SUPPRESSING DENDRITIC GROWTH DURING ZINC ELECTRODEPOSITION USING POLYETHYLENIMINE AS AN ELECTROLYTE ADDITIVE FOR RECHARGEABLE ZINC BATTERIES

by

Stephen J. Banik II

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Thesis Advisor: Professor Rohan Akolkar

Department of Chemical & Biomolecular Engineering
CASE WESTERN RESERVE UNIVERSITY

May, 2016
We hereby approve the dissertation of

Stephen J. Banik II

Candidate for the Doctor of Philosophy degree*

(signed) Prof. Rohan Akolkar

(chair of the committee)

Prof. Uziel Landau

Prof. Chung-Chiun Liu

Prof. Mark De Guire

Date: March 23, 2016

*We also certify that written approval has been obtained for any proprietary material contained therein.
DEDICATION

This thesis is dedicated to my wife and family for their unwavering love and support.
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<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>$A$</td>
<td>Electrode area, cm$^2$</td>
</tr>
<tr>
<td>$C$</td>
<td>Concentration, mol/cm$^3$</td>
</tr>
<tr>
<td>$\bar{c}$</td>
<td>Concentration, dimensionless</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusion coefficient, cm$^2$/s</td>
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<tr>
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<td>$h$</td>
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<tr>
<td>$\dot{h}$</td>
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</tr>
<tr>
<td>$I$</td>
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<tr>
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<tr>
<td>$i_0$</td>
<td>Exchange current density, mA/cm$^2$</td>
</tr>
<tr>
<td>$K$</td>
<td>Molar volume of zinc (9.2 cm$^3$/mol)</td>
</tr>
<tr>
<td>$K_{eq}$</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>$k_{ads}$</td>
<td>Adsorption rate constant, cm/s</td>
</tr>
<tr>
<td>$k_{des}$</td>
<td>Desorption rate constant, mol/cm$^2$ s</td>
</tr>
</tbody>
</table>
$k_D$  Diffusion-limited rate constant, cm/s
$L$  Length of PEI molecule, nm
$l$  Characteristic length of electrode, cm
$M$  Molecular weight of zinc (65.38 g/mol)
$\Delta m$  Mass change, µg/cm$^2$
$N_A$  Avogadro’s Number ($6.022 \times 10^{-23}$ molecules/mole)
$n$  Number of electrons transferred during electrodeposition (=2)
$Q$  Charge, Cb
$R_a$  Activation resistance, $\Omega$ cm$^2$
$R_O$  Ohmic resistance, $\Omega$ cm$^2$
$R_{rms}$  Root mean square roughness, µm
$R$  Universal gas constant (8.314 J/mol K)
$T$  Temperature, K
$t$  Time, s
$\tau$  Time, dimensionless
$t_+$  Transport number, dimensionless
$V$  Volume of PEI molecule, nm$^3$
$V_{app}$  Applied voltage, V
$W$  Width of PEI molecule, nm
$Wa$  Wagner number, dimensionless
$\bar{x}$  Distance, dimensionless
\( y_i \)  
Surface height, µm

**Greek**

\( \alpha_a \)  
Anodic charge transfer coefficient

\( \alpha_c \)  
Cathodic charge transfer coefficient

\( \Gamma \)  
Saturation surface concentration, mol/cm\(^2\)

\( \gamma \)  
Surface tension at zinc-electrolyte interface \((7.9 \times 10^{-5} \text{ J/cm}^2)\)

\( \delta \)  
Diffusion boundary layer thickness, cm

\( \eta_a \)  
Activation overpotential, V

\( \eta_\Omega \)  
Ohmic overpotential, V

\( \eta_c \)  
Concentration overpotential, V

\( \eta_s \)  
Surface curvature overpotential, V

\( \Delta \eta_a \)  
Activation overpotential difference, V

\( \theta \)  
Surface coverage, dimensionless

\( \kappa \)  
Electrolyte conductivity, mS/cm

\( \nu \)  
Kinematic viscosity, cm\(^2\)/s

\( \xi \)  
Dendrite suppression factor, dimensionless

\( \rho \)  
Density of zinc \((7.14 \text{ g/cm}^3)\)

\( \tau \)  
Time constant, s

\( \Phi \)  
Plating current efficiency, %

\( \omega \)  
Angular rotation rate, rad/s
Subscripts

$avg$  Average value

$b$  Bulk value

$e$  Value at electrode surface

$flat$  On flat electrode

$H$  Hydrogen

$NoAdd$  No additive

$PEI$  Contains polyethylenimine (PEI)

$rod$  PEI in rod shape

$sphere$  PEI in sphere shape

$SS$  Steady state value

$tip$  At dendrite tip

$Zn$  Zinc

$Zn+H$  Refers to zinc deposition and hydrogen co-evolution
Suppressing Dendritic Growth during Zinc Electrodeposition using Polyethylenimine as an Electrolyte Additive for Rechargeable Zinc Batteries

Abstract

by

STEPHEN J. BANIK II

Energy storage devices, e.g., batteries, are central to the United States’ clean energy revolution. Load-leveling batteries are needed to store energy from intermittent renewable energy sources and high energy density batteries are required for electric vehicles and portable electronics. Zinc-air batteries are a promising alternative to the current state-of-the-art lithium-ion batteries. Zinc-air batteries offer high energy densities (about twice the energy density of lithium-ion batteries). The Zinc-air battery anode contains metallic zinc, which is an earth-abundant, environmentally benign metal. The use of aqueous electrolytes makes zinc-air batteries inherently cheaper and safer compared to lithium-ion batteries, which use expensive and flammable organic electrolytes. However, a major roadblock in the development of rechargeable zinc batteries is the dendritic morphology evolution during zinc electrodeposition (i.e., during battery charging). Zinc dendrites can detach from the electrode surface leading to capacity loss or pierce through the separator causing early cell failures.

In the present work, polyethylenimine (PEI, M.W. = 800 g/mol) is employed as an electrolyte additive to suppress dendrite formation during zinc electrodeposition from typical alkaline electrolytes used in rechargeable zinc-air batteries. Dendrite suppression is characterized as a function of the PEI concentration in the bulk electrolyte using in situ
optical microscopy. Steady-state and transient electrochemical polarization measurements on a rotating disk electrode, combined with electrochemical quartz crystal microgravimetry and scanning electron microscopy reveal the mechanism by which PEI suppresses dendrites. That is, PEI adsorbs on the zinc surface leading to suppression of the zinc electrodeposition kinetics, thereby suppressing activation-controlled dendrite growth. PEI is also effective in suppressing roughness evolution during charge-discharge cycling of zinc anodes. At current densities corresponding to typical zinc-air battery charging rates, PEI does not affect the zinc deposition current efficiency.

Additive injection studies coupled with transport-kinetics modeling provides insights into the diffusion and surface-adsorption properties of PEI during zinc electrodeposition. At typical PEI concentrations required for zinc dendrite suppression, PEI adsorption on the electrode surface is limited by its diffusional transport and not by its surface adsorption kinetics. For branched PEI (M.W. = 800 g/mol) in alkaline media, the diffusion coefficient ($D_{PEI}$) was measured to be $1.87 \times 10^{-6}$ cm$^2$/s and the adsorption rate constant was estimated to be $k_{ads} \geq 0.1$ cm/s.
CHAPTER 1. Introduction

1.1 Motivation: To Enable High Energy Density Rechargeable Zinc Batteries

Energy storage devices, e.g., batteries, are central to the United States’ clean energy revolution. Since renewable energy sources such as wind and solar are intermittent by nature, load-leveling batteries are needed to store the excess harvested energy and release it during periods of high demand.\textsuperscript{1-3} Furthermore, zero-emission electric vehicles (EVs) and portable electronics require high energy density and high power density batteries.\textsuperscript{4-7} The development of reliable, rechargeable battery systems is critical to realize the clean energy revolution in the United States and around the world. Transportation and grid-storage applications require battery technologies with high energy densities, \textit{i.e.}, kWhr of energy stored per unit mass or volume of the battery.\textsuperscript{4-5}

Figure 1.1 shows the practical energy densities of various battery technologies: lead-acid, nickel-metal-hydride, lithium-ion (Li-ion), zinc-air (Zn-air), and lithium-air (Li-Air). Among these battery technologies, rechargeable Li-ion batteries with energy density of \(~\text{160 Whr/kg}\) are commercially available. Compared to the state-of-the-art Li-ion battery, metal-air batteries have the potential to offer increased energy densities. For example, the Zn-air battery offers an energy density of \(~\text{350 Whr/kg}\), roughly twice the energy density of the Li-ion battery.\textsuperscript{8} In addition to increased energy density, the Zn-air battery has many other advantages: (i) It uses metallic zinc, an abundant and environmentally benign material, as the battery anode; and (ii) It uses aqueous electrolytes that are inherently cheaper and safer than organic solvents used in Li-ion and
Li-Air batteries. Thus, the Zn-air battery holds great potential for next-generation energy storage.7,9

![Figure 1.1. Practical energy density of various energy storage technologies. Data taken from Girishkumar, et al.](image)

Batteries utilizing zinc-metal anodes involve zinc (Zn) electrodeposition during battery charging and Zn electrodissolution during battery discharging, as shown in Eq. 1.1:

$$Zn^{2+}_{(aq)} + 2e^{-} \overset{\text{charge}}{\longrightarrow} Zn^{0}_{(s)} \hspace{1cm} (E_0 = -0.76 \ V \ vs. \ SHE) \ [1.1]$$

In alkaline electrolytes as employed in Zn-air batteries, the deposition-dissolution reactions involve the zincate anion [Zn(OH)₄]²⁻, which is the stable solution-phase species at high pH], and thus the anode half-reaction is:
A schematic representation of a rechargeable Zn-air battery is shown in Figure 1.2, illustrating the electrode half-reactions occurring during charging and discharging.

![Figure 1.2. Schematic of an alkaline Zn-air battery showing the two half-reactions. During charging, metallic Zn is electrodeposited on the anode, and oxygen evolves on the cathode. This battery has practical energy density around 350 Whr/kg, substantially exceeding that of state-of-the-art Li-ion battery.][8]

While the anode half-reaction is represented by Eq. 1.2, the cathode half-reaction is shown in Eq. 1.3:

\[ \frac{1}{2} O_2 (g) + H_2 O(l) + 2e^{-} \xrightarrow{charge} 2OH^- (aq) \]  \hspace{1cm} (E_{0,cathode} = +0.40 \text{ V vs. SHE}) \quad [1.3]
The theoretical equilibrium cell potential \( E_{eq} = E_{0,\text{cathode}} - E_{0,\text{anode}} \) of a Zn-air battery is 1.65 V. Zn-air battery electrolytes contain 0.1–0.5 M ZnO and 4–6 M KOH for optimal ZnO solubility and conductivity. Furthermore, operation at high pH ensures moderately fast oxygen reduction kinetics on low-cost carbon-based cathode materials.\(^4\)

In spite of numerous attractive characteristics of Zn-air batteries, development and commercial deployment of rechargeable Zn-air battery systems has been impeded by numerous technical challenges. For commercialization readiness, stable charge-discharge cycling performance over ~1000 cycles is required. Such performance has not been achieved to date. A critical hurdle in achieving rechargeable Zn-air batteries is the formation of Zn dendrites at the anode during the Zn electrodeposition reaction (charging). Figure 1.3 illustrates the problem of dendritic Zn growth on the electrode surface during Zn electrodeposition. While dendrites can detach from the electrode surface leading to capacity loss, needle-like dendrites can pierce through the separator and cause shorting that leads to early cell failures.\(^7\)

![Figure 1.3. Dendritic Zn electrodeposit after high rate electrodeposition (30 min at \(-1.57\) V vs. Hg|HgO; \(i \approx -12.5\) mA/cm\(^2\)) from a 0.1 M ZnO + 4.0 M KOH electrolyte.](image)
While the present thesis focuses on the problems associated with Zn dendrite formation at the battery anode, it must be noted that several challenges exist in realizing cycleable cathodes for Zn-air batteries. A major challenge at the cathode is minimizing electrode passivation from carbonate formation due to the reaction between the alkaline electrolyte (KOH) and CO₂ from air. This problem is not addressed in the present work.

1.2 Mechanism of Dendrite Formation during Electrodeposition

Numerous studies over the last 50 years have addressed the mechanism of Zn dendrite formation.\textsuperscript{11–13} The accepted mechanism\textsuperscript{12} is as follows: Tiny micro-scale roughness elements are present on any practically relevant Zn surface. During Zn electrodeposition, micro-scale roughness elements on the Zn surface experience enhanced three-dimensional (3D) diffusional transport of Zn ions, releasing them from diffusion-limitations. As a result, deposition proceeds at an accelerated rate at the tips of these roughness elements, leading to the formation of needle-like dendrites.

Imagine a roughness element on a Zn electrode surface as shown in Figure 1.4. On the flat portion of the electrode surface, the total overpotential that develops ($\eta_{\text{flat}}$) is the sum of the activation overpotential ($\eta_{a,\text{flat}}$) and the concentration overpotential ($\eta_{c,\text{flat}}$). Assuming Tafel kinetics for the activation overpotential, the total overpotential at the flat electrode surface is given as Eq. 1.4:

$$\eta_{\text{flat}} = \eta_{a,\text{flat}} + \eta_{c,\text{flat}} = -\frac{RT}{\alpha_e F} \ln \left( \frac{i_{\text{flat}}}{i_0} \right) + \eta_{c,\text{flat}} \quad [1.4]$$
In Eq. 1.4, $\alpha_c$ is the cathodic transfer coefficient and $i_0$ is the exchange current density. Since Eq. 1.4 relates to cathodic processes, all overpotentials have negative values.

Figure 1.4. Mechanism of dendrite formation during Zn electrodeposition: accelerated dendrite growth is aided by 3D transport to the tip of a micro-scale dendrite precursor element.

The total overpotential at the tip of the dendrite precursor ($\eta_{tip}$) is the sum of the activation overpotential ($\eta_{a,tip}$), concentration overpotential ($\eta_{c,tip}$) and the overpotential due to the surface energy of a curved dendrite tip ($\eta_{s,tip}$). For simplifying the following discussion, the surface curvature overpotential ($\eta_{s,tip}$) is assumed to be negligible (this is verified in Appendix A and Ref. 14). Thus, the total overpotential at the dendrite tip is given by Eq. 1.5:

$$\eta_{tip} = \eta_{a,tip} + \eta_{c,tip}$$

For the dendrite precursor tip to grow more rapidly than the flat surface, it is essential that the concentration overpotential at the tip be negligibly small. Physically, this
condition is met due to ‘spherical’ 3D diffusion to a micro-scale dendrite tip. This releases the tip from mass transport limitations and causes the dendrite to propagate primarily under kinetic limitations, \textit{i.e.}, dendrite propagation is activation-controlled. This has been demonstrated in several metal electrodeposition systems.\textsuperscript{12,15} Thus, assuming that the concentration overpotential at the dendrite tip is negligible, the total overpotential at the dendrite tip is:

\[ \eta_{\text{tip}} = \eta_{a,\text{tip}} = -\frac{RT}{\alpha_c F} \ln \left( \frac{i_{\text{tip}}}{i_o} \right) \] \[ \text{[1.6]} \]

Since the flat surface and the dendrite tip form an equipotential surface,\textsuperscript{16–17} one can write:

\[ \eta_{\text{flat}} = \eta_{\text{tip}} \] \[ \text{[1.7]} \]

Inserting the overpotential expressions from Eq. 1.4 and 1.6 into Eq. 1.7 results in Eq. 1.8:

\[ -\frac{RT}{\alpha_c F} \ln \left( \frac{i_{\text{flat}}}{i_o} \right) + \eta_{c,\text{flat}} = -\frac{RT}{\alpha_c F} \ln \left( \frac{i_{\text{tip}}}{i_o} \right) \] \[ \text{[1.8]} \]

Rearranging Eq. 1.8 yields Eq. 1.9:
Since $\eta_{c,\text{flat}}$ is a negative number, it can be concluded from Eq. 1.9 that the ratio $i_{\text{tip}}/i_{\text{flat}}$ is always larger than one. As the magnitude of $\eta_{c,\text{flat}}$ increases (as the system approaches mass-transport limitations), $i_{\text{tip}}$ becomes much larger compared to $i_{\text{flat}}$ and dendrite formation is favored.

1.3 Prior Strategies to Suppress Dendrite Growth during Electrodeposition

In the context of Zn electrodeposition, suppressing dendrite formation has been a focus of researchers worldwide since the 1960s. Notable studies include those by Naybour et al.\textsuperscript{18} who characterized the crystal orientation of the electroformed Zn dendrites, Bockris et al. who studied Zn electrodeposition kinetics from alkaline zincate electrolytes,\textsuperscript{19} and Oren and Landau who reported Zn dendrite growth characteristics in acidic chloride electrolytes.\textsuperscript{20} Additionally, Chen and Jorné have characterized fractal-like morphologies during Zn electrodeposition from sulfate electrolytes,\textsuperscript{21} while Barkey and coworkers have studied the formation of branched Zn aggregates also in sulfate electrolytes.\textsuperscript{22–23} Many early attempts to control the Zn electrodeposit morphology focused on optimization of the applied current or potential waveform. Arouete et al. experimented with pulsed-current electrodeposition for surface smoothening,\textsuperscript{24} whereas Despic and Popov showed Zn dendrite suppression using high-frequency square-wave potential pulses.\textsuperscript{25}
Other strategies to suppress Zn dendrites have involved the use of ppm-levels of electrolyte additives to lower the kinetics associated with the Zn electrodeposition reaction.\textsuperscript{10,26–36} Banik and Akolkar reported on the use of polyethylene glycol for suppressing dendritic growth during Zn electrodeposition from an acidic, halide-containing electrolyte (Appendix A and Ref. 14). Bass \textit{et al.} documented additives relevant to alkaline Zn battery applications,\textsuperscript{37} including surfactants, ammonium salts, and lead and bismuth compounds.\textsuperscript{38–47} While several promising additive candidates have been identified, a thorough and in-depth mechanistic analysis of the additive effect on the Zn electrodeposition process is lacking.

1.4 **Strategy: Polyethylenimine as an Electrolyte Additive for Dendrite Suppression during Zinc Electrodeposition**

In the present work, polyethylenimine (PEI) is used as an electrolyte additive to suppress Zn dendrites during alkaline Zn electrodeposition. This work is motivated by the fact that PEI is a widely studied polarizer during copper (Cu) electrodeposition\textsuperscript{48–49} and is also stable in the alkaline electrolytes relevant to Zn-air batteries\textsuperscript{50–51} Branched PEI was purchased from Sigma-Aldrich. Average PEI molecular weight (M.W.) was 800 g/mol. A schematic of the PEI additive polymer structure is shown in Figure 1.5.
1.5 Objectives

The specific objectives of the present research are:

1) Characterize the efficacy of the electrolyte additive PEI in suppressing dendritic growth and roughness evolution during potentiostatic and galvanostatic Zn electrodeposition from alkaline electrolytes;

2) Characterize the effect of PEI on kinetics of the Zn electrodeposition reaction and the hydrogen co-evolution reaction, thereby quantifying the effect of PEI on the Zn deposition current efficiency;

3) Using injection studies on a rotating disc electrode combined with analytical diffusion-adsorption modeling, characterize the fundamental transport and adsorption properties (diffusion coefficient, adsorption rate constant) associated with PEI during Zn electrodeposition from alkaline electrolytes.

The above objectives are addressed in Chapters 2–4 and key conclusions are summarized in Chapter 5.

In Chapter 2, in situ optical microscopy is used to monitor the growth of Zn dendrites and characterize the dendrite suppression efficacy of PEI as a function of the
PEI concentration. Dendrite suppression is demonstrated under both potentiostatic and galvanostatic Zn electrodeposition conditions. Scanning electron microscopy and surface profilometry illustrate distinct smoothening of the electrodeposit surface morphology in the presence of PEI. The efficacy of PEI in suppressing roughness under cycling conditions is confirmed through galvanostatic deposition-dissolution tests.

In Chapter 3, polarization measurements during Zn electrodeposition on a rotating disk electrode (RDE) are reported. The effect of PEI on the kinetic parameters associated with Zn electrodeposition ($\alpha_c$, $i_0$) is quantified. Electrochemical quartz crystal microgravimetry (e-QCM) is employed to demonstrate PEI adsorption on the electrode surface during Zn electrodeposition. Anodic stripping coulometry and hydrogen evolution polarization measurements provide the Zn electrodeposition current efficiency in the presence and absence of PEI.

In Chapter 4, PEI injection studies using a RDE are conducted to characterize the diffusion and adsorption properties of PEI during Zn electrodeposition. The transient response of the surface potential upon PEI injection is measured and compared to predictions of the transient PEI surface coverage evolution modeled using diffusion-adsorption theory. This leads to determination of the PEI diffusion coefficient ($D_{PEI}$) and an estimate of the PEI adsorption rate constant ($k_{ads}$).
CHAPTER 2. Polyethylenimine Additive to Suppress Dendrite Growth during Zinc Electrodeposition

As discussed in the introduction, a key issue preventing wide-scale implementation of Zn rechargeable batteries is the evolution of dendritic Zn electrodeposit morphology at the battery anode during the battery charging process. In this chapter, polyethylenimine (PEI) is used as an additive to suppress Zn dendrites during Zn electrodeposition from an alkaline electrolyte. This work is motivated by the fact that PEI is a widely studied polarizer during copper (Cu) electrodeposition\textsuperscript{48–49} and is also stable in alkaline media.\textsuperscript{50–51} In this chapter, it is shown, using a combination of electrochemical and surface microscopy techniques that PEI effectively suppresses the formation of Zn dendrites.

Since the 1970s, numerous efforts have focused on characterizing and suppressing roughness and dendrite evolution during Zn electrodeposition through the use of ppm-levels of additives in the plating electrolyte.\textsuperscript{10,26–32} Several studies reporting the use of additives to control the Zn deposit quality and appearance have also been published. These studies include additives such as polyvinyl alcohols,\textsuperscript{33–34} polyamines,\textsuperscript{35} and carbonyl compounds.\textsuperscript{36} Bass \textit{et al.} documented additives relevant to alkaline Zn battery applications,\textsuperscript{37} including surfactants, ammonium salts, lead ions (Pb\textsuperscript{2+}), bismuth compounds, and metal oxides.\textsuperscript{38–47} While several promising additive candidates have been identified in prior studies, an in-depth characterization and systematic study of the mechanism through which these additives suppress Zn dendrite formation is still lacking.

In this chapter, \textit{in situ} optical microscopy is used to monitor the growth of Zn dendrites and characterize the dendrite suppression efficacy of PEI as a function of the
PEI concentration in the electrolyte. Dendrite suppression is demonstrated under both potentiostatic and galvanostatic Zn electrodeposition conditions. Scanning electron microscopy images illustrate distinct differences in the electrodeposit surface morphology when PEI is added to the electrolyte. Surface profilometry is used to evaluate the electrodeposit roughness and to quantify the roughness-suppression ability of PEI. Galvanostatic deposition-dissolution tests are used to demonstrate the efficacy of PEI in suppressing roughness under cycling conditions.

2.1 Experimental Procedure

2.1.1 Materials

Electrodeposition of Zn was studied from an aqueous solution of zinc oxide (ZnO) and potassium hydroxide (KOH). Both chemicals were procured from Fisher Scientific. The branched additive polyethylenimine (PEI) was purchased from Sigma-Aldrich. Average PEI molecular weight (M.W.) was 800 g/mol. Millipore-spec (18.2 MΩ) deionized water was used to prepare all electrolytes. Prior to each experiment, argon (Ar) gas was bubbled through the electrolyte for ~1 hr to remove dissolved oxygen.

2.1.2 Methods

A National 410 stereo microscope enabled live observation of dendrite evolution during Zn electrodeposition. The three-electrode setup consisted of a Petri dish containing the electrolyte (0.1 M ZnO + 4.0 M KOH with varying levels of PEI). A 1 mm diameter Zn wire (99.95% purity, purchased from Alfa-Aesar) was used as the counter electrode (CE). A mercury/mercury oxide electrode (Hg|HgO) filled with 4.0 M KOH
(from Koslow Scientific) served as the reference electrode (RE, $E_{Hg/HgO} = +0.098$ V vs. SHE). The working electrode was a 1 mm diameter Zn wire, coated with Loctite underwater repair epoxy. Zn electrodeposition was performed at the exposed tip of the wire electrode with an active surface area of 0.008 cm$^2$. Prior to each experiment, the wire electrode tip was sanded with 1000 grit sand paper, then mechanically hand-polished using 5 µm alumina slurry on a nylon polishing pad (Pine Research Instrumentation). A schematic and photograph of the setup are shown in Figure 2.1 and Figure 2.2, respectively.

**Figure 2.1.** Schematic of optical microscopy setup used for *in situ* dendrite tracking during Zn electrodeposition. Setup is comprised of a 5 cm diameter glass cell positioned below an optical microscope with digital camera for imaging. Working electrode (WE) = 1 mm diameter Zn wire coated with Loctite underwater repair epoxy; Counter electrode (CE) = 1 mm diameter Zn wire; reference electrode (RE) = Hg/HgO filled with 4.0 M KOH.
Deposit characteristics were also analyzed ex situ using electron microscopy and surface profilometry. Scanning electron microscopy (SEM) using FEI Helios Nanolab 650 provided high-resolution ex situ imaging of the Zn electrodeposits. A KLA-Tencor P-6 Stylus Profiler was used to conduct contact-mode surface profilometry of the electrodeposited Zn to quantify roughness. Profilometry scan length was 500 µm, and scan was taken at the center of the working electrode with a scan rate of 5 µm/s and a data acquisition rate of 1000 Hz. A Solartron model 1287A potentiostat/galvanostat with automated data acquisition was used for all electrochemical measurements.

### 2.2 Zinc Dendrite Suppression Evaluated under Potentiostatic Conditions

#### 2.2.1 Dendrite Suppression as a Function of PEI Concentration

In this section, Zn dendrite suppression efficacy of PEI is reported as a function of the PEI concentration in the electrolyte. First, dendritic Zn deposits were obtained by
electrodeposition onto the epoxy-coated Zn wire electrode from the additive-free electrolyte (0.1 M ZnO + 4.0 M KOH) at an applied potential of –1.57 V (vs. Hg|HgO reference). This potential was selected after conducting linear sweep voltammetry (LSV) on the wire electrode and determining that –1.57 V (vs. Hg|HgO) provides mass-transport limited electrodeposition on the wire electrode. Under these conditions, dendritic morphology evolution is anticipated. Figure 2.3 shows LSV at 5 mV/s scan rate. As the potential becomes increasingly negative, the current density continues to increase until it levels off at around –12.5 mA/cm². This value of the current corresponds to the system limiting current density (i_L), shown as dashed red line. Accordingly, –1.57 V (vs. Hg|HgO) was selected for Zn dendrite growth studies (shown as dashed black line). As is also seen in Figure 2.3, potentials cathodic with respect to –1.6 V (vs. Hg|HgO) should be avoided as these potentials cause excessive hydrogen co-evolution.
Figure 2.3. Linear sweep voltammogram on a Zn wire electrode illustrating limiting current conditions (as represented via dashed red line) at $\sim -12.5$ mA/cm$^2$. Dashed black line at $-1.57$ V vs. Hg|HgO shows potential at which dendrite growth studies were conducted. At potentials cathodic to $-1.6$ V vs. Hg|HgO, an increase in current density beyond $-12.5$ mA/cm$^2$ is likely due to hydrogen co-evolution. Electrolyte contains 0.1 M ZnO + 4.0 M KOH.

As shown in Figure 2.4, Zn dendrites form on the wire electrode and propagate with time when Zn is electrodeposited potentiostatically at $-1.57$ V (vs Hg|HgO). The microscopy setup enabled ‘live’ tracking of the evolution of dendrite height (as shown in the optical images of Figure 2.4), and chronoamperometry enabled indirect quantification of the electrochemically active surface area (as shown by the increase in the magnitude of the measured current with time in Figure 2.4). The optical images shown in Figure 2.4 correspond to various times: $t_0 = 0$, $t_1 = 600$ s, $t_2 = 1200$ s, and $t_3 = 1800$ s as labeled on the chronoamperometry plot. The four-fold increase in current at time $t_3$ (compared to $t_0$)
is attributed to the increase in the electrode surface area caused by dendritic morphology evolution. [Note that the sign convention used in this thesis denotes cathodic currents and overpotentials as negative. Thus, a current change from –0.1 mA to –0.4 mA is recognized as an increase in cathodic current.] The dendrite tip propagation rate can be estimated from Figure 2.4. In 1800 s, the tip grows to a height of ~600 µm. Faraday’s law (Eq. 2.1) can then be used to convert dendrite height, $h$, reached over a given time, $t$, to a current density at the dendrite tip, $i_{tip}$:

$$\frac{h}{t} = \frac{M i_{tip}}{nF \rho}$$

[2.1]

where $M$ is the molecular weight of Zn (65.38 g/mol), $n$ is the number of electrons transferred ($n = 2$) during the electrodeposition reaction, $F$ is Faraday’s constant (96485 Cb/mol), and $\rho$ is the density of Zn (7.14 g/cm$^3$). Calculating the dendrite tip current density results in a value of about –0.7 A/cm$^2$, which is typical of activation-controlled growth of Zn dendrite tips. As discussed in the introduction section, the Zn dendrites of Figure 2.4 initiate and propagate because local micro-scale roughness elements present on the electrode surface are released from mass-transport (diffusion) limitations and thereby grow purely under activation control at large current densities in the A/cm$^2$ range.
Figure 2.4. Tracking the Zn dendrite growth on a wire electrode using optical microscopy (left), and corresponding chronoamperometry (right) indicating surface area increase due to dendritic morphology evolution. Zn is electrodeposited potentiostatically at $-1.57 \text{ V vs. Hg|HgO}$ on a Zn wire electrode for a period of 1800 s. Electrolyte contains 0.1 M ZnO + 4.0 M KOH.$^{53}$

It is worthwhile to note that, at long deposition times (>1000 s), the Zn dendrite length (on the order of 100–1000 μm, as seen in Figure 2.4) is significantly larger than the typical diffusion boundary layer thickness ($\delta$ on the order of 10–100 μm).$^{12}$

In spite of micro-scale non-uniformities of the current distribution that lead to Zn dendrite formation (Figure 2.4), the overall macro-scale current distribution during the very early stages of Zn deposition on the wire electrode is expected to be fairly uniform. A parameter used to assess the latter macro-scale uniformity is the Wagner number,$^{54}$ which describes the secondary current distribution uniformity, i.e., when surface activation and electrolyte resistances are dominant. The Wagner number ($Wa$) relates to the ratio of the activation resistance ($R_a$) to the ohmic resistance ($R_\Omega$) of the electrolyte, as defined in Eq. 2.2.
\[ \text{Wa} = \frac{R_a}{R_{\text{eff}}} = \frac{R T \kappa}{\alpha_c F i_{\text{avg}} l} \]  

where \( R \) is the universal gas constant, \( T \) is the temperature, \( \kappa \) is the electrolyte conductivity, \( \alpha_c \) is the cathodic charge transfer coefficient, \( F \) is Faraday’s constant, \( i_{\text{avg}} \) is average current density on the electrode, and \( l \) is the characteristic length of the electrode (in Figure 2.4, \( l \) is of the order of magnitude of the wire diameter)\(^5\). \( \text{Wa} < 0.2 \) indicates a highly non-uniform current distribution, whereas \( \text{Wa} > 5 \) indicates a highly uniform current distribution. Assuming electrolyte conductivity of 570 mS/cm (Ref. 56) and \( \alpha_c = 1.76 \) (determined later in section 3.2), Zn plating on the wire electrode at \(-12.5 \text{ mA/cm}^2\) results in \( \text{Wa} = 6.7 \). Thus, it can be concluded that the macro-scale current distribution on the wire electrode is highly uniform.

Figure 2.5 shows the effect of PEI concentration on Zn dendrite suppression. With the addition of 10 ppm PEI to the electrolyte (Figure 2.5 (b)), Zn dendrite growth was significantly suppressed (compared to the additive-free case in Figure 2.5 (a)) with only a few small dendrites appearing after 30 min of Zn plating. In Figure 2.5 (b), it is evident that dendrites are concentrated near the bottom edge of the wire electrode. Given the high \( \text{Wa} \) number (as computed above), this non-uniformity is likely due to non-uniform transport effects which are not captured by scaling analysis using the Wagner number.

At PEI concentration of 50 ppm or greater (Figure 2.5 (c) or (d)), dendrite growth was completely eliminated and bright Zn electrodeposits were produced that were \( \sim 10 \mu\text{m} \) in thickness. These observations demonstrate the concentration-dependent dendrite suppression efficacy of PEI. In comparison to previous work on suppressing dendrite
formation in acid Zn plating using 1000–10000 ppm polyethylene glycol (PEG) additive,\textsuperscript{14} PEI produces substantial dendrite suppression in the alkaline Zn system at a bulk concentration of merely 50–100 ppm.

Figure 2.5. \textit{In situ} optical microscopy of a Zn wire electrode after potentiostatic Zn electrodeposition at \(-1.57 \, \text{V vs. Hg|HgO}\) for 30 min. Electrolyte contains 0.1 M ZnO + 4.0 M KOH with various concentrations of PEI: 0 ppm (a), 10 ppm (b), 50 ppm (c), and 100 ppm (d). At a PEI concentration of 50 ppm or higher, dendritic growth during Zn plating is eliminated.\textsuperscript{53}

Figure 2.6 shows chronoamperometry plots corresponding to the optical microscopy images of Figure 2.5. At short times \((t < 250 \, \text{s})\), a pseudo steady-state current of about \(-0.1 \, \text{mA}\) is reached at the applied potential of \(-1.57 \, \text{V (vs. Hg|HgO)}\), independent of the PEI concentration in the electrolyte. This current corresponds to Zn deposition under diffusion limitations, because it translates to a current density of \(-12.5 \, \text{mA/cm}^2\) and thus very close to the limiting current density on the wire electrode. During this short time period, no visible dendritic morphology evolution is seen during \textit{in situ}
optical microscopy inspections of the wire electrode. After $t > 250$ s, the current gradually rises in magnitude for the case of additive-free Zn electrodeposition due to dendritic morphology evolution (see also Figure 2.4 and associated text). In contrast to the additive-free electrolyte, the current increases only slightly with time in the presence of 10 ppm PEI. Moreover, at PEI concentrations of 50 and 100 ppm in the electrolyte, the current remains fairly constant, (close to the mass-transport limit), indicating no surface-area increase, i.e., complete elimination of dendritic growth. Chronoamperometry (Figure 2.6) complements the optical microscopy images (Figure 2.5), validating the functionality of PEI as a dendrite suppressor in alkaline Zn plating.

Figure 2.6. Chronoamperometry during potentiostatic Zn plating on the wire electrode (shown in Figure 2.5) at $-1.57$ V vs. Hg|HgO. Electrolyte contains 0.1 M ZnO + 4.0 M KOH with various concentrations of PEI additive.53
In addition to optically tracking the macro-scale growth of Zn electrodeposits, the micro-scale dendrite morphology were examined more closely using scanning electron microscopy (SEM). SEM images (Figure 2.7) show high-resolution Zn dendritic structure obtained from 0.1 M ZnO + 4.0 M KOH electrolyte (Figure 2.7 (a)) and that from a 10 ppm PEI-containing electrolyte (Figure 2.7 (b)). As seen in Figure 2.7 (a), the dendrites formed in an additive-free electrolyte have a characteristic fern-like structure, similar to that reported by Wranglén for lead (Pb) dendrites\textsuperscript{57} and more recently by Lopez and Choi for Zn dendrites.\textsuperscript{58} Dendrites formed in the 10 ppm PEI-containing electrolyte showed nodular and rounded dendrite tips (Figure 2.7 (b)). The transition from sharp-tip morphology (in the absence of PEI) to a rounded-tip morphology (in the presence of PEI) may be attributed to the modulation of the local current distribution near the tip due to PEI adsorption, which increases the surface polarization and results in a more uniform current distribution.\textsuperscript{59–60}

![Figure 2.7](image-url)  
**Figure 2.7.** SEM images of Zn dendrites electrodeposited from an additive-free electrolyte (a) and from an electrolyte containing 10 ppm PEI (b). Electrolyte contains 0.1 M ZnO + 4.0 M KOH.\textsuperscript{53}
2.2.2 PEI Injection to Retard Dendrite Growth

In section 2.2.1, the role of PEI in suppressing Zn dendrite growth was demonstrated when starting with a relatively smooth and flat electrode surface. In this section, the transient effect of adding PEI to the electrolyte when using a pre-formed dendritic substrate is reported.

For this study, Zn dendrite evolution during electrodeposition onto a wire electrode was tracked using \textit{in situ} optical microscopy (same as in Figure 2.4 and Figure 2.5) from the additive-free electrolyte. After electrodepositing Zn for 1000 s at an applied potential of $-1.57 \text{ V}$ (vs. Hg|HgO), the Zn surface evolved into the fern-like dendritic morphology classical of high-rate Zn electrodeposition (Figure 2.8 (a) and (c)). In one experiment, no additive was injected into the electrolyte and dendrite evolution was tracked for another 800 s (Figure 2.8 (b)). In another experiment, 100 ppm PEI was injected at $t = 1000 \text{ s}$, and the dendrite evolution was tracked (Figure 2.8 (d)). In both experiments, chronoamperometry provided time-dependent surface area tracking. In the optical images of Figure 2.8 (a) and (b), an increasingly large mass of fern-like dendrites is observed to grow over time, consistent with the gradual rise in total current. On the contrast, when 100 ppm PEI is injected at $t = 1000 \text{ s}$, the dendritic growth and associated surface area increase are instantly halted (Figure 2.8 (c) and (d)). Pre-formed dendrites (\textit{i.e.}, dendrites formed prior to PEI injection) show no further tip growth after PEI injection. Moreover, the gradual rise in current (before PEI injection) is transformed into a steady, time-invariant current after PEI injection, confirming that PEI suppresses Zn dendrite propagation.
Figure 2.8. Optical microscopy and chronoamperometry during a PEI injection experiment. Zn was electrodeposited onto a wire electrode at $-1.57 \text{ V}$ (vs. Hg|HgO) from additive-free electrolyte ($0.1 \text{ M ZnO} + 4.0 \text{ M KOH}$). At $t = 1000 \text{ s}$, the electrode showed substantial Zn dendrite growth ((a), (c)). The red curve corresponds to injection of 100 ppm PEI after 1000 s of plating (whereas the blue curve received no additive injection). After 800 s of additional plating following the PEI injection, no further dendrite propagation was observed (d), and the total current remained nearly constant indicating no surface area increase.\textsuperscript{53}
Close inspection of Figure 2.8 (d) reveals that while Zn electrodeposition continues after PEI injection, the deposit growth is uniform, spreading over the entire dendrite surface rather than concentrating at the tips. This produces thicker dendrites with more rounded tips, while the overall dendrite length remains relatively unchanged.

2.3 Zinc Dendrite Suppression Evaluated under Galvanostatic Conditions

2.3.1 Effect of PEI during Galvanostatic Zinc Electrodeposition

In section 2.2, Zn dendrite suppression using PEI additive was characterized under potentiostatic Zn electrodeposition conditions. However, for applications in rechargeable Zn-metal batteries, galvanostatic electrodeposition is more relevant because rechargeable batteries predominantly use constant-current charging mode. Accordingly, in this section, the effect of PEI on dendrite growth and roughness evolution during galvanostatic Zn electrodeposition is characterized using the wire-electrode setup described earlier in Figure 2.4 and Figure 2.5).

A Zn electrodeposit was obtained by plating onto a wire electrode from 0.1 M ZnO + 4.0 M KOH at a constant current of –0.1 mA for 40 min. This current corresponds approximately to the limiting current density on the flat wire electrode (–12.5 mA/cm²) at which dendritic morphology is expected to develop. After 40 min of electrodeposition, the electrode was removed from the electrolyte, quickly rinsed in deionized water, thoroughly dried, and stored under vacuum awaiting SEM characterization. This experiment was then repeated on a separate wire electrode in an electrolyte containing 0.1 M ZnO + 4.0 M KOH with 100 ppm PEI. Both samples were
characterized using scanning electron microscopy. SEM images (Figure 2.9) reveal the surface morphology of Zn electrodeposits obtained from 0.1 M ZnO + 4.0 M KOH electrolyte (Figure 2.9 (a)) and that from a 100 ppm PEI-containing electrolyte (Figure 2.9 (b)). As seen, the electrodeposits formed in an additive-free electrolyte (Figure 2.9 (a)) is visibly rough. On the other hand, electrodeposits formed in the 100 ppm PEI-containing electrolyte (Figure 2.9 (b)) are substantially smoother with minimal surface protrusions. This conclusively establishes that PEI suppresses roughness evolution during Zn electrodeposition under galvanostatic conditions.

![Figure 2.9](image.png)

**Figure 2.9.** SEM images of a rough Zn film electrodeposited from an additive-free electrolyte (a) and a smooth Zn film electrodeposited from an electrolyte containing 100 ppm PEI (b). Base electrolyte contains 0.1 M ZnO + 4.0 M KOH. Deposition was performed at –0.1 mA for 40 min. Electrode area is 0.008 cm².

After imaging via SEM, the Zn electrodeposits from Figure 2.9 were analyzed using contact-mode surface profilometry. Raw profilometry data was post-processed to remove artifacts such as those introduced due to slight substrate tilt with respect to the profilometer stage. A 500 µm long profilometry scan was obtained. Surface profilometry
data are shown in Figure 2.10, confirming that the Zn deposit obtained from an additive-free electrolyte (Figure 2.10 (a)) is significantly rougher than that obtained from an electrolyte containing 100 ppm of PEI (Figure 2.10 (b)).

**Figure 2.10.** Contact-mode surface profilometry measurements of Zn electrodeposits galvanostatically plated on a wire electrode from an additive-free electrolyte (panel (a) in blue) and from an electrolyte containing 100 ppm PEI (panel (b) in red). Base electrolyte contains 0.1 M ZnO + 4.0 M KOH.

To quantify the electrodeposit roughness of the two samples in Figure 2.10, their root mean square roughness ($R_{\text{rms}}$) was calculated using Eq. 2.3.

$$R_{\text{rms}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \left( y_i - y_{\text{avg}} \right)^2} \quad [2.3]$$

where $n = \text{number of surface height measurements}$, $y_i$ is the value of each height measurement, and $y_{\text{avg}}$ is the average of all $y_i$. $R_{\text{rms}}$ values for each sample are reported in Table 2.1. Roughness was suppressed by an order of magnitude with the addition of 100
ppm PEI to the electrolyte, consistent with the qualitative observations made in the SEM data of Figure 2.9.

Table 2.1. RMS roughness of Zn electrodeposits obtained in the presence or absence of PEI additive. Base electrolyte contains 0.1 M ZnO + 4.0 M KOH. Galvanostatic plating was performed at –0.1 mA for 40 min. Electrode area = 0.008 cm².

<table>
<thead>
<tr>
<th>PEI Concentration (ppm)</th>
<th>RMS roughness ($R_{rms}$, µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.02</td>
</tr>
<tr>
<td>100</td>
<td>0.36</td>
</tr>
</tbody>
</table>

2.3.2 Effect of PEI on Multiple Zinc Deposition-Dissolution Cycles

For rechargeable battery applications, it is essential to characterize the effect of PEI additive on Zn deposition (i.e., charging) as well as Zn dissolution (i.e., discharging). Thus, electrode polarization was measured on a wire electrode ($A = 0.008$ cm²) during Zn electrodeposition at an average current density of –10 mA/cm² for 28 min followed by Zn stripping at +10 mA/cm² for 28 min. This sequence of deposition followed by dissolution constituted one cycle. The electrode potential response over 5 deposition-dissolution cycles is shown in Figure 2.11. It is observed that 100 ppm PEI polarizes the electrode surface during deposition as well as during dissolution. In a battery, polarization due to PEI during Zn deposition and Zn dissolution will manifest as voltaic efficiency loss. After various numbers of cycles (using the waveform described in Figure 2.11), the surface roughness of the wire electrode was measured using profilometry, and the RMS roughness was quantified using Eq. 2.3.
Figure 2.11. Applied current waveform (top) and measured electrode potential response (bottom) during galvanostatic Zn deposition-dissolution cycles on a wire electrode. Zn was electrodeposited at –0.08 mA for 28 min, then stripped at +0.08 mA for 28 min. Electrode area = 0.008 cm². Electrolyte contains 0.1 M ZnO + 4.0 M KOH with (red) or without (blue) PEI additive. 100 ppm PEI polarizes the Zn electrode during deposition as well as during dissolution.

Shown in Figure 2.12 are RMS roughness values for wire electrodes analyzed after various deposition-dissolution cycles. Electrodeposits from additive-free electrolyte are shown in blue, and electrodeposits from 100 ppm PEI-containing electrolyte are shown in red. The trend observed in Figure 2.12 demonstrates that the additive PEI suppresses roughness evolution after Zn deposition-dissolution cycling.
2.4 Conclusions

In this chapter, the polymeric additive PEI was shown to effectively suppress dendritic morphology evolution during Zn electrodeposition from alkaline electrolytes. Over a concentration range of 10–100 ppm, PEI substantially suppresses dendrite formation and roughness evolution. The degree of dendrite suppression depends on the PEI concentration. Dendrite suppression is more effective at higher PEI concentrations. Optical microscopy and scanning electron microscopy were used to confirm dendrite and roughness suppression attributes of PEI, and surface profilometry provided quantitative
roughness suppression metrics. PEI effectively suppressed roughness evolution during electrode cycling (deposition-dissolution) as necessitated for application in rechargeable alkaline Zn-air batteries.
CHAPTER 3. Characterizing the Effect of Polyethylenimine on Zinc Electrodeposition Kinetics and Current Efficiency

In the previous chapter, it was demonstrated that the electrolyte additive polyethylenimine (PEI) effectively suppresses dendrite growth during Zn electrodeposition from an alkaline electrolyte. In this chapter, polarization measurements during Zn electrodeposition on a rotating disk electrode (RDE) are reported, which aid in characterizing the role of PEI on the Zn electrodeposition kinetics. It is shown that PEI suppresses Zn electrodeposition kinetics by adsorbing onto the Zn electrode surface. In addition, the effect of PEI on current efficiency during Zn electrodeposition is reported.

Diggle et al. developed the model of activation-controlled dendrite propagation for Zn electrodeposition from an alkaline zincate electrolyte.\textsuperscript{12} In Appendix A, this model is employed to correlate additive-assisted Zn dendrite suppression in acidic electrolytes to changes in the Zn electrodeposition kinetic parameters.\textsuperscript{14} For activation-controlled dendrite growth, it follows that an additive that adsorbs on the Zn electrode surface and lowers the exchange current density ($i_0$) associated with Zn electrodeposition also retards deposition at dendrite tips. Under potentiostatic conditions, this effect leads to dendrite suppression. In addition to dendrite and roughness suppression, electrolyte additives such as weak acids,\textsuperscript{61} surfactants,\textsuperscript{62} organics,\textsuperscript{63} and metal oxides\textsuperscript{64} may suppress hydrogen co-evolution during Zn electrodeposition.

In this chapter, polarization measurements during Zn electrodeposition on a RDE are reported. The effect of PEI concentration on the kinetic parameters associated with Zn electrodeposition ($\alpha_c$, $i_0$) from 0.1 M ZnO + 4.0 M KOH electrolyte is quantified. Electrochemical quartz crystal micro-gravimetry (e-QCM) is employed to demonstrate
PEI adsorption on the electrode surface during Zn electrodeposition. Anodic stripping coulometry and hydrogen evolution polarization measurements provide the Zn electrodeposition current efficiency in the presence and absence of PEI.

3.1 Experimental Procedure

3.1.1 Materials

Electrodeposition of Zn was studied from an aqueous solution of 0.1 M ZnO and 4.0 M KOH. Both chemicals were procured from Fisher Scientific. Polarization studies of hydrogen evolution were conducted in 4.0 M KOH (in the absence of dissolved ZnO). The branched additive polyethylenimine (PEI) was purchased from Sigma-Aldrich. Average PEI molecular weight (M.W.) was 800 g/mol. Millipore-spec (18.2 MΩ) deionized water was used to prepare all electrolytes. Prior to each experiment, argon (Ar) gas was bubbled through the electrolyte for ~1 hr to remove dissolved oxygen.

3.1.2 Methods

Polarization studies.— To study the effect of PEI on Zn electrodeposition, experiments were performed on a 0.5 cm diameter platinum (Pt) rotating disk electrode (RDE, Pine Research Instrumentation). The Pt RDE was galvanostatically pre-plated with ~1 μm thick layer of Zn at –10 mA/cm² from an additive-free electrolyte (0.1 M ZnO + 4.0 M KOH) prior to each experiment. The Zn pre-plated RDE was submerged to a depth of ~0.5 cm in a 250 mL electrolyte and the RDE rotation speed was set to 1000 rpm. A 1 mm diameter Zn wire (99.95% purity, purchased from Alfa-Aesar) was used as the counter electrode (CE). A mercury/mercury oxide electrode (Hg|HgO, Koslow Scientific)
containing 4.0 M KOH served as the reference electrode (RE). The electrochemical cell is shown in Figure 3.1. A Solartron model 1287A potentiostat/galvanostat with automated data acquisition was used for electrochemical measurements.

![Diagram of electrochemical cell with labels: WE (Zn RDE), RE (Hg|HgO), CE (Zn wire), 5 cm, 10 cm.]

**Figure 3.1.** Schematic (left) and photograph (right) of RDE setup used to study the effect of PEI on Zn electrodeposition kinetics. Electrolyte contained 0.1 M ZnO + 4.0 M KOH. Counter electrode (CE) is a coiled Zn wire, working electrode (WE) is a Zn-plated RDE, and reference electrode (RE) is a Hg|HgO electrode with 4.0 M KOH.

*Electrochemical quartz crystal microbalance studies.*— PEI adsorption onto the electrode surface during Zn electrodeposition was studied using a Stanford Research Systems QCM-200 quartz crystal microbalance. The QCM used 5 MHz AT-cut gold-coated quartz crystals from Fil-Tec. Prior to each experiment, the gold crystal was gently rinsed in ethanol followed by deionized water rinse, and then dried under N$_2$. The crystal was then galvanostatically pre-plated with a uniform layer of Zn (~250 nm thick) at −10 mA/cm$^2$ from an additive-free electrolyte (0.1 M ZnO + 4.0 M KOH) under moderate agitation. Various quantities of PEI were injected into the electrolyte and the QCM frequency
response during Zn electrodeposition was recorded. The e-QCM setup used is shown in Figure 3.2. Electrolyte volume was about 500 mL. A Princeton Applied Research VersaSTAT-4 potentiostat/galvanostat was used for e-QCM studies.

**Figure 3.2.** Quartz crystal microbalance setup consisting of 500 mL of 0.1 M ZnO + 4.0 M KOH electrolyte in 12 cm diameter glass cell with gentle agitation provided by a stir bar. Ar gas was continually bubbled through the electrolyte. WE is Au-coated QCM crystal with a thin layer of Zn pre-plated onto the Au. CE is Pt wire and RE is Hg|HgO.

*Current efficiency measurements.*— The effect of PEI on the current efficiency during Zn electrodeposition was studied using galvanostatic plating followed by anodic stripping coulometry on a Pt RDE rotated at 2000 rpm. In a typical experiment, Zn was first galvanostatically plated onto the Pt RDE (at –20 mA/cm²) and then anodically stripped. The measured stripping charge provided the current efficiency, as discussed below.

Current efficiency values were also obtained by performing polarization measurements on the hydrogen evolution reaction in the presence and absence of PEI. Polarization curves for hydrogen evolution were obtained on a Zn RDE. The Zn RDE
surface was polished using 1000 grit sand paper to remove surface oxides, followed by a polishing sequence that used 5 µm, 0.3 µm, and 0.05 µm alumina slurries to produce a mirror finish. Hydrogen evolution polarization experiments used Pt wire in an isolation tube as counter electrode and Hg/HgO electrode with 4.0 M KOH as reference electrode.

3.2 Polarization Studies of the Effect of PEI on Zn Electrodeposition Kinetics

The effect of PEI on Zn electrodeposition kinetics was characterized via electrochemical polarization studies on a Zn pre-plated RDE. For each polarization measurement, a constant current ($I$) was applied and the electrode potential ($V_{app}$) was monitored until it reached a steady, time-invariant value. For each electrolyte composition, this procedure was repeated for various average current densities ($i = I/A$, where $A$ is the electrode area) in the range $-2$ to $-24$ mA/cm$^2$. This current density range corresponds to a Wagner number (as discussed in section 2.2.1 of Chapter 2), $Wa = 1.4–5.0$, indicating moderate to highly uniform current distribution on the RDE. PEI concentration in the electrolyte was varied between 0–100 ppm.

Figure 3.3 shows polarization curves for Zn electrodeposition from a 0.1 M ZnO + 4.0 M KOH electrolyte containing various concentrations of PEI. Activation polarization ($\eta_a$) was obtained from the measured electrode potential ($V_{app}$) by subtracting the ohmic overpotential ($\eta_\Omega$), the concentration overpotential ($\eta_c$), and the thermodynamic Zn reduction potential ($E_{Zn}$) as shown in Eq. 3.1.

$$\eta_a = V_{app} - \eta_\Omega - \eta_c - E_{Zn} \quad [3.1]$$
Newman’s formula\textsuperscript{65} for ohmic resistance of a disk electrode was used for determining \( \eta_\Omega \). For a RDE of radius, \( r \), the ohmic overpotential is:

\[
\eta_\Omega = \frac{\pi}{4} \frac{ir}{\kappa}
\]  \[3.2\]

where \( \kappa \) is the electrolyte conductivity. For 0.1 M ZnO + 4.0 M KOH, \( \kappa = 570 \text{ mS/cm}\textsuperscript{56} \). The calculation of the concentration overpotential requires knowledge of the magnitude of the diffusion-limited current density, which was determined using the Levich Equation,\textsuperscript{66} shown in Eq. 3.3.

\[
i_L = 0.62 nF D^{2/3} \omega^{1/2} \nu^{-1/6} C
\]  \[3.3\]

where \( D \) is the diffusion coefficient (\( D = 4.9 \times 10^{-6} \text{ cm}^2/\text{s}, \) typical for the zincate ion),\textsuperscript{67–68} \( \omega \) is the angular rotation rate, \( \nu \) is the kinematic viscosity (\( \nu = 0.0124 \text{ cm}^2/\text{s}, \)\textsuperscript{69–70} and \( C \) is the zincate ion concentration (0.1 M). At RDE rotation speed of 1000 rpm employed in polarization studies, the magnitude of the limiting current density (\( i_L \)) was determined to be 74 mA/cm\textsuperscript{2}. The concentration overpotential is calculated according to Eq. 3.4:

\[
\eta_c = \frac{RT}{nF} \ln \left( 1 - \frac{i}{i_L} \right)
\]  \[3.4\]
where $R$ is the universal gas constant (8.314 J/mol K), $T$ is the temperature (298 K), $n$ is the number of electrons transferred ($n = 2$), $F$ is Faraday’s constant (96485 Cb/mol), and $i_L$ is the limiting current (from Eq. 3.3).

Since polarization measurements were carried out in a high-conductivity alkaline electrolyte (large $\kappa$) away from mass-transport limitations ($i \ll i_L$), the contribution of the ohmic and the concentration overpotentials to the total overpotential was small. This also ensured minimal surface area change during polarization measurements. In the absence of Zn electrodeposition, the reduction potential ($E_{Zn}$) was measured, under open circuit conditions, to be close to $-1.36$ V vs. Hg|HgO.

From Figure 3.3, it is observed that the addition of PEI to the base electrolyte polarizes the Zn electrode. The polarization behavior of PEI during Zn electrodeposition is analogous to the electrode polarization provided by polymeric additives during Cu electrodeposition.\textsuperscript{71–72} The extent of electrode polarization increases with PEI concentration. At a current density of $-10$ mA/cm$^2$, 10 ppm PEI provides a $-70$ mV increase in the magnitude of the activation overpotential compared to the additive-free electrolyte. However, the extent of electrode polarization saturates at higher PEI concentrations with 50 ppm and 100 ppm PEI providing almost the same magnitude of polarization. This saturation behavior has been observed in other additives-assisted electrodeposition systems,\textsuperscript{71} and may be explained in the framework of the Langmuir-adsorption isotherm. This is discussed in detail in section 4.2 of Chapter 4.
The dependence of the electrodeposition rate (current density, $i$) on the driving force (activation overpotential, $\eta_a$) is given by the Butler-Volmer Equation, shown in Eq. 3.5:

$$i = i_0 \left\{ \exp \left( \frac{\alpha_a F}{RT} \eta_a \right) - \exp \left( -\frac{\alpha_c F}{RT} \eta_a \right) \right\}$$  \[3.5\]

where $\alpha_a$, $\alpha_c$, and $i_0$ represent the anodic charge transfer coefficient, cathodic charge transfer coefficient, and the exchange current density, respectively.
At large cathodic overpotentials, electrodeposition kinetics are governed by the Tafel approximation to the Butler-Volmer equation, shown in Eq. 3.6:

\[ i = -i_0 \exp \left( \frac{-\alpha_c F \eta_a}{RT} \right) \]  

[3.6]

Eq. 3.6 can be rearranged as shown in Eq. 3.7:

\[ \ln \left( \frac{|i|}{i_0} \right) = \frac{RT}{\alpha_c F} |\eta_a| - \ln (i_0) \]  

[3.7]

Data from Figure 3.3 are plotted as \( \ln(|i|) \) vs. \( |\eta_a| \) (Tafel plot) in Figure 3.4 below. Figure 3.4 shows that the slope of the \( \ln(|i|) \) vs. \( |\eta_a| \) curve essentially remains unaltered for all concentrations of PEI tested in the range 0–100 ppm. Since the slope is related to the cathodic charge transfer coefficient (\( \alpha_c \)), the constant slope suggests that PEI has minimal effect on \( \alpha_c \) associated with Zn electrodeposition. From Figure 3.4, \( \alpha_c \) was determined to be 1.76. The solid lines shown in Figure 3.4 are drawn with a slope that corresponds to this best-fit value of \( \alpha_c \). While PEI does not affect the Tafel slope during Zn plating, it substantially alters the \( y \)-intercept of the \( \ln(|i|) \) vs. \( |\eta_a| \) curve. That is, it significantly lowers the exchange current density (\( i_0 \)) associated with Zn electrodeposition. Exchange current densities at various PEI concentrations were determined from the \( y \)-intercept of Figure 3.4 and are listed in Table 3.1.
Figure 3.4. Tafel plot for Zn electrodeposition (in the presence of 0–100 ppm of PEI) obtained on a Zn-coated Pt RDE at 1000 rpm. Plots show that PEI additive suppresses Zn electrodeposition kinetics by lowering the exchange current density (Table 3.1). PEI does not affect the Tafel slope (shown as solid lines over each polarization data set) during Zn plating.

<table>
<thead>
<tr>
<th>PEI Concentration (ppm)</th>
<th>Exchange Current Density ($i_0$, mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.01</td>
</tr>
<tr>
<td>10</td>
<td>0.027</td>
</tr>
<tr>
<td>50</td>
<td>0.0047</td>
</tr>
<tr>
<td>100</td>
<td>0.0031</td>
</tr>
</tbody>
</table>
It can be seen from Table 3.1 that the exchange current density is lowered by almost two orders of magnitude with the addition of 10 ppm PEI to the electrolyte. At a PEI concentration of 100 ppm, \( i_0 \) is reduced by three orders of magnitude compared to the additive-free case. The effect of PEI on \( i_0 \) (but not on \( \alpha_c \)) indicates that PEI most likely suppresses deposition kinetics through a surface site-blocking mechanism, \( i.e., \) PEI adsorbs on the electrode surface and lowers the vacant sites available for Zn electrodeposition.\(^71\) The extent of PEI surface coverage in turn depends on the bulk PEI concentration.\(^44-45\) The active (additive-free) surface area fraction available for Zn deposition is lowered in the presence of PEI, which manifests as a reduction in the apparent exchange current density associated with Zn electrodeposition. This effect is modeled in section 4.2 of Chapter 4.

### 3.3 E-QCM Studies of PEI Adsorption during Zn Electrodeposition

Electrochemical quartz crystal microgravimetry (e-QCM) provides valuable insights into additive adsorption on charged surfaces.\(^73-74\) PEI adsorption on the electrode surface during Zn electrodeposition was studied by injecting various concentrations of PEI into the electrolyte and measuring the e-QCM frequency response. The base electrolyte in the cell was 0.1 M ZnO + 4.0 M KOH. The QCM crystal surface was pre-coated with a Zn layer before use in QCM studies, as described in the experimental section 3.1 above. During e-QCM studies, Zn was galvanostatically electrodeposited onto the QCM crystal surface at an average plating current density of \( \sim 50 \, \mu A/cm^2 \). As a control, Figure 3.5 (a) shows the injection of blank electrolyte (\( i.e., \) electrolyte containing no PEI injected at \( t = 60 \, s \)) to ensure no interference of convective mixing with the QCM
As seen, the injection of blank electrolyte shows no response in the measured rate of the frequency change. Figure 3.5 (b) shows the injection of 10 ppm of PEI at \( t = 180 \) s. Before injection of PEI, the frequency decreases at the rate of \(-0.5 \) Hz/s, which corresponds to the applied current density of \(-50 \) µA/cm\(^2\). Within a few seconds after PEI injection, the frequency (\( \Delta f \)) drops sharply by about \(-15 \) Hz, then returns to the pre-injection slope of \(-0.5 \) Hz/s.

Assuming that PEI adsorbs rigidly on the electrode surface and is distributed uniformly across the surface, its mass may be estimated using the Sauerbrey Equation,\(^{75}\) shown in Eq. 3.8.

\[
\Delta m = \frac{\Delta f}{-56.6 \left( \text{Hz cm}^2 \mu\text{g}^{-1} \right)}
\]  

where the denominator on the right hand side of the equation represents the QCM sensitivity factor.\(^{54}\) The observed frequency shift (\( \Delta f_{\text{PEI}} = -15 \) Hz observed in Figure 3.5 (b)) corresponds to a PEI mass of about 265 ng/cm\(^2\). The frequency shift due to PEI adsorption on Zn is similar to that observed by Kelly and West\(^{74}\) when studying adsorption of polyethylene glycol (PEG) additive on Cu-coated QCM crystals. In the above discussion, the adsorbed PEI mass was estimated using Eq. 3.8; however, it should be noted that the Sauerbrey equation (Eq. 3.8) may introduce errors when estimating the mass of non-rigid polymers such as PEI.
Figure 3.5. Frequency response of an e-QCM to (a) blank electrolyte that does not contain PEI and (b) injection of 10 ppm PEI. E-QCM response suggests PEI adsorption during Zn electrodeposition corresponding to a frequency change of –15 Hz. Blank electrolyte injection was performed at $t = 60$ s; PEI injection was performed at $t = 180$ s, during galvanostatic Zn electrodeposition at an average plating current density of 50 $\mu$A/cm$^2$. Base electrolyte contains 0.1 M ZnO + 4.0 M KOH.\textsuperscript{53}
The magnitude of the e-QCM frequency change due to PEI adsorption (|Δf_{PEI}|) as a function of the bulk PEI concentration is shown in Figure 3.6. In the PEI concentration range 10–50 ppm, the PEI mass added to the electrode surface is nearly constant as indicated by a concentration-independent frequency change close to –15 Hz. This is again indicative of near-saturation surface concentration of PEI, which is unaltered by changes in the bulk PEI concentration in the 10–50 ppm range.

The e-QCM data (Figure 3.5 and Figure 3.6) provides direct evidence that PEI adsorbs on the Zn surface during electrodeposition. It is through this adsorption process that PEI affects the Zn electrodeposition kinetics.

![Figure 3.6](image)

**Figure 3.6.** Magnitude of the steady-state frequency change (measured from PEI injection experiments as shown in Figure 3.5 (b)) as a function of the bulk PEI concentration. Frequency change indicates that the PEI surface concentration is independent of the bulk PEI concentration in the 10–50 ppm range.53
3.4 Effect of PEI on Current Efficiency during Zn Electrodeposition

In this section, the effect of PEI on current (faradaic) efficiency during Zn electrodeposition is examined. High Zn electrodeposition current efficiencies are desirable during charging of batteries utilizing Zn anodes to maximize the battery round-trip energy efficiency. However, in aqueous electrolytes, Zn electrodeposition is accompanied by hydrogen co-evolution, which can lower the plating current efficiency. The two competing reactions are shown in Eq. 3.9 (Ref. 4) and Eq. 3.10 (Ref. 76), with reduction potentials adjusted for species concentrations (0.1 M ZnO, 4.0 M KOH, pH ≈ 14.7) via the Nernst Equation:

\[
\text{Zn(OH)}_{4}^{2-} (aq) + 2e^- \rightleftharpoons \text{Zn}^{0} (s) + 4\text{OH}^- (aq) \quad (E_{Zn} = -1.36 \text{ V vs. } \text{Hg}|\text{HgO}) \quad [3.9]
\]

\[
\text{H}_2\text{O}(l) + e^- \rightleftharpoons \frac{1}{2}\text{H}_2 (g) + \text{OH}^- (aq) \quad (E_{H} = -0.97 \text{ V vs. } \text{Hg}|\text{HgO}) \quad [3.10]
\]

While hydrogen evolution is thermodynamically favored during Zn electrodeposition, the kinetics of hydrogen evolution on Zn are quite sluggish. This is seen in Figure 3.7, which reports hydrogen evolution polarization curves in 1.0 M sulfuric acid on various substrates (data taken from Pourbaix\textsuperscript{76}). On Zn, the H\textsubscript{2} evolution reaction requires an overpotential of close to –1.0 V before appreciable reaction rates are achieved. While this data is for acidic electrolytes in the absence of electrolyte additives, hydrogen evolution polarization data for alkaline electrolytes in the presence of additive
PEI are not readily available. In the present study, polarization behavior of hydrogen evolution on Zn electrodes from alkaline electrolytes containing PEI is provided. This study aids in characterizing the effect of PEI on Zn electrodeposition current efficiency.

![Polarization curves for the hydrogen evolution reaction on various metal substrates from 1.0 M H₂SO₄. Data taken from Pourbaix.](image)

**Figure 3.7.** Polarization curves for the hydrogen evolution reaction on various metal substrates from 1.0 M H₂SO₄. Data taken from Pourbaix.⁷⁶

### 3.4.1 Effect of PEI on Current Efficiency of Zinc Electrodeposition Measured Using Anodic Stripping Coulometry

In this section, the effect of PEI on the current efficiency during Zn electrodeposition is characterized. Galvanostatic Zn plating followed by potentiostatic (anodic) stripping provides the Zn plating and stripping charge, the ratio of which provides a measure of the plating current efficiency.
The procedure used for anodic stripping coulometry is as follows. First, Zn was electrodeposited galvanostatically at –20 mA/cm² for 1055 s onto a freshly polished Pt RDE at 1000 rpm from an electrolyte containing 0.1 M ZnO + 4.0 M KOH. This current density is towards the upper limit of typical charge/discharge current densities used in practical Zn-air cells. Immediately following the Zn plating step, the electrode was held potentiostatically at –1.35 V vs. Hg|HgO, i.e., slightly positive with respect to the Zn reduction potential of –1.36 V, which provided anodic stripping of the plated Zn. The choice of the anodic stripping potential, i.e., –1.35 V, ensured minimal side reactions such as hydrogen evolution (confirmed in section 3.4.2) on the Zn electrode or on the underlying Pt substrate once all Zn is stripped. A plot of the measured current during the galvanostatic plating step followed by the potentiostatic stripping step is shown in Figure 3.8.
Figure 3.8. Measured current as a function of time during galvanostatic ($I = -4$ mA for 1055 s) plating of Zn followed by its potentiostatic stripping at $-1.35$ V vs. Hg|HgO. Experiment was performed on a Pt RDE with an electrode area of 0.2 cm$^2$. Electrolyte was 0.1 M ZnO + 4.0 M KOH with no additives. The areas under the plating and stripping current traces provided the integrated charge associated with plating ($Q_{Zn+H}$) and stripping ($Q_{Zn}$). Zn plating current efficiency was determined to be 95.9%.

The integrated charge associated with Zn plating ($Q_{Zn+H}$) represents simultaneous electrochemical processes involving Zn electrodeposition as well as hydrogen co-evolution. The integrated stripping charge ($Q_{Zn}$), on the other hand, does not involve any parasitic reactions and is truly a measure of the Zn deposited during the preceding plating step. Thus, the Zn plating current efficiency ($\Phi$) can be defined as in Eq. 3.11:

$$\Phi = \frac{Q_{Zn}}{Q_{Zn+H}} \times 100\%$$  \[3.11\]
\(Q_{Zn+H}\) and \(Q_{Zn}\) were determined from Figure 3.8 and the Zn electrodeposition current efficiency for the additive-free case was calculated to be 95.9%.

The above protocol for determining the Zn plating current efficiency was repeated for the case of a PEI-containing (100 ppm) electrolyte. The procedure followed was identical to that described above for the additive-free case with one difference: potentiostatic Zn stripping was performed at \(-1.31\) V vs. Hg|HgO in the PEI-containing electrolyte (instead of \(-1.35\) V used in the additive-free case). The rationale for this is that the presence of PEI in the electrolyte suppresses the Zn electrodissolution kinetics, such that the anodic stripping current at \(-1.35\) V is extremely small. Thus, to achieve Zn stripping at reasonable rates, a stripping potential of \(-1.31\) V was employed.

Plating and stripping currents measured for 100 ppm PEI-containing electrolyte is shown in Figure 3.9. \(Q_{Zn+H}\) and \(Q_{Zn}\) were determined from Figure 3.9 and the Zn electrodeposition current efficiency in the presence of PEI was determined to be 95.4%, which is very close (within experimental error) to that measured above for Zn electrodeposition in the absence of PEI. To characterize the Zn plating current efficiency further, polarization measurements of the hydrogen evolution reaction on Zn electrodes were performed and the effect of PEI on the hydrogen evolution kinetics was studied. This is reported in the next section.
Figure 3.9. Measured current as a function of time during galvanostatic ($I = -4$ mA for 1055 s) plating of Zn followed by its potentiostatic stripping at $-1.31$ V vs. Hg|HgO. Experiment was performed on a Pt RDE with an electrode area of 0.2 cm$^2$. Electrolyte was 0.1 M ZnO + 4.0 M KOH with 100 ppm of PEI additive. Zn plating current efficiency was determined to be 95.4%.

3.4.2 Polarization Measurements of the Hydrogen Evolution Reaction on Zn Substrates

Polarization measurements were performed to characterize the hydrogen evolution kinetics on a Zn RDE. The electrolyte used was 4.0 M KOH (with or without PEI added to the electrolyte). Electrolyte was kept deoxygenated by continually bubbling Ar. The RDE rotation speed was set to 2000 rpm. The rotation rate of 2000 rpm ensured that evolved gas bubbles did not accumulate and block the RDE surface. The electrode potential was scanned slowly at a rate of 2 mV/s in the negative direction starting from
the open-circuit potential and terminating the scan at a cathodic potential that provides an average cathodic current density of –25 mA/cm².

Figure 3.10 compares polarization curves for the hydrogen evolution reaction on a Zn RDE in the presence and absence of PEI in the electrolyte. In Figure 3.10, hydrogen evolution current density is plotted on the y-axis and the IR-corrected electrode potential \((V_{app} - \eta_\Omega)\) is plotted on the x-axis. This allows comparison of polarization curves for multiple simultaneous electrochemical reactions, as discussed below. As expected, Figure 3.10 shows that appreciable hydrogen evolution commences at electrode potentials cathodic to –1.6 V vs. Hg|HgO, i.e., activation overpotentials in excess of –0.6 V (recall that \(E_H = –0.97\) V vs. Hg|HgO). Furthermore, it is observed that 100 ppm of PEI in the electrolyte catalyzes the hydrogen evolution reaction. This is seen clearly in Figure 3.10 at electrode potentials cathodic with respect to –1.6 V vs. Hg|HgO.
Figure 3.10. Polarization curves for the hydrogen evolution reaction on a Zn RDE at 2000 rpm from a 4.0 M KOH electrolyte with no additive (blue) or with 100 ppm PEI (red). Curves were obtained by sweeping the applied electrode potential in the cathodic direction at 2 mV/s sweep rate. Plot shows that PEI accelerates hydrogen evolution on a Zn substrate at potentials cathodic with respect to –1.6 V vs. Hg|HgO. At potentials positive of –1.6 V, hydrogen evolution is practically absent.

The polarization plots for the hydrogen evolution reaction (Figure 3.10) and the Zn electrodeposition reaction are overlaid in Figure 3.11. The Zn electrodeposition polarization curves were obtained using a procedure similar to that used for the hydrogen evolution polarization measurements in Figure 3.10. The electrolyte used for the Zn electrodeposition polarization measurements was 0.1 M ZnO + 4.0 M KOH with or without 100 ppm PEI additive. All four polarization curves in Figure 3.11 were IR-corrected and the IR-corrected electrode potential ($V_{app} - \eta_D$) was plotted on the $x$-axis.
Figure 3.11. IR-corrected polarization curves collected on a Zn RDE at 2000 rpm from a 4.0 M KOH electrolyte (dashed lines) and from a 0.1 M ZnO + 4.0 M KOH electrolyte (solid lines). **Blue** curves represent additive-free electrolytes and **red** curves represent electrolytes containing 100 ppm.

The hydrogen evolution current ($i_H$, dashed lines) and the combined Zn deposition and hydrogen evolution current ($i_{Zn+H}$, solid lines) obtained in Figure 3.11 can be used to get a qualitative assessment of the current efficiency, which can be defined as seen in Eq. 3.12.

\[ \Phi = \frac{i_{Zn+H} - i_H}{i_{Zn+H}} \times 100\% \]  

[3.12]

It can be observed from Figure 3.11 that, in the range $i_{Zn+H}$ from 0 to –25 mA/cm$^2$, the hydrogen evolution current ($i_H$) is extremely small (smaller in magnitude than –1
mA/cm²). This indicates, from Eq. 3.12, that the current efficiency associated with Zn electrodeposition is very large, consistent with > 95% efficiency measured using anodic stripping coulometry in the previous section. Furthermore, for $0 < |i_{Zn+H}| < 25$ mA/cm², the hydrogen evolution current stays small even in the presence of PEI, which explains why PEI does not appreciably lower the Zn plating current efficiency.

### 3.5 Conclusions

The polymeric additive PEI effectively suppresses dendritic morphology evolution during Zn electrodeposition from an alkaline electrolyte by adsorbing onto the Zn surface and suppressing Zn electrodeposition kinetics. Specifically, PEI lowers the plating exchange current density ($i_0$). The higher the PEI concentration, the lower the exchange current density, thus resulting in a higher dendrite suppression efficacy. In the range of current densities relevant to Zn battery charging, PEI has a negligibly small effect on the Zn electrodeposition current efficiency.
CHAPTER 4. Characterization of the Transport and Adsorption Properties of Polyethylenimine during Zinc Electrodeposition

As has been demonstrated in Chapters 2 and 3, the additive PEI affects various aspects of Zn electrodeposition including surface morphology (i.e., PEI suppresses dendritic growth), kinetics (i.e., PEI lowers the exchange current density during Zn electrodeposition), and faradaic efficiency (i.e., PEI mildly accelerates the hydrogen co-evolution during Zn electrodeposition). Like most additives, PEI functions by adsorbing onto the electrode surface, thereby modifying the Zn deposition kinetics. The rate of PEI build-up on the Zn surface maybe limited by the PEI transport to the electrode surface via diffusion, or by the rate of PEI adsorption once it reaches the Zn electrode surface. In this chapter, transport (diffusion) and adsorption properties of PEI are analyzed to gain insights into the rate-limiting processes associated with PEI adsorption during Zn electrodeposition.

Prior work measuring the transport and adsorption properties of PEI in aqueous solutions was conducted by Hostetler and Swanson in the early 1970s.78–79 These investigators measured the PEI diffusion coefficient as a function of the PEI molecular weight using the “free-diffusion method.” This method utilized synthetic boundary cells—small capillary channels with minimal convective flow, filled with two solutions containing different amounts of PEI where concentration across the boundary region was recorded as a function of time using a Rayleigh optical system.78 A more detailed description of the technique is provided by Gosting.80 Hostetler and Swanson also characterized PEI adsorption onto a porous silica gel substrate. The amount of PEI adsorbed was determined by measuring the concentration change of the adsorption
solution using a spectrophotometric method based on the formation of a complex between PEI and cupric ions.\textsuperscript{78–79} While these studies provide much insight, the PEI used was of a higher molecular weight than that used in the present study, and the silica gel substrate differs in surface structure and characteristics compared to metallic Zn. Additionally, because the size of PEI in solution is a strong function of pH (due to chain conformations from differing degrees of protonation), the diffusion coefficient is also a strong function of pH.\textsuperscript{81} Pulsed-gradient nuclear magnetic resonance (NMR) can be used to measure diffusion coefficients in the medium of interest; however, this technique suffers from limitations: NMR is not widely accessible, often involves intricate sample preparation, and may pose challenges with data interpretations.\textsuperscript{82–83}

In this chapter, PEI injection studies are reported using a rotating disk electrode (RDE) to characterize the diffusion and adsorption properties of PEI during Zn electrodeposition. The transient response of the Zn deposition current (or the Zn electrode potential) to PEI injection provides the PEI surface adsorption time constant. This measured time constant is analyzed in the framework of a diffusion-adsorption model, which leads to determination of the PEI diffusion coefficient ($D_{PEI}$) and its adsorption rate constant ($k_{ads}$). These parameters ($D_{PEI}$ and $k_{ads}$) provide insights into the rate-limiting processes that govern the PEI adsorption during Zn electrodeposition.

### 4.1 Experimental Procedure

#### 4.1.1 Materials

Zn electrodeposition was performed from an alkaline electrolyte containing 0.1 M zinc oxide (ZnO) and 4.0 M potassium hydroxide (KOH). Both chemicals were procured
from Fisher Scientific. The branched additive polyethylenimine (PEI) was purchased from Sigma-Aldrich, average M.W. = 800 g/mol. Millipore-spec (18.2 MΩ) deionized water was used to prepare all electrolytes. Prior to each experiment, argon gas was bubbled through the electrolyte for ~ 1 hr to remove dissolved oxygen.

4.1.2 Methods

To study the diffusion and adsorption properties of PEI, injection experiments were performed using a three-electrode configuration (Figure 4.1). A 0.5 cm diameter Pt RDE, pre-plated with 0.5 µm Zn, served as the working electrode. The RDE was submerged to a depth of ~0.5 cm in a 7 cm diameter glass cell containing 100 mL of the electrolyte. A 1 mm diameter Zn wire was used as the counter electrode. A mercury/mercury oxide reference electrode (Hg|HgO) containing 4.0 M KOH was used as the reference. A schematic illustrating the electrode placements in the cell is shown in the left panel of Figure 4.1. A 1 mL quantity of PEI-containing solution was injected into the electrolyte using a micropipette. The red ‘X’ in the right panel of Figure 4.1 shows the approximate location of PEI injection. The tip of the micropipette was submerged approximately 1 cm beneath the electrolyte surface, and the solution was ejected in less than 1 s. The system response (current or potential) was recorded using a Solartron model 1287A potentiostat/galvanostat with automated data acquisition.
Figure 4.1. Side view (left) and top-down view (right) of RDE setup used for injection experiments. Electrolyte contained 0.1 M ZnO + 4.0 M KOH. Counter electrode (CE) = 1 mm diameter Zn wire; working electrode (WE) = 0.5 cm diameter Zn RDE; reference electrode (RE) = Hg|HgO with 4.0 M KOH. Various concentrations of PEI were injected at injection site shown.

Note that the size of the cell and the volume of electrolyte used herein are smaller than those used in previous RDE experiments (i.e., Chapters 2 and 3, where 250 mL electrolyