported by various researchers is provided in Table 2.2. In our work, the three independent measurements, *i.e.*, CV combined with diffusion–reaction modeling (DRM), conventional polarization on RDE, and microelectrode polarization, all provided self– consistent values of α_c (= 0.49–0.54) and i_0 (= 1.72–1.88 mA/cm²). This leads us to believe that these values truly represent the kinetics limitations encountered in the redox reaction Cu²⁺ + $e^- \rightleftharpoons$ Cu¹⁺ in ethaline–based deep eutectic solvents.



Figure 2.11. Tafel plot obtained from a linear scan voltammogram collected on a Pt microelectrode immersed in ethaline containing 100 mM Cu²⁺ and 100 mM Cu¹⁺. The electrode potential is scanned at 2 mV/s. The *red* portion represents portion of the data fitted using Eq. 2.20, which provided α_c and i_0 .

Source	Measurement	D_{2+}	D_{1+}	α	$k_0 ~(\times 10^4 ~{\rm cm/s})$
	Technique	$(\times 10^7 \text{ cm}^2/\text{s})$	$(\times 10^7 \text{ cm}^2/\text{s})$		
Abbott et al. ⁴⁰	CV	2.4			
Ghosh et al. ³⁸	CV	1.22			
Lloyd et al. ⁴²	EIS	1.5	2.6	0.3	8
	CV	1.45	2.7	0.2	11
	CA (Cottrell)	1.6	2.8		
This work ⁵⁷	$i_{\rm L}$ on RDE	1.56	2.57		
	DRM			0.5	1.95
	LSV on RDE			0.49	1.78
	LSV on μE			0.54	1.79

Table 2.2. Transport and kinetic parameters for Cu^{2+}/Cu^{1+} redox transition from ethaline electrolyte.

CV = cyclic voltammetry, EIS = electrochemical impedance spectroscopy, CA = chronoamperometry, DRM = diffusion–reaction modeling, LSV = linear scan voltammetry, μE = microelectrode

2.6 Conclusions

The present study emphasizes the following steps to avoid pitfalls in kinetics measurements of electrochemical reactions in resistive DES systems such as ethaline. For DES systems that are more viscous than ethaline, such as ZnCl₂–ethylene glycol or choline chloride–CrCl₃,⁷ the following conclusions become even more critical for reliably determining the kinetic parameters.

- (i) High concentrations of electroactive species should be used in kinetics analysis so as to minimize the interference due to parasitic background reactions.
- (ii) Due to the resistive nature of DES electrolytes, accurate IR_{Ω} compensation must be applied during unsteady-state CV or steady-state polarization measurements.
- (iii) DES electrolyte composition must be chosen such that the equilibrium potential (E_{eq}) is well–defined and reproducible. Use of open circuit potentials where the thermodynamic equilibrium state is poorly defined must be avoided as this may lead to erroneous measurements of surface overpotentials.
- (iv) Polarization studies on RDE can yield reliable kinetic data; however, care must be taken to ensure that the current distribution on the RDE is relatively uniform. For highly resistive DES systems, kinetics studies on microelectrodes is recommended.
- (v) It is recommended that kinetics studies using cyclic voltammetry be performed in conjunction with diffusion–reaction modeling so that the CV response is interpreted correctly as being due to reversible or irreversible reaction conditions.

Specific to the Cu^{2+}/Cu^{1+} redox reaction in ethaline investigated in this chapter, following conclusions are drawn. For the conditions employed in the present study, the cathodic charge transfer coefficient and the reaction rate constant were accurately

determined: $\alpha_c = 0.49-0.54$; $k_0 = (1.78-1.95) \times 10^{-4}$ cm/s. The reaction rate constant corresponds to an exchange current density of $i_0 = 1.72-1.88$ mA/cm² in 100 mM CuCl₂ + 100 mM CuCl in ethaline. The α_c value resulting from the present study is close to 0.5 and indicates a symmetric polarization behavior unlike previous reports.⁴² The exchange current density is 1–2 orders of magnitude lower than that known for Cu²⁺/Cu¹⁺ in aqueous media, suggesting a kinetic hindrance, the mechanistic nature of which is explored in the next chapter. Given the increasing interest in DES electrolytes for applications in energy storage, such findings present opportunities for future experimental and modeling studies.

CHAPTER 3. Unraveling the Mechanistic Underpinnings of Sluggish Kinetics in Ethaline–based Deep Eutectic Solvents

For energy storage applications, such as redox flow batteries, solution phase redox reactions are preferred over electrodeposition because redox reactions which undergo a soluble-soluble transition are typically reversible, *i.e.*, with fast kinetics, and do not cause electrode 'shape change'. To investigate ethaline as a potential electrolyte for future redox flow batteries, it is important to study and characterize the kinetics of redox reactions. The $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$ redox reaction, due to its anodic reduction potential, could be used as a redox couple at the battery cathode. Lloyd et al.⁴² were among the first to report on the $Cu^{2+} + e^- \rightarrow Cu^{1+}$ kinetics in ethaline medium. They reported a cathodic charge transfer coefficient α_c of 0.2 – 0.3 and a reaction rate constant k_0 of $(8-10) \times 10^{-4}$ cm/s. Their α_c value suggested an asymmetric current response under cathodic vs. anodic polarization, which stood in contrast to the CV experiments conducted by Abbott *et al.*⁴⁰ Such low α_c values also contradicted the commonly accepted symmetric ($\alpha_c \sim 0.5$) behavior of the Cu²⁺/Cu¹⁺ redox transition in aqueous media. For example, Kiekens *et al.*⁴³ reported $\alpha_c = 0.49$ and $k_0 = 4.6 \times 10^{-3}$ cm/s in a chloride-containing aqueous solution. Besides the discrepancy in the charge transfer coefficient, the nearly order of magnitude difference in reaction rate constant between DES and aqueous media was also unexplained.

In the previous chapter, we developed guidelines to accurately measure the kinetics of the Cu²⁺/Cu¹⁺ redox transition in ethaline DES. The measurements yielded an expected symmetric behavior with $\alpha_c = 0.49 - 0.54$ and $k_0 = (1.78 - 1.95) \times 10^{-4}$

72
cm/s. This was confirmed using three independent techniques – slow scan linear sweep voltammetry (LSV) on Pt RDE, fast scan cyclic voltammetry (CV) on Pt PDE, and slow scan LSV on Pt microelectrode. Consequently, this study established beyond doubt that the Cu^{2+}/Cu^{1+} redox transition proceeds slowly in DES.

Building on the foundational work presented in chapter 2, the work presented in this chapter aims to investigate further the origins of sluggish kinetics of the Cu²⁺/Cu¹⁺ redox transition in ethaline with the ultimate goal of revealing the mechanistic underpinnings behind such irreversible behavior. The charge transfer kinetics was measured under a wide variety of experimental conditions to investigate the effect of system variables such as species concentration and temperature on kinetics. New mixtures that deviated from the 1:2 ChCl:EG eutectic composition were formulated and charge transfer kinetics constants in them were measured. It was shown that the kinetics depended on the complexation of Cu^{n+} species with chloride. Senanayake and $Muir^{58,59}$ had previously identified that for most aqueous and organic solvents containing excess chloride, the metal ions are stabilized by forming a chloro-complex. In the DES system too, the metal ions tend to form chloro-complexes as shown by EXAFS studies.^{60,61} In the case of Zn electrodeposition, the high chloride activity of the ethaline DES changed the effective concentration of the electroactive Zn species again via complexation.⁶² In this chapter, we investigate further the complexation of Cu^{n+} ions by excess Cl^{-} which is found to be the root cause underlying the sluggish charge transfer kinetics for the Cu^{2+}/Cu^{1+} redox transition in Cl⁻ rich DES such as ethaline.

3.1 Experimental Procedure

The experimental setup in this chapter closely follows that reported in chapter 2. The ethaline–based electrolyte was prepared by mixing choline chloride (ChCl, 99% purity, Acro Organics) and ethylene glycol (EG, anhydrous, 99.8% purity, Sigma-Aldrich) at various molar ratios (ChCl:EG = 1:5, 1:4, 1:3, 1:2) at 80 °C until a homogeneous solution was obtained.⁵⁷ Cupric chloride dihydrate (CuCl₂·2H₂O, 99% purity, Acros Organics) and cuprous chloride (CuCl, anhydrous, 99% purity, Acros Organics) were then added to provide Cu²⁺ and Cu¹⁺ concentrations ranging between 50 and 200 mM. In the various electrolytes prepared, the choline chloride from the bare ChCl:EG electrolyte provided base chloride concentrations of 2.5, 2.9, 3.5 and 4.3 M and the addition of Cu^{n+} salts at 100 mM concentrations provided an additional 0.3 M Cl⁻. The electrolyte containing CuCl₂·2H₂O was dried at 100 °C for 2 hours to reduce the moisture content. The typical moisture content in the various electrolyte mixtures was measured by a Karl Fischer moisture meter to be 3–4 wt.%. The water content likely did not affect the Cu^{2+}/Cu^{1+} redox transition which occurs at potentials within the water electrochemical stability window. The CuCl₂–containing electrolyte was then bubbled with Ar gas to remove dissolved O₂ before CuCl was added. The Ar purge was a preventive measure to remove dissolved O_2 which may oxidize Cu^{1+} to Cu^{2+} in the bulk electrolyte. The electrolytes were stored inside an Ar-filled glovebox until usage and were used as soon as possible to avoid further moisture and oxygen uptake. Parafilm[®] was used to seal all openings of the electrochemical cell to slow down the moisture and oxygen uptake from ambient during experimentation. For careful analysis, as described in

previous chapter, both Cu^{2+} and Cu^{1+} were added to the electrolyte, so that the equilibrium potential of the working electrode was stable and reproducible.

The electrochemical cell consisted of a Pine[®] RDE cell with a water jacket through which warm water was circulated using an Anova[®] water bath to provide the desired electrolyte temperatures of 30, 40, 50 or 70 °C. The electrolyte temperature was monitored by a thermometer to ± 0.5 °C. During electrochemical experiments, a threeelectrode configuration was employed. The working electrode was a 0.5 cm diameter platinum RDE (mirror polished, Pine Research Instrumentation, Inc) with electrode area of 0.196 cm². The RDE rotation was maintained at 1500 RPM by a Pine[®] rotator. The counter electrode was a 0.32 cm diameter graphite rod (Graphite store). The reference electrode was a silver (Ag) wire (99.9% purity, Rio Grande) anodized in ethaline. By holding the Ag wire at a positive potential, a thin, white AgCl layer formed, which provided a pseudo Ag/AgCl reference electrode for experiments. Such reference electrodes have been employed in previous studies of ethaline.^{40,48} All electrochemical measurements were acquired using a Princeton Applied Research PARSTAT-4000 potentiostat. The near steady-state polarization measurements were conducted at a slow scan rate (1 mV/s) to minimize transient effects. An automated viscometer (RheoSense *micro*VISCTM) and density meter (DMATM 4500 M) took multiple measurements and provided the electrolyte viscosity and density as a function of temperature to the number of significant digits reported below.

3.2 Experimental Determination of Kinetics and Transport Parameters

3.2.1 Slow–Scan Linear Sweep Voltammetry

To experimentally determine the charge transfer kinetics of Cu^{2+}/Cu^{1+} redox reaction, slow–scan LSV was performed on the Pt RDE in a Cu^{2+} and Cu^{1+} –containing electrolyte. In chapter 2, the kinetic measurements conducted on both the Pt RDE and Pt microelectrode showed negligible difference.

During the slow–scan LSV, the electrode potential was scanned from the equilibrium potential to -0.2 V vs. Ag/AgCl at 1 mV/s. The initial equilibrium potential was established by the concentrations of redox active species, and the slow scan rate ensured the system was under pseudo steady–state conditions. As the electrode potential (E) was scanned, the surface overpotential (η_s) at the Pt RDE changed according to Eq. 2.19,

$$\eta_{s} = E - E_{eq} = (V - IR_{\Omega}) - E_{eq}$$
[2.19]
(revisited)

where E_{eq} is the equilibrium potential, V is the potential applied by the potentiostat, and IR_{Ω} is the ohmic loss due to the electrolyte resistance. The ohmic resistance R_{Ω} was measured using electrochemical impedance spectroscopy (EIS) and IR_{Ω} -correction was applied as per Eq. 2.19.

As the surface overpotential increased in the cathodic ($\eta_s < 0$) direction, the rate of reduction of Cu²⁺ + $e^- \rightarrow$ Cu¹⁺ increased gradually and eventually reached a mass transport limited plateau at higher overpotentials, as shown by the current response in Fig. 3.1. The effect of Cu^{2+} and Cu^{1+} bulk concentrations on the current response was examined in a 1:2 molar ratio ChCl:EG DES at 30 °C (Fig. 3.1(a)). The mass transport limited current at high overpotential ($\eta_s < -0.4$ V) was observed to be a function of the Cu^{2+} bulk concentration only. For example, the limiting current doubled when the bulk Cu^{2+} concentration doubled (*green*, *black* and *red* curves), but not when Cu^{1+} was doubled (compare *black* vs. *blue* curve). On the other hand, the current response at low overpotentials (kinetics dominated regime) depended on both Cu^{2+} and Cu^{1+} bulk concentrations. When Cu^{1+} concentration doubled, the initial current also increased while tending towards the same limiting current (Fig. 3.1(a), *black* vs. *blue* curves).

The effect of temperature on the current response was also examined in a 1:2 molar ratio ChCl:EG electrolyte containing equimolar (100 mM) Cu²⁺ and Cu¹⁺ (Fig. 3.1(b)). As the temperature increased, the rate of Cu²⁺ + $e^- \rightarrow$ Cu¹⁺ reduction also increased. The mass transport limited current at high overpotential ($\eta_s < -0.4$ V) indicated that the temperature impacted the mass transport parameters. Thus, the diffusion coefficient was carefully measured.



Figure 3.1. Slow–scan linear sweep voltammetry (1 mV/s) on a Pt RDE immersed in 1:2 molar ratio ChCl:EG DES. (a) Cu²⁺ concentration controls the diffusion limited current, whereas Cu¹⁺ only affects the current response at low overpotentials. (b) Operating temperature affects the current response in the kinetics and mass transport limited regions of the polarization curve (Cu²⁺ and Cu¹⁺ concentrations were 100 mM).

3.2.2 Determination of Cu²⁺ and Cu¹⁺ Diffusion Coefficients

The diffusion coefficients were determined from limiting current measurements on a Pt RDE. The electrolyte was kept at constant Cu^{2+} and Cu^{1+} concentrations (100 mM), but the total chloride concentration and operating temperature were varied. The chloride concentration (2.8, 3.2, 3.8 or 4.6 M) was modulated by using different molar ratios (1:5, 1:4, 1:3 or 1:2) of the ChCl:EG mixture. The temperature was maintained at 30, 40, 50 or 70 °C. Using the Levich equation,⁵⁰ the diffusion coefficient was calculated, as was performed in chapter 2, from the anodic and cathodic limiting currents (Eq. 2.4 and 2.5):

$$i_{\rm L}^{\rm c} = -0.62 {\rm nF} D_{2+}^{\frac{2}{3}} \left[\frac{\mu}{\rho}\right]^{-\frac{1}{6}} [{\rm Cu}^{2+}]_{\rm b} \omega^{\frac{1}{2}}$$
[2.4]
(revisited)

$$i_{\rm L}^{\rm a} = 0.62 {\rm nF} D_{1+}^{\frac{2}{3}} \left[\frac{\mu}{\rho} \right]^{-\frac{1}{6}} [{\rm Cu}^{1+}]_{\rm b} \omega^{\frac{1}{2}}$$
 [2.5]
(revisited)

where $i_{\rm L}$ is the limiting current density (superscript 'c' and 'a' denote cathodic and anodic reactions, respectively), n is the number of electrons transferred, F is the Faraday's constant, D_{2+} and D_{1+} are the diffusion coefficients, μ is the viscosity of the electrolyte, ρ is the density, $[{\rm Cu}^{2+}]_{\rm b}$ and $[{\rm Cu}^{1+}]_{\rm b}$ are the concentrations in the bulk electrolyte, and ω is the RDE rotation speed. Because the viscosity and density of the electrolyte are a function of the electrolyte composition and temperature, both were carefully measured using a viscometer and density meter up to 50 °C. The data point for 70 °C was extrapolated using the Vogel–Fulcher–Tamman (VFT) model for viscosity and linear regression for density, as has been done previously in literature.³⁸ The viscosity was found to depend on the moisture content. Therefore, efforts were taken to maintain the same moisture content (3–4 wt.%) across all samples. The viscosity and density values agree with literature measurements and are listed in Table 3.1.

The cathodic and anodic limiting currents were measured at RDE rotation speeds ranging from 500 to 1500 RPM. A linear relationship between $i_{\rm L}$ and $\omega^{\frac{1}{2}}$ was confirmed, indicating Levich behavior. The application of the Levich equation to extract diffusion coefficients was discussed in detail in chapter 2. The same technique was applied here, and the measured diffusion coefficients at various chloride concentrations and temperatures are listed in Table 3.1. It is noteworthy that the diffusion coefficients reported in Table 3.1 are those of the respective chloro–complexes of Cu¹⁺ and Cu²⁺. In general, the diffusion coefficients of the chloro–complexes decreased with increasing chloride concentration (Fig. 3.2) at any given temperature. This decrease is due to an increase in the electrolyte viscosity as more ChCl was added to the electrolyte to raise the chloride concentration. With increasing temperature, the diffusion coefficients of the Cuⁿ⁺–complexes were observed to increase (Fig. 3.2). As tabulated in Table 3.1, the viscosity of the electrolyte decreased at higher temperatures thereby resulting in faster species diffusion.



Figure 3.2. The diffusion coefficients of (a) Cu^{2+} and (b) Cu^{1+} complexes extracted from diffusion–limited current response measured on a Pt RDE immersed in equimolar (100 mM) Cu^{2+} and Cu^{1+} –containing ChCl:EG (=1:5, 1:4, 1:3 or 1:2) mixtures. The electrolyte composition and temperature both affected the diffusion coefficients.

To investigate the relationship between diffusion coefficients and electrolyte viscosity, the D_{2+} and D_{1+} values were plotted as a function of viscosity regardless of chloride concentration or temperature (Fig. 3.3(a)). The diffusion coefficients exhibited a strong linear dependence on the inverse of viscosity (Fig. 3.3(b)), which suggests Stokes–Einstein behavior. The Stokes–Einstein equation⁶³ describes the diffusion of a spherical object with radius r_{sphere} as it moves through a medium with viscosity μ at temperature T.

$$D = \frac{k_{\rm B} T}{6\pi r_{\rm sphere} \mu}$$
[3.1]

By applying this equation, the Cu^{2+} – Cl_n complex was estimated to have a solvation sphere of 2.2 Å in radius. The Cu^{1+} – Cl_m complex solvation sphere was 1.3 Å in radius. The constant sizes of the solvation spheres of the chloro–complex of Cu^{1+} and Cu^{2+} indicate that the coordination number is relatively unaffected in the range of experimental parameters studied and that the key modulator of diffusivity is the electrolyte viscosity.



Figure 3.3. (a) The diffusion coefficients of the Cu^{2+} and Cu^{1+} complexes decrease with increasing viscosity; (b) The diffusion coefficients obey the Stokes–Einstein relation.

3.2.3 Determination of $Cu^{2+} + e^- \rightarrow Cu^{1+}$ Reduction Kinetics

To measure the charge transfer kinetics of the $Cu^{2+} + e^- \rightarrow Cu^{1+}$ reduction reaction, slow scan (1 mV/s) linear sweep voltammetry was deployed on the Pt RDE immersed in the various ChCl:EG mixtures. The Cu^{n+} concentration, chloride concentration and operating temperature were varied systematically within the ranges described above. The surface overpotential at the electrode was scanned in the cathodic direction and the current response was measured, then analyzed by applying the Tafel equation (Eq. 2.20), as described in chapter 2:

$$i = i_0 \left(1 - \frac{i}{i_{\rm L}} \right) \exp\left(-\frac{\alpha_{\rm c} F}{\rm RT} \eta_{\rm s} \right)$$
[2.20]
(revisited)

where i_0 is the exchange current density, α_c is the cathodic charge transfer coefficient, and all other variables have their usual meanings. As expected,⁵⁷ the current reached a limiting current plateau at large overpotentials and its value corresponded to the reported diffusion coefficients (Table 3.1). At moderate overpotentials, the Tafel equation could be fitted to the polarization data, as shown in Fig. 3.4(a).

While the measured current response depended on the Cu²⁺, Cu¹⁺ and Cl⁻ concentrations (Fig. 3.4(b)), the Tafel slope obtained remained constant providing a relatively unchanged value of the charge transfer coefficient α_c of ~0.5 (indicating symmetric behavior in cathodic and anodic polarization). In addition, the charge transfer coefficient remained ~0.5 for various compositions of the ChCl:EG mixture as well as over the entire operating temperature range studied (Fig. 3.5).



Figure 3.4. (a) Tafel plot from which the charge transfer kinetics parameters were extracted at 30 °C. The red portion represents the region where the Tafel equation (Eq. 2.20) was applied to extract α_c and i_0 . (b) A series of Tafel curves at various Cu¹⁺ and Cu²⁺ concentrations showing constant slope (*black* guide line) corresponding to $\alpha_c \sim 0.5$.



Figure 3.5. The charge transfer coefficients were extracted from Tafel plots shown in Fig. 3.4. The coefficient remained constant ($\alpha_c \sim 0.5$) independent of the Cu^{*n*+} concentration (a) or the total Cl⁻ concentration and temperature (b). The *dashed* lines are for visual guide.

From the y-intercept of the Tafel plots (Fig. 3.4), the exchange current density was extracted (Table 3.1). According to the classical Butler–Volmer theory, the exchange current density can be expressed as:

$$i_0 = nFk_0 [Cu^{2+}]^{1-\beta} [Cu^{1+}]^{\beta}$$
[3.2]

where k_0 is the reaction rate constant and β is the charge transfer symmetry factor ($\beta \times$ n = α_c , and $\alpha_c = \beta$ in this case because n = 1). Assuming $\beta = \alpha_c = 0.5$, i_0 is expected to increase in proportion to ([Cu²⁺][Cu¹⁺])^{0.5}. This linear proportionality could be clearly observed in a 1:2 ChCl:EG DES at 30 °C (Fig. 3.6(a)). From the slope, the reaction rate constant was calculated as $k_0 = 2.4 \times 10^{-4}$ cm/s, which is in reasonable agreement with measurement reported in the previous chapter.

ChCl:EG composition	[Cl ⁻] (M)	T (°C)	μ (cP)	ρ (g/cm ³)	$D_{2+} \times 10^7$ (cm ² /s)	$D_{1+} \times 10^7$ (cm ² /s)	i_0 (mA/cm ²)
and $[Cu^n]_b$	<u> </u>	20	01.4	1 1056			70
1:5 ChCl:EG	2.8	30	21.4	1.1256	4.6	8.2	7.9
$100 \text{ mM } \text{Cu}^{2+}$		40	15.1	1.1193	6.9	12.0	11.8
100 mM Cu^{1+}		50	11.4	1.1130	9.5	16.0	17.4
		70	7.3	1.1003	18.1	28.2	23.0
1:4 ChCl:EG	3.2	30	23.7	1.1272	4.6	8.1	6.6
$100 \text{ mM } \text{Cu}^{2+}$		40	16.8	1.1209	6.6	11.3	10.1
$100 \text{ mM } \text{Cu}^{1+}$		50	12.5	1.1147	9.0	15.1	12.3
		70	7.8	1.1023	16.8	26.2	18.2
1:3 ChCl:EG	3.8	30	26.0	1.1277	3.8	6.5	5.0
100 mM Cu ²⁺		40	18.2	1.1217	5.5	9.2	7.1
$100 \text{ mM } \mathrm{Cu}^{1+}$		50	13.5	1.1157	7.5	12.2	8.7
		70	8.6	1.1036	13.9	21.5	15.1
1:2 ChCl:EG	4.6	30	36.3	1.1278	2.6	4.6	3.0
100 mM Cu ²⁺		40	24.9	1.1220	3.9	6.8	4.4
$100 \mathrm{~mM~Cu^{1+}}$		50	18.2	1.1162	5.4	9.5	5.6
		70	11.1	1.1047	10.4	17.9	9.5
1:2 ChCl:EG							
50 mM Cu ²⁺		30					1.0
$50 \text{ mM } \text{Cu}^{1+}$							
1:2 ChCl:EG							
100 mM Cu ²⁺		30					2.0
50 mM Cu ¹⁺							
1:2 ChCl:EG							
50 mM Cu ²⁺		30					2.5
$200 \text{ mM } \mathrm{Cu}^{1+}$							
1:2 ChCl:EG							
$200 \text{ mM } \mathrm{Cu}^{2+}$		30					4.3
$200 \text{ mM } \mathrm{Cu}^{1+}$							

Table 3.1. Transport and kinetic parameters for $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$ redox transition in ChCl:EG mixtures.

T = temperature; μ = viscosity; ρ = density; D_{2+} = Cu²⁺ diffusion coefficient, D_{1+} = Cu¹⁺ diffusion coefficient, i_0 = exchange current density



Figure 3.6. (a) The exchange current density measured on a Pt RDE in 1:2 molar ratio ChCl:EG DES at 30 °C was linearly dependent on the square root of the product of the Cu^{n+} species concentrations. The *dashed* line represents the best fit line. (b) In equimolar (100 mM) Cu^{2+} and Cu^{1+} -containing ChCl:EG mixtures, the exchange current decreased with increasing Cl⁻ concentrations but it increased with increasing temperature.

The observed reaction rate constant ($k_0 = 2.4 \times 10^{-4}$ cm/s) in 1:2 ChCl:EG DES at 30 °C is much lower than that reported for the same reaction in an aqueous medium. Kiekens *et al.*⁴³ using aqueous electrolytes reported $\alpha_c = 0.49$ and $k_0 = 46 \times 10^{-4}$ cm/s for the $Cu^{2+} + e^- \rightarrow Cu^{1+}$ reduction reaction. The sluggish kinetics in DES is likely not due to surface adsorbed species of chloride⁶⁴ because of their presence in large excess (>1 M) in the electrolyte. In such excess concentration and in the potential region of Cu^{2+}/Cu^{1+} redox transition, the electrode surface will experience nearly saturated Cl^{-} coverage^{65,66} and not one which gradually increases with bulk Cl⁻ concentration to produce a monotonically decreasing exchange current density as in Fig. 3.6(b). Besides adsorption, solvation is also not the likely cause for the observed sluggish kinetics. Halley *et al.*⁶⁷ reported that Cu^{2+}/Cu^{1+} redox transition in an aqueous solution is not dominated by solvent rearrangement, but by the energetics of solvated species approaching the electrode surface. We believe that such effects are not dominant in our DES system because when we compared voltammetry response on a glassy carbon (GC) RDE to that on a Pt RDE (Fig. 3.7), the kinetics of the Cu^{2+}/Cu^{1+} reaction were measurably different. The dependence of kinetics on the substrate suggests that solvent effects (like reorientation) are likely not the rate determining factors.



Figure 3.7. Slow–scan linear sweep voltammetry (1 mV/s) on a Pt RDE (*black*) and glassy carbon RDE (*red*) immersed in a 1:5 molar ratio ChCl:EG electrolyte containing equimolar (100 mM) of Cu²⁺ and Cu¹⁺ at (a) 30 °C, (b) 40 °C, (c) 50 °C and (d) 70 °C. The polarization response is observed to depend on the substrate (Pt vs. GC).

It is known that metal ions, such as Cu^{2+} and Cu^{1+} , form metal chloride complexes in aqueous solutions with high chloride content.^{68–71} Abbott *et al.*⁷² showed that the Cu speciation in a ChCl:EG DES displayed similar UV–Vis spectrum as in an 8 M LiCl aqueous solution. They further determined that the Cu(II) tetrachloro complex, CuCl4^{2–}, is the predominant species for Cu²⁺, and CuCl₂[–] is the predominant form of Cu¹⁺ although lower order complexes are present in tandem.⁷³ Therefore, the higher order CuCl_n complexes could stabilize the Cuⁿ⁺ and impede its participation in electron transfer reactions whereas the less stable (less coordinated) species may be available to participate in reactions.

As the ChCI:EG ratio shifted from 1:5 to 1:2, the total chloride concentration in the electrolyte increased from 2.8 M to 4.6 M. The exchange current density as a function of the total chloride concentration is plotted in Fig. 3.6(b). The kinetics became more sluggish when the chloride concentration increased. This supports the role of chloro– complex formation mentioned in the preceding paragraph. From aqueous Cu speciation data,^{68–71} Cu ions form CuCl_n complexes at high chloride concentrations. As the chloride concentration increases (> 1 M), the complex shifts to higher order species (n = 4). The same is known about Cu speciation in DES.⁶¹ Thus, as the chloride concentration increases, one would expect a reduced number of 'free' Cu ions (*i.e.*, lower concentration of weakly coordinated Cuⁿ⁺) to be available for direct electrochemical reaction. A consequence of this effect would be a decrease in the exchange current density (i_0) value per Eq. 3.2.

Note that this dependence of kinetics on 'free' or loosely coordinated Cu^{n+} is distinct from the system behavior when under diffusion limitations. Under mass transport control, the electroactive species near the electrode surface are exhausted. While more electroactive species may be brought to the electrode surface via diffusion, the higher order complexes of Cu^{n+} near the electrode can also gradually generate the 'free' electroactive species by dissociation whereby they (higher order complexes) too develop a diffusion–limited concentration gradient. A net result of all this is a depletion of the total Cu species concentration in the boundary layer thus explaining why mass transport limitations are sensitive to the total Cu^{n+} concentration.⁵⁷

By varying the operating temperature, its effect on charge transfer kinetics could be studied. The exchange current density is directly proportional to the operating temperature (Fig. 3.6(b)). This dependence, together with the dependence of i_0 on the Cu^{*n*+} and chloride concentration, is analyzed in the model section below.

3.3 Mathematical Modeling of Complexation Effects on Reaction Kinetics

3.3.1 Model Setup and Comparison to Experimental Results

To evaluate the effects of complexation on exchange current density, a mathematical model was formulated. The model is based on the assumption that Cu^{n+} ions form chloro–complexes in ChCl:EG mixtures. The electroactive chloro–complexes assumed are Cu(II)Cl_n and Cu(I)Cl_m where *n* and *m* represents the number of Cl⁻ needed to complex Cu²⁺ and Cu¹⁺, respectively. We assume that Cu(II)Cl_n and Cu(I)Cl_m are in equilibrium with higher order Cl⁻ complexes as shown in Eq. 3.3 and 3.4. Previous studies by Hartley *et al.* indicated that CuCl₄^{2–} and CuCl₂⁻ are the predominant higher order complexes in 1:2 molar ratio ChCl:EG DES;⁷² however, we develop here a generalized model in which the value of *n* and *m* – although fixed – are *a priori* unknown:

$$\operatorname{CuCl}_{n}^{2-n} + \operatorname{xCl}^{-} \rightleftharpoons \operatorname{CuCl}_{n+x}^{2-n-x}$$

$$[3.3]$$

$$\operatorname{CuCl}_{m}^{1-m} + \operatorname{yCl}^{-} \rightleftharpoons \operatorname{CuCl}_{m+y}^{1-m-y}$$
[3.4]

 $\operatorname{CuCl}_{n}^{2-n} + e^{-} \rightleftharpoons \operatorname{CuCl}_{m}^{1-m}$ [3.5]

where $\operatorname{CuCl}_{n+x}^{2-n-x}$ and $\operatorname{CuCl}_{m+y}^{1-m-y}$ are the higher order complexes for Cu^{2+} and Cu^{1+} and $\operatorname{CuCl}_{n}^{2-n}$ and $\operatorname{CuCl}_{m}^{1-m}$ are the lower order electroactive complexes involved in the charge transfer reaction Eq. 3.5. Thus, the exchange current density from classical Butler– Volmer theory (Eq. 3.2) can now be written as:

$$i_0 = \mathrm{nF}k_0[\mathrm{Cu}\mathrm{Cl}_n^{2-n}]^{1-\alpha_c}[\mathrm{Cu}\mathrm{Cl}_m^{1-m}]^{\alpha_c}$$
[3.6]

Since the concentrations of $CuCl_n^{2-n}$ and $CuCl_m^{1-m}$ are not known *a priori*, we involve the equilibrium constants K₂₊ and K₁₊ of reactions 3.3 and 3.4 above:

$$K_{2+} = \frac{[\operatorname{CuCl}_{n+x}^{2-n-x}]}{[\operatorname{CuCl}_{n}^{2-n}][\operatorname{Cl}^{-}]^{x}}$$
[3.7]

$$K_{1+} = \frac{\left[\operatorname{CuCl}_{m+y}^{1-m-y}\right]}{\left[\operatorname{CuCl}_{m}^{1-m}\right]\left[\operatorname{Cl}^{-}\right]^{y}}$$
[3.8]

Additionally, since the total Cu^{n+} and Cl^{-} is fixed, $[Cu^{2+}]_{total}$, $[Cu^{1+}]_{total}$ and $[Cl^{-}]_{total}$ are known quantities. Mass balance on the species then provides:

$$1 \times [\operatorname{CuCl}_{n}^{2-n}] + 1 \times [\operatorname{CuCl}_{n+x}^{2-n-x}] = [\operatorname{Cu}^{2+}]_{\text{total}}$$
[3.9]

$$1 \times [\operatorname{CuCl}_{m}^{1-m}] + 1 \times [\operatorname{CuCl}_{m+y}^{1-m-y}] = [\operatorname{Cu}^{1+}]_{\text{total}}$$
[3.10]

$$n \times [CuCl_{n}^{2-n}] + (n + x) \times [CuCl_{n+x}^{2-n-x}] + m \times [CuCl_{m}^{1-m}] + (m + y)$$

$$\times [CuCl_{m+y}^{1-m-y}] + [Cl^{-}] = [Cl^{-}]_{total}$$
[3.11]

Because our experiments are done under conditions of excess chloride and $[Cu^{n+}]_{total} \ll [Cl^{-}]_{total}$, we can assume that most of the bulk chloride is 'free', simplifying Eq. 3.11 to

$$[Cl^{-}] \approx [Cl^{-}]_{total}$$

$$[3.12]$$

Eq. 3.7–3.12 combined with Eq. 3.6 yields

$$i_{0} = nFk_{0} \left(\frac{[Cu^{2+}]_{total}}{1 + [Cl^{-}]_{total}^{x} K_{2+}} \right)^{1-\alpha_{c}} \left(\frac{[Cu^{1+}]_{total}}{1 + [Cl^{-}]_{total}^{y} K_{1+}} \right)^{\alpha_{c}}$$
[3.13]

As shown by the experiments (Fig. 3.5) above, the charge transfer coefficient α_c remains ~0.5 under conditions studied herein. Eq. 3.13 can hence be written as

$$i_0 = nFk_0 ([Cu^{2+}]_{total} [Cu^{1+}]_{total})^{0.5} \left(\frac{1}{1 + [Cl^{-}]_{total}^x K_{2+}} \frac{1}{1 + [Cl^{-}]_{total}^y K_{1+}}\right)^{0.5} [3.14]$$

The model (Eq. 3.14) predicts the exchange current density dependencies on system parameters that are in good qualitative agreement with the experimental observations reported in Fig. 3.6:

a) Eq. 3.14 shows that the exchange current density is expected to be a linear function of the square root of the product of the Cu^{n+} species concentration, $i_0 \propto ([Cu^{2+}]_{total}[Cu^{1+}]_{total})^{0.5}$ which is consistent with Fig. 3.6(a) data.

b) As the total chloride concentration $[Cl^-]_{total}$ increased in Fig. 3.6(b), i_0 decreased. This again is consistent with the inverse dependence of i_0 on $[Cl^-]_{total}$ in Eq. 3.14.

The equilibrium constants K_{2+} and K_{1+} are temperature dependent. Meng and Bard reported that, as the temperature shifted higher, a lower coordination number was favored by the Cu^{2+} – Cl_n complex in aqueous media.⁷¹ Hartley suggested that the K values are different in DES than in aqueous media,⁷² hence no quantitative analysis can be done unless K values are experimentally measured in DES. However, a qualitative assessment is still possible and useful. The equilibrium constants depend on the enthalpy of formation. For some chloro–complexes, such as CuCl₂ and CuCl, available data⁷⁴ suggests that complex formation is exothermic. As temperature increases, the equilibrium in Eq. 3.3 and 3.4 is expected to shift to the left, *i.e.*, higher order complexation is hindered. This would imply that the concentration of the weakly coordinated, *i.e.*, electroactive, Cu^{n+} species would be higher at elevated temperatures, thus explaining the increase in the exchange current density per Eq. 3.6. Additionally, temperature may also directly affect k_0 in Eq. 3.6. All this supports the experimental observation that charge transfer kinetics will be accelerated at elevated temperatures (consistent with Fig. 3.6(b) data).

3.4 Conclusions

In this chapter, the charge transfer kinetics of the $Cu^{2+} + e^- \rightleftharpoons Cu^{1+}$ redox transition was analyzed in a chloride-containing ChCl:EG deep eutectic solvent. The charge transfer coefficient (α_c) and the exchange current density (i_0), as well as the mass transport parameters $(D_{2+} \text{ and } D_{1+})$ were precisely measured as a function of species concentrations and temperature. Upon analysis, the charge transfer kinetics were found to be sluggish as indicated by an order of magnitude lower i_0 in the chosen DES than that known for the same reaction in aqueous media. The dependence of i_0 on the Cuⁿ⁺ concentration, Cl⁻ concentration and temperature pointed towards the role of complexation, *i.e.*, Cu¹⁺ and Cu²⁺ undergoes complexation with Cl⁻ whereby the lower coordination number species (least complexed with Cl⁻) are available for participating in charge transfer reactions. Invoking arguments of equilibrium in a simple mathematical model, it was shown that this complexation effect explains qualitatively the key dependencies observed in experimental kinetics data. The findings in this chapter will guide future experimental work on prevention or circumvention of complexation leading potentially to identification of reversible redox chemistries in DES media.

As discussed in the introduction, rare earth elements enable important functions in numerous applications.^{15,16,30,31,75} For future sustainable use of rare earth metals, the recovery and recycling of these materials from product waste is of great practical importance.¹⁹ For energy–efficient recovery of rare earth elements, such as neodymium (Nd), one promising technique is the electrolytic refining process using high temperature molten salt.²⁰

Significant empirical work on Nd electrodeposition from molten salts has been reported in literature. The early feasibility of Nd electrowinning from chloride and oxide–fluoride melts was achieved at the U.S. Bureau of Mines.^{76,77} A commonly reported observation in prior studies using molten salts is the low current efficiency (only ~30%) of Nd electrodeposition.^{78,79} The loss of efficiency has been attributed to Nd dissolution via the comproportionation reaction which is prevalent in systems that exhibit multivalency.^{20,79,80} Low current efficiency is also a characteristic feature in the electrodeposition of other multivalent metals such as titanium.^{81,82} In the latter case, the use of diaphragms to retard redox–shuttling processes was found to increase the deposition efficiency.^{82–84} In Nd electro–extraction, Liu *et al.* employed a liquid gallium (Ga) electrode to suppress multi–stage redox transitions so as to obtain high current efficiencies.⁸⁵ In their work, it was demonstrated that the Nd electrodeposition on liquid Ga underwent a one–step reduction to Nd metal, implying that no soluble intermediates (which typically lower the efficiency by diffusing away from the electrode) were

generated. Through such an approach, current efficiency exceeding 90% was achieved; however, the electrodeposited Nd was observed to form an alloy with the Ga electrode.

In addition to the aforementioned application–oriented studies of Nd electrodeposition, many researchers have investigated the fundamental physical, chemical and electrochemical properties pertinent to Nd electrolysis from halide melts. These studies include the examination of the solubility of Nd³⁺ in molten LiCl–KCl eutectic mixtures.^{86–88} Furthermore, Sridharan *et al.* constructed a phase diagram of the NdCl₃– LiCl–KCl melt.⁸⁹ Of particular relevance to electrowinning and electrorefining, it has been demonstrated (using cyclic voltammetry and potentiometric measurements) that Nd electrodeposition from NdCl₃–LiCl–KCl melts proceeds via a two–stage reduction process:^{85,86,89–93}

$$\mathrm{Nd}^{3+} + e^- \to \mathrm{Nd}^{2+}$$

$$[4.1]$$

$$\mathrm{Nd}^{2+} + 2e^{-} \to \mathrm{Nd}^{0}$$

$$[4.2]$$

Yamana *et al.* reported the reduction potentials for reactions 4.1 and 4.2 to be -1.915 V and -2.023 V vs. Ag/AgCl–LiCl–KCl reference electrode, respectively.⁹³ In the two– stage reduction of Nd³⁺ to Nd metal, reaction 4.1 involves the change in oxidation state from one soluble (solution–phase) species (Nd³⁺) to another (Nd²⁺), and is thus referred to as the soluble–soluble transition.^{85,86,89–92} On the other hand, reaction 4.2 involves the reduction of a soluble species (Nd²⁺) to an insoluble (solid Nd⁰) product, which gets deposited on the electrode surface. The latter reaction is thus referred to as soluble–insoluble transition.^{89–92} Cyclic voltammetry (CV) studies have confirmed that reaction

4.2 involves a two–electron transfer process.^{89,91} In prior studies, the peak potential, *i.e.*, the electrode potential at which the current is maximal, exhibited little dependence on the scan rates during CV. Thus, both reactions 4.1 and 4.2 were treated as reversible systems, *i.e.*, they have fast kinetics.^{85,89,91–93} However, the peak potential for reaction 4.2 has been noted to vary slightly depending on the scan rate.^{89,93} As a result, reaction 4.2 is known to exhibit some irreversibility.

In reversible systems, fast kinetics implies that transport (diffusion) is often the rate–limiting factor. Sridharan *et al.* and Masset *et al.* have independently determined the diffusion coefficient of Nd³⁺ in LiCl–KCl.^{89,92} At temperatures in the range 450–500 °C, the diffusion coefficient was in the range of 1.2×10^{-5} – 2.6×10^{-5} cm²/s and it decreased linearly with Nd³⁺ concentration. Unlike Nd³⁺, the Nd²⁺ diffusion coefficient could not be reliably measured,^{86,89,90,93} because of its disproportionation via:

$$3Nd^{2+} \rightleftharpoons 2Nd^{3+} + Nd^0$$
[4.3]

In reversible electrochemical systems, the CV behavior can be analyzed using the well–known Randles–Sevcik^{34,35} and Berzins–Delahay⁹⁴ equations for the soluble– soluble and the soluble–insoluble redox transitions, respectively.^{37,89,90,92} These equations incorporate the diffusional transport of the reacting species towards the electrode surface followed by instantaneous surface reaction. Fast surface reaction implies that the species' near–surface concentration obeys Nernstian equilibrium. While this description is widely adopted in the study of reversible redox reactions, its simplistic application to systems

involving multiple redox transitions (such as the Nd system with two–stage reduction: reactions 4.1 and 4.2 above) can be erroneous.

The CV behavior of reversible electrochemical systems that exhibit multivalency has been studied previously. As early as 1960, Gokhshtein and Gokhshtein developed a mathematical model analyzing the electrochemical behavior of reversible, multivalent systems.⁹⁵ They showed that, when the two consecutive current peaks (corresponding to the two steps in a reaction sequence) in a potential scan were separated by at least 177 mV, the two redox transitions exerted no influence on one other and thus could be analyzed independently. However, when the two peak occurred closer together, as in the case of redox transitions in the Nd system (discussed below), interactions must be accounted for in interpreting the current-potential behavior. Polcyn and Shain examined the multi-stage copper deposition reaction ($Cu^{2+} + e^- \rightarrow Cu^{1+}$ followed by $Cu^{1+} + e^$ $e^- \rightarrow Cu^0$) using stationary electrode polarography and transient diffusion modeling.⁹⁶ Cotarta et al. electrodeposited chromium (Cr) from CrCl₃-LiCl-KCl and determined that only the first reduction step ($Cr^{3+} + e^- \rightarrow Cr^{2+}$) is reversible.⁹⁷ The second step $(Cr^{2+} + 2e^- \rightarrow Cr^0)$ requires incorporation of surface reaction kinetics.⁹⁸ Martinet *et* al. developed a complex numerical code invoking numerous adjustable parameters for simulating the voltammetry response during two-step deposition at an inert electrode including adsorption.⁹⁸ Salmi et al. too simulated numerically the transport of multivalent species during the electrodeposition of titanium and niobium on an inert electrode.⁹⁹ Again, surface adsorption was incorporated in their model. Prior models do not comprehensively discuss the electrodeposition of Nd which is the subject of the present work. Also, in this chapter as shown below, it is seen that general characteristics of the

voltammetry response can be simulated by incorporating Butler–Volmer kinetics without surface adsorption.

In the present investigation concerning the electrochemistry of Nd in a molten LiCl–KCl eutectic mixture, it is first demonstrated that the peak current in a voltammetry scan does not strictly obey the simplistic Berzins–Delahay equation particularly for the soluble-insoluble transition. To address the deficiency in existing models, we develop a mathematical framework that incorporates the diffusion of multivalent Nd species (Nd³⁺ and Nd^{2+}) and their electrochemical reaction (deposition) at the electrode surface. This approach takes into consideration the multivalent nature of the Nd species and their interactions, thereby enables the precise and quantitative modeling of the voltammetry behavior during Nd electrodeposition. This approach of combining experiments and theory is an extension of the model developed previously in chapter 2 and it has been demonstrated in chapter 2 to yield accurate kinetics parameters that agree with independent experimental determination.⁵⁷ The work in this chapter builds on the model approach developed in chapter 2 to describe the multi-stage reduction reaction of multivalent Nd. The work reported in this chapter therefore provides reliable access to the kinetic parameters associated with Nd electrodeposition which otherwise are difficult to quantify¹⁰⁰ using conventional polarization methods.

4.1 Experimental Procedure

In this chapter, molten salt electrolysis of neodymium (Nd) metal was investigated using cyclic voltammetry. The electrochemical cell consisted of a 5 cm diameter cylindrical quartz tube with a flat bottom, similar to the setup in the previous chapters. The cell was filled with a LiCl-KCl (55–45 mol.%) eutectic mixture, prepared from anhydrous LiCl (>99% purity, Sigma Aldrich) and KCl (>99% purity, Sigma Aldrich). Anhydrous NdCl₃ (99.9% purity, Alfa Aesar) was added to the salt mixture in amounts that provided Nd³⁺ concentrations of 60 mM or 120 mM in the molten salt. A three–electrode configuration was employed, in which the working electrode was a 0.16 cm diameter tungsten rod (99.5% purity, Anchor Brand) and the counter electrode was a 0.32 cm diameter graphite rod (Graphite store). The working and counter electrodes were placed 3 cm apart inside the quartz cell. A specialized reference electrode was constructed. The reference electrode consisted of a silver (Ag) wire (99.9% purity, Rio Grande) placed inside a 0.5 cm diameter borosilicate glass tube (Fisher Scientific). The tube was filled with the LiCl-KCl eutectic salt containing 1 wt.% AgCl (99.9999% purity, Acros). The reference electrode was then placed midway between the working and the counter electrodes. At the operating temperature, the borosilicate glass tube becomes porous enough to be ionically conductive, therefore rendering itself as an excellent reference electrode. Such a pseudo-reference electrode has been employed in previous studies of electrolysis from molten halide melts.^{89,91,101,102} All electrode potentials below are referenced to this Ag/AgCl–LiCl–KCl electrode (referred to simply as Ag/AgCl). After placement of all three electrodes inside the quartz electrochemical cell, the quartz

cell was placed along the axis of a vertical tube furnace that allowed precise control of the electrolyte temperature. All experiments reported herein were conducted at 475 °C. After the electrolyte was in its molten state, the electrodes were immersed to a depth of 2.4 cm below the surface of the electrolyte. All current densities reported below are determined based on the immersed electrode area of 1.2 cm². Before a typical experimental run, the molten electrolyte was purged with Ar gas to minimize oxygen or moisture contamination. Furthermore, the entire experimental apparatus was placed inside an MBraun controlled–environment, Ar–purged glove box. Oxygen and moisture levels inside the glove box were maintained below 0.5 ppm. For cyclic voltammetry studies, scan rates were varied between 50–500 mV/s. A Princeton Applied Research PARSTAT-4000 potentiostat with automated data acquisition was used for all electrochemical measurements. Electrochemical impedance spectroscopy (EIS) was used to measure the electrolyte resistance and estimate the electrolyte IR-drop correction. Unlike the DES electrolyte reported in the previous chapters, the molten LiCl-KCl electrolyte possessed a high conductivity (1.74 S/cm, reported in literature²¹), which led to the low ohmic resistance (0.38 Ω) measured by EIS. As a result, IR correction was small (merely 10–20 mV) and thus was not applied in this chapter.

4.2 Cyclic Voltammetry Studies of Redox Transitions during Nd Electrodeposition

Cyclic voltammetry (CV) was employed to study the redox transitions during Nd electrodeposition. Fig. 4.1 shows cyclic voltammograms (at 100 mV/s) measured on a W working electrode immersed in molten LiCl-KCl eutectic electrolyte in the presence (black curve) and in the absence (red curve) of dissolved NdCl₃. In the absence of NdCl₃, the background current was nearly zero in the range of potentials from -1.4 V to -2.2 V, indicating good electrochemical stability. In the presence of NdCl₃, CV showed two distinct regions of cathodic activity. During the cathodic scan, a broad cathodic wave was observed in the potential range between -1.4 and -2.05 V. This wave corresponds to the soluble-soluble redox transition (Nd³⁺ + $e^- \rightarrow$ Nd²⁺) described by reaction 4.1. This is in accordance with previous literature reports.^{89,91} At potentials negative compared to – 2.05 V, a second reduction peak was observed. Since this potential range is cathodic with respect to the reduction potential⁹³ of reaction 4.2 (Nd²⁺ + 2 $e^- \rightarrow$ Nd⁰), this much sharper peak is associated with the electrodeposition of Nd. In fact, at potentials negative with respect to -2.05 V, a combination of reactions 4.1 and 4.2 provides the source of the measured electrochemical current. During the anodic scan direction, electrochemical stripping of Nd manifests as an oxidation peak located at -1.96 V.



Figure 4.1. Cyclic voltammograms (100 mV/s) measured on a W working electrode immersed in molten LiCl–KCl electrolyte at 475 °C in the presence (*black* curve) and in the absence (*red* curve) of NdCl₃. In region A (potential range: -1.4 to -2.05 V), Nd³⁺ is reduced to Nd²⁺. In region B (potential range: negative to -2.05 V), both Nd³⁺ and Nd²⁺ reduction occur at the electrode leading to Nd electrodeposition.

For clarity, we define the two potential regions in the CV scan (Fig. 4.1) as: 'Region A' corresponding to potential range between -1.4 and -2.05 V, *i.e.*, reaction 4.1, and 'Region B' corresponding to potentials negative to -2.05 V, *i.e.*, reactions 4.1 and 4.2 proceeding in parallel. The CV behavior at various scan rates (100–300 mV/s) is shown in Fig. 4.2. Clearly, the peak potential in region A does not exhibit strong dependency on the scan rate, which is a manifestation of diffusion–limited reversible system behavior.³² The peak potential in region B, on the other hand, shifts slightly depending on the scan rate as also observed by others.^{89,93} From Fig. 4.2, the maximal (peak) cathodic current densities were extracted for regions A and B as a function of the scan rate. For region A, the peak current density corresponded to the diffusion–limited current plateau observed at electrode potentials close to -2.04 V. For region B, the peak position was around -2.1 V (varying slightly with scan rate) as seen in Fig. 4.2. The peak current densities were plotted versus the square root of the scan rate in the range of scan rates from 50–500 mV/s. This is shown in Fig. 4.3. A linear dependence of the peak current density on the square root of the scan rate is confirmed.







Figure 4.3. The cathodic peak current densities in regions A and B of cyclic voltammograms (from Fig. 4.1 and 4.2) show a linear dependence on the square root of potential scan rate. Cyclic voltammograms were measured under conditions outlined in Fig. 4.1 and 4.2.

4.3 Limitations of Classical Models of Diffusion–Limited Reversible Redox Reactions

As described in previous chapters, the basis of a linear dependence of the cathodic peak current density on the square root of the scan rate is presented by classical mathematical models that treat diffusion–limited reversible electrochemical reactions. For soluble–soluble redox transitions such as in region A, the dependence of the cathodic
peak current (i_{peak}) on the scan rate (v) is given by the Randles–Sevcik equation³² (Eq. 1.5), which can be written for the Nd system as:

$$i_{\text{peak}} = -0.4463 \left(\frac{F^3}{RT}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D^{\frac{1}{2}} [\text{Nd}^{3+}]_{\text{b}} \nu^{\frac{1}{2}}$$
[4.4]

where *D* is the Nd³⁺ diffusion coefficient, $[Nd^{3+}]_b$ is the Nd³⁺ bulk concentration, and *v* is the scan rate, and all other variables have their usual meaning. For region A, taking n = 1, $D = 2.2 \times 10^{-5}$ cm²/s based on literature reports,^{89,92} and $[Nd^{3+}]_b = 60$ mM, the peak current density predicted using Eq. 4.4 was compared to experimental data in Fig. 4.3. This comparison is shown in Fig. 4.4. It is observed that the peak current density (*i*_{peak}) predicted using Eq. 4.4 (*dashed green* line) closely matches that measured experimentally. This further confirms that region A represents a reversible soluble– soluble process (Nd³⁺ + $e^- \rightarrow$ Nd²⁺) with n = 1.



Figure 4.4. Comparison between the cathodic peak current densities in regions A and B of CVs measured experimentally (data points from Fig. 4.3) and computed using the Randles–Sevcik (Eq. 4.4, *dashed green* line) and the Berzins–Delahay (Eq. 4.5, *dashed blue* line) models. For region B, the discrepancy between the experimental peak current densities and the Berzins–Delahay model predictions is noted.

For soluble–insoluble transition such as in region B, the peak current density is described using the Berzins–Delahay equation (Eq. 1.6) employed in electrodeposition studies.^{37,94} It is written for the Nd system as

$$i_{\text{peak}} = -0.6105 \left(\frac{F^3}{\text{RT}}\right)^{\frac{1}{2}} n^{\frac{3}{2}} D^{\frac{1}{2}} [\text{Nd}^{3+}]_{\text{b}} \nu^{\frac{1}{2}}$$
[4.5]

Fig. 4.4 shows a comparison of the peak current density predicted using Eq. 4.5 (n = 3)and that measured in region B of the CV scan (Fig. 4.3). A clear lack of agreement between the two is noted. Eq. 4.5, which is commonly used in studies of molten salt electrolysis of multivalent metals,⁹² assumes a one-step electrodeposition process that encounters mass-transport resistance as the electrode potential is cathodically scanned. However, this simplistic picture is inconsistent with the complex multivalent redox transitions (reactions 4.1 and 4.2 above) prevalent in Nd electrodeposition. Specifically, in potential region B, the Nd³⁺ concentration is already depleted on account of the soluble–soluble transition (Nd³⁺ + $e^- \rightarrow$ Nd²⁺) that precedes it in region A. Furthermore, in region B, as Nd³⁺ is reduced to Nd⁰ through a combination of reactions 4.1 and 4.2, a portion of the intermediate Nd²⁺ species may out–diffuse away from the electrode surface. This 'loss' of Nd²⁺ may be viewed as a source of inefficiency that lowers the available Nd^{2+} near the electrode, thereby lowering the peak reaction rate achievable in region B. As a consequence of these effects, the experimentally measured current density is substantially lower than (nearly half of) that predicted by the Berzins-Delahay model (Eq. 4.5). If the Nd²⁺ concentration were known and were used in Eq. 4.5 with n = 2, the Berzins–Delahay model may predict more reliably the peak current densities in region B. However in fact, during the electrodeposition of Nd from Nd³⁺, the intermediate Nd²⁺ concentration and its profile are not *a priori* known nor easily measurable. Thus, determining Nd²⁺ concentration requires comprehensive diffusionreaction modeling as performed in the section below. In the work of Novoselova and Smolenski on CV of Nd deposition from NdCl₃-LiCl-KCl-CsCl, their measured

cathodic peak currents were also consistently lower than the predictions of the Berzins– Delahay equation.¹⁰³

To capture the complex phenomena involving multi–stage reduction of Nd³⁺ to Nd⁰ in region B, the transient diffusion–reaction modeling, as developed in chapter 2, was again employed. Through detailed numerical analysis of the transient diffusion of multivalent Nd species (Nd³⁺, Nd²⁺) and their electrochemical reactions (Eq. 4.1 and 4.2 above), this work developed a theory–guided approach for characterizing the CV behavior during electrodeposition of Nd. Specifically, as demonstrated in the subsequent section, such approach of incorporating transient multi–component diffusion and surface reactions can predict reliably and accurately the CV behavior in systems that exhibit multivalency.

4.4 Mathematical Modeling of Nd Electrodeposition via Multi-step Reduction of Nd³⁺

4.4.1 Diffusion-Reaction Model Setup

Consider an electrode surface brought in contact with a molten salt electrolyte as shown schematically in Fig. 4.5. Initially, *i.e.*, before any electrochemical reactions are initiated, the NdCl₃–LiCl–KCl electrolyte comprises of Nd ions in their +3 oxidation state (Nd³⁺). Near the electrode surface, within the zone $0 \le x \le \delta$, diffusion is the predominant mode of ionic transport. Thus, when the electrode potential is scanned in the negative (cathodic) direction, the two–stage reduction process (described earlier in Fig. 4.1 and related text) leads to the development of a Nd³⁺ concentration gradient. Specifically, in the potential range –1.4 V to –2.05 V (region A in Fig. 4.1), Nd³⁺ diffuses

towards the electrode surface from the bulk electrolyte and is reduced to Nd²⁺, which then diffuses away from the electrode surface. As the potential is scanned further negative with respect to -2.05 V (region B in Fig. 4.1), Nd²⁺ formed at the electrode surface via reaction 4.1 is at least partially reduced further into Nd metal (Nd⁰). At the same time, unreacted Nd²⁺ diffuses away from the electrode surface towards the bulk electrolyte. The transport of soluble species (Nd³⁺ and Nd²⁺) within the zone $0 \le x \le \delta$ is assumed to obey Fickian diffusion:

$$\frac{\partial [\mathrm{Nd}^{3+}]}{\partial t} = D_{3+} \frac{\partial^2 [\mathrm{Nd}^{3+}]}{\partial x^2}$$
[4.6]

$$\frac{\partial [\mathrm{Nd}^{2+}]}{\partial t} = D_{2+} \frac{\partial^2 [\mathrm{Nd}^{2+}]}{\partial x^2}$$

$$\tag{4.7}$$

In Eq. 4.6 and 4.7, $[Nd^{3+}]$ and $[Nd^{2+}]$ represent ion concentrations, D_{3+} and D_{2+} are their respective diffusion coefficients, *x* represents position within the space domain, and *t* is time. In modeling the Nd²⁺ and Nd³⁺ species transport, transport due to field–assisted electric migration was neglected because of the well–supported molten salt electrolyte.



Figure 4.5. Schematic representation of the diffusion–reaction process during stepwise reduction of Nd³⁺ leading to Nd electrodeposition. This mechanistic picture forms the basis of the mathematical model developed in this chapter.

During an electrode potential scan, the potential E has the following time

dependence, as described in chapter 2:

$$E = E_i - \nu t$$
 [2.11]
(revisited)

where E_i is the initial potential (-1.4 V, consistent with experiment) and *v* is the scan rate. Initially (*t* = 0), the concentration of Nd³⁺ in the vicinity of the electrode is uniform and is equal to its bulk value. Also, at *t* = 0, the Nd²⁺ concentration is zero. Thus:

$$t = 0$$
 $0 \le x \le \delta$: $[Nd^{3+}] = [Nd^{3+}]_b$ [4.8]

$$t = 0$$
 $0 \le x \le \delta$: $[Nd^{2+}] = 0$ [4.9]

Under semi–infinite diffusion, the concentration of Nd³⁺ far away from the electrode surface stays constant and is equal to the Nd³⁺ bulk concentration. Practically, when δ is very large (as in the present case of a stagnant electrolyte), the boundary conditions at $x = \delta$ can be formulated as:

$$t > 0$$
 $x = \delta$: $[Nd^{3+}] = [Nd^{3+}]_b$ [4.10]

$$t > 0$$
 $x = \delta$: $[Nd^{2+}] = 0$ [4.11]

In region A of the electrode potential scan, *i.e.*, at potentials in the range between -1.4 V to -2.05 V, the reversible nature of the soluble–soluble redox transition between Nd³⁺ and Nd²⁺ implies that the Nernst equation is valid:

$$t > 0$$
 $x = 0$: $E = E_i - \nu t = E_{3+/2+}^0 + \frac{RT}{nF} \ln \frac{[Nd^{3+}]}{[Nd^{2+}]}\Big|_{x=0}$ [4.12]

where the concentrations are taken at the electrode surface. Additionally, in region A of the electrode potential scan, mass balance dictates that:

$$t > 0$$
 $x = 0$: $-D_{3+} \frac{\partial [\mathrm{Nd}^{3+}]}{\partial x} \Big|_{x=0} = D_{2+} \frac{\partial [\mathrm{Nd}^{2+}]}{\partial x} \Big|_{x=0}$ [4.13]

Eq. 4.6 and 4.7, together with the initial conditions (Eq. 4.8 and 4.9) and the boundary conditions (Eq. 4.10–4.13) were solved numerically (using COMSOL Multiphysics simulation software) to determine the concentration profiles of Nd³⁺ and Nd²⁺ in the vicinity of the electrode surface as a function of the time–dependent electrode potential.

In region B of the electrode potential scan, *i.e.*, at potentials negative with respect to -2.05 V, Nd²⁺ formed at the electrode surface is reduced further into Nd metal (Nd⁰). In this range of potentials, the mass balance represented by Eq. 4.13 is modified further to incorporate the Nd²⁺–reduction reaction as:

$$-D_{3+}\frac{\partial[\mathrm{Nd}^{3+}]}{\partial x} = D_{2+}\frac{\partial[\mathrm{Nd}^{2+}]}{\partial x} + k_0[\mathrm{Nd}^{2+}]^{1-\beta} \left\{ e^{\frac{(1-\beta)\mathrm{nF}}{\mathrm{RT}}\eta_s} - e^{\frac{-\beta\mathrm{nF}}{\mathrm{RT}}\eta_s} \right\}$$
(4.14)

where the second term on the right hand side represents the Butler–Volmer kinetics associated with the Nd electrodeposition reaction.⁴⁹ The parameter k_0 is the reaction rate constant (related to exchange current density) and β is the charge transfer symmetry factor, where β is related to the charge transfer coefficient $\alpha_c \text{ via } \beta \times n = \alpha_c$. The surface overpotential η_s is the deviation of the electrode potential from the reduction potential (–2.05 V) of the reaction: Nd²⁺ + 2e⁻ \Rightarrow Nd⁰. For various values of k_0 and β , Eq. 4.14 can be used (instead of Eq. 4.13) as a boundary condition to solve the Fickian diffusion Eq. 4.6 and 4.7, yielding the Nd^{3+} and Nd^{2+} concentration profiles during potential scan in region B.

For direct comparison of model results to experiment, current density must be computed. For this, the diffusion–reaction flux is converted into current density via:

In region A:
$$i = -FD_{3+} \frac{\partial [Nd^{3+}]}{\partial x}$$
 [4.15]

In region B:
$$i = -FD_{3+} \frac{\partial [Nd^{3+}]}{\partial x} + 2Fk_0 [Nd^{2+}]^{1-\beta} \left\{ e^{\frac{(1-\beta)2F}{RT}\eta_s} - e^{\frac{-\beta2F}{RT}\eta_s} \right\}$$
 [4.16]

Eq. 4.15 and 4.16 provide the cathodic reduction current densities in regions A and B.

4.4.2 Model Parameters and Simulation Results

The current response during a cathodic potential sweep was simulated by numerically solving the mathematical model discussed above. The parameters used for simulating the current response are provided in Table 4.1. For consistency with experimental conditions, the bulk Nd³⁺ concentration was maintained at 60 mM. The electrode potential was scanned from $E_i = -1.4$ V at various scan rates (v = 50, 100, 200, 300 and 500 mV/s) also consistent with experimental conditions (Fig. 4.3). The diffusion coefficient of Nd³⁺ (D_{3+}) was obtained from literature.^{89,92} Due to the unavailability of reliable Nd²⁺ diffusion coefficient data,^{86,89,90,93} it was assumed that $D_{2+} = D_{3+}$. This assumption is supported by the fact that the diffusion coefficients of the various soluble species (with different oxidation states) of titanium or europium in molten chloride melts are similar.^{104,105} The charge transfer coefficient α_c , and through which the symmetry factor β , was selected based on previous studies of the electrodeposition of other divalent metals in molten chloride media. For example, Borresen *et al.*¹⁰⁶ provided the charge transfer coefficient of Mg²⁺/Mg to be around 0.1 – 0.2 on GC and Mo substrates, largely consistent with other literature reports²⁴ on the kinetics of divalent metal (Cd, Zn, Ag, Ni, Pt) electrodeposition in chloride–based molten salts.

Table 4.1. Parameters f	or simulating	the current ve	s. potential	response	using the
diffusion-reaction mod	el developed i	in chapter 4.			

Parameter	Value	Source		
$[Nd^{3+}]_{b}$	60 mM	Experiment		
E_i	-1.4 V vs. Ag/AgCl-LiCl-KCl	Experiment		
ν	50, 100, 200, 300, 500 mV/s	Experiment		
D_{3+}	$2.2 \times 10^{-5} \text{ cm}^2/\text{s}$	Ref. 89,92		
D_{2+}	$2.2 \times 10^{-5} \text{ cm}^2/\text{s}$	Selected		
δ	0.1 cm	Selected		
β	0.1	Ref. 24,106		
k_0	$2.4 \times 10^{-3} \text{ (cm/s)}(\text{mol/cm}^3)^{0.1}$	Determined via optimization		



Figure 4.6. Comparison between experimental voltammetry data (*red* curve) and predictions of the diffusion–reaction model (*black* curve) developed herein. Both curves represent a 60 mM NdCl₃ containing LiCl–KCl electrolyte at 475 °C. Scan rate was 200 mV/s. Good agreement between experiments and model predictions is noted.

The reaction rate constant k_0 is not available *a priori*; however, since this is the only adjustable parameter in the model system, it can be determined by comparison of model results to experiments. In this case, the value of k_0 [units = (cm/s)(mol/cm³)^{0.1}] was varied in the range between $10^{-2} - 10^{-4}$ and determined that $k_0 = 2.4 \times 10^{-3}$ provides the best agreement between theory and experiment. This is shown in Fig. 4.6. At $k_0 = 2.4 \times 10^{-3}$, the simulated peak current density (at -2.12 V) is 65 mA/cm², which is consistent with experimental data. However, the model predicts a somewhat higher

current density compared to experimental data at potentials cathodic with respect to -2.12V. This discrepancy although small may be due to non-linear kinetics or transport effects which to date are not completely understood. Nonetheless, this optimal value of k_0 can be used to estimate the exchange current density: $i_0 \approx 2Fk_0[Nd^{2+}]^{1-\beta}$. The maximum value of $[Nd^{2+}]$ is equal to $[Nd^{3+}]_b$, which is 60 mM. For this condition, $i_0 \approx 74$ mA/cm². This value is generally in agreement with exchange current densities of metal electrodeposition systems employing high temperature molten halide media. For example, Rose *et al.* determined the exchange current density for the reaction U^{3+} + $3e^- \rightleftharpoons U^0$ in molten LiCl-KCl to be 100 mA/cm² at 500 °C.¹⁰⁷ Triaca *et al.* found that the exchange current density for chlorine evolution $(2Cl^- \rightleftharpoons Cl_2 + 2e^-)$ from a chloride melt is in the range of 130–190 mA/cm², depending on the electrode material.¹⁰⁸ This general agreement in the value of i_0 provides confidence that, once again, the approach of coupling diffusion-reaction modeling to experimental CV data, as presented in both this chapter and previously in chapter 2, can unravel system kinetic parameters such as exchange current density. More importantly, this chapter proves that the modeling approach is also suitable for multi-stage redox transitions, where the concentration of the intermediate species is unknown. This approach to estimate kinetics in multivalent electrodeposition systems in molten salt has several advantages and can alleviate some of the challenges mentioned in chapter 1.

It is noteworthy that, if the current–potential response is simulated at $k_0 >>$ 2.4×10⁻³, *i.e.*, approaching very fast (reversible) kinetics, the simulated peak current density is much larger than the experimentally measured peak current density. This behavior is expected since we already know (based on Fig. 4.4) that the Berzins–Delahay

equation (which too assumes reversibility) substantially overpredicts the peak current. Therefore, it may be stated that reaction 4.2 is not completely reversible in nature.



Figure 4.7. Comparison between the cathodic peak current densities in regions A and B of CVs measured experimentally (data points from Fig. 4.3) and those computed using the diffusion–reaction model developed in the present work (*dashed* lines). The model accurately predicts the peak current densities for both the soluble–soluble (region A) and the soluble–insoluble (region B) transitions during Nd electrodeposition. NdCl₃ concentration was set to 60 mM.

Using the optimized reaction rate constant ($k_0 = 2.4 \times 10^{-3}$), the current–potential response was simulated at a variety of potential scan rates in the range 50-500 mV/s. The simulated peak current densities in potential regions A and B were compared to those available from experimental observations (Fig. 4.3). This comparison is shown in Fig. 4.7. As seen in this figure, the simulated peak current densities are in excellent agreement with experimental data for both potential regions A and B over a wide range of scan rates. The agreement in region A is not surprising, because our diffusion-reaction model uses the same underlying physics that govern the Randles–Sevcik equation (Eq. 4.4), which we already know predicts the peak current densities in region A correctly (see Fig. 4.4). The agreement between our numerical model and the experimental data in region B is rather unique. As discussed previously (Fig. 4.4 and related text), the Berzins–Delahay equation (Eq. 4.5) for the soluble-insoluble redox transition does not agree with experimental CV data because it neglects critical transport-kinetics interactions which dominate the system behavior in potential region B. Our modeling strategy eliminates this deficiency and thereby enables precise and quantitative prediction of the CV behavior during electrolysis investigations involving multi-stage redox transitions.



Figure 4.8. Comparison between the cathodic peak current densities in regions A and B of CVs measured experimentally (data points) and those computed using the diffusion–reaction model developed in the present work (*dashed* lines). The model accurately predicts the peak current densities for both the soluble–soluble (region A) and the soluble–insoluble (region B) transitions during Nd electrodeposition. NdCl₃ concentration was set to 120 mM.

To further confirm the validity of the extracted kinetics parameters, we performed simulations using the same set of parameters as in Fig. 4.7 except at higher [Nd³⁺] bulk concentration, *i.e.*, [Nd³⁺]_b = 120 mM, and compared the results to experimentally obtained CV data. The simulations incorporated the same value of the kinetic parameter $k_0 = 2.4 \times 10^{-3}$ as determined via optimization for the 60 mM condition (Fig. 4.6) because k_0 should be concentration–independent. A comparison between the peak current densities measured experimentally and simulated numerically at $[Nd^{3+}]_b = 120 \text{ mM}$ for various scan rates is shown in Fig. 4.8. Once again, excellent agreement is noted. This further indicates the validity of the model and the parameter values used in computing the current–potential response. In Fig. 4.7 and 4.8, it is noted that the simulated peak currents are linearly proportional to the $[Nd^{3+}]$ bulk concentration. This dependency is qualitatively consistent with that observed in the conventional Berzins–Delahay equation. The agreement between the predictions of our diffusion–reaction model and the experimental voltammetry data over a range of concentrations and scan rates leads us to believe that the model developed herein captures the key physicochemical processes that govern the multi–step reduction of Nd^{3+} to Nd metal.

4.5 Conclusions

In this chapter, the following conclusions are drawn pertaining to the multivalent electrodeposition of Nd from NdCl₃-containing halide melts:

- (i) Nd electrodeposition proceeds via a multi–stage reduction process in which Nd³⁺ ions are first reduced to an intermediate Nd²⁺ species, followed by the reduction of Nd²⁺ to Nd metal.
- (ii) Nd electrodeposition was investigated using cyclic voltammetry. It was demonstrated that the peak current density measured in region B of the voltammogram (corresponding to Nd electrodeposition) is inconsistent with that predicted by applying the classical Berzins–Delahay model.

(iii) A diffusion-reaction model was developed, which incorporates the diffusional transport and surface electrochemical reactions involving multivalent Nd species. Through such a theory-guided approach, the voltammetry response during Nd electrodeposition could be precisely and quantitatively modeled. The diffusion-reaction model incorporates a single adjustable parameter, *i.e.*, the electrodeposition rate constant (*k*₀), which could be estimated by comparing the simulated voltammetry response to experiments over a wide range of process variables. This technique of parameter estimation has the potential to provide reliable access to exchange current densities in molten salt electrodeposition systems, where conventional polarization measurements are often cumbersome and where a high degree of reversibility makes rate constant measurements unreliable.

5.1 Summary and Conclusions

The present work developed guidelines to accurately measure the kinetics of metal redox couples in resistive electrolyte, such as ethaline DES. Using the Cu²⁺/Cu¹⁺ redox transition as a model system, we pursued a comprehensive study of the kinetics and transport properties of this redox reaction. The measurements yielded kinetic parameters of $\alpha_{\rm c} = 0.49 - 0.54$ and $k_0 = (1.78 - 1.95) \times 10^{-4}$ cm/s. This was confirmed using three independent techniques – slow scan linear sweep voltammetry (LSV) on Pt RDE, fast scan cyclic voltammetry (CV) on Pt PDE coupled with diffusion-reaction modeling, and slow scan LSV on Pt microelectrode. Consequently, this study established beyond doubt that the Cu^{2+}/Cu^{1+} redox transition proceeds slowly in chloride–containing DES. Furthermore, the effects of DES composition and temperature on kinetics provide important insights into the origins of the rate-limiting factor related to species complexation. Specifically, the role of Cl⁻ in complexing the cations and thereby hindering charge-transfer is demonstrated. To explain how charge transfer kinetics depend on the various system parameters, a model incorporating complexation phenomena was developed and its predictions were compared to experiments.

Regarding the multivalent electrodeposition of Nd form NdCl₃-containing halide melts, the multi-step electrodeposition reaction was investigated using cyclic voltammetry. The analysis demonstrated an inconsistency with existing classical model. As a result, a diffusion-reaction model was once again developed, this time incorporating

the diffusional transport and surface electrochemical reaction involving multivalent Nd species. Through such a theory–guided approach, the voltammetry response during Nd electrodeposition could be precisely and quantitatively modeled. Through this approach, the reaction rate constant (k_0) associated with the multivalent Nd electrodeposition was obtained.

5.2 Outlook and Future Work

As renewable energy sources become more prevalent, so arises the need for grid– scale energy storage. Deep eutectic solvents are a promising candidate as electrolyte for redox flow batteries, due to their numerous advantages. However, as indicated in this work, metal redox couples form undesirable complexes with the DES constituents, thus hinder the reaction kinetics. By applying techniques such as extended X–ray absorption fine structure (EXAFS) and UV–Vis spectroscopy,⁶¹ further insight into the structure and concentration of these complexes can be gained. To eliminate the formation of unwanted complexes, future works in this area needs to focus on two components: the redox couple and the DES electrolyte.

Given the tendency for most metal ions to form complexes with chloride,⁵⁸ organic redox couples could be a promising substitute. Quinones, (2,2,6,6– Tetramethylpiperidin–1–yl)oxyl (TEMPO), and phenols are known electroactive species that dissolve in conventional DES.^{109–111} Since they do not form complexes, their charge transfer kinetics in DES are expected to be comparable to that in water. However, their

solubility limit and mass transport parameters have first to be ascertained, so that they provide comparable energy and power output as conventional aqueous RFBs.

DES are formed from two different constituents whose mixture has a lower melting point compared to its parents.⁸ They feature a large variety of potential starting materials, thus enabling the design of a mixture that does not form complexes with metal ions. Starting materials that don't contain chloride–based salts, but rather fluoride– or acetate–based salts could alleviate the undesirable chloro–complex formation. In addition, the structures of the DES components could be fine–tuned by altering their functional groups to lower the viscosity of the resulting mixture. The fine–tuning of the DES structure could also benefit the electrochemical stability window of the mixture, which when combined with the proper anode/cathode reaction chemistries can thereby improve the power output of the RFB.

In developing an energy–efficient recycling process for Nd, this work has focused solely on the cathode chemistry. However, several key challenges remain for the overall electrolytic process. First of all, electrorefining of Nd from a Nd–Fe–B alloy requires selective electrochemical dissolution of Nd from the alloy anode without dissolving Fe or B. Such an anode chemistry is yet to be developed. Secondly, despite the intrinsic advantages of molten salt electrolysis (high electrochemical reaction rates), sluggish transport of Nd in the solid state Nd–Fe–B anode can limit the overall electrorefining process rates. One solution could be to crush the anode into small particulates and place them in an anode basket during dissolution. The small dimensions of the solid phase could minimize the impact of sluggish solid state diffusion. Another solution could be to implement a variable duty cycle pulsing algorithm when dissolving the anode. By pulsing

the current, more Nd deep within the metal anode would be given the time to diffuse towards the surface, thereby achieving more complete dissolution. Thirdly, prior attempts at Nd electrorefining have encountered low current (and energy) efficiencies due to redox shuttling of multivalent Nd ions.²⁰ Nd²⁺ species generated during electrodeposition at the cathode migrate to the anode where they are oxidized back to Nd³⁺, thereby lowering the current efficiency. Consequently, a porous separator needs to be implemented in the reactor design, such that the redox shuttling of multivalent Nd species (Nd³⁺ and Nd²⁺) are hindered and high current efficiency can be achieved.

While this thesis focused on developing a recycling process for Nd, the principles of operation herein can be extended to the electrorefining of other rare earth metals, as well as the electrowinning of refractory metals such as titanium and zirconium. More importantly, the techniques applied in this work can be extended to analyzing the charge transfer kinetics of other multivalent metals, which is crucial in developing their electrorefining and electrowinning processes. 1. M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli, and M. Saleem, *J. Electrochem. Soc.*, **158**, R55 (2011).

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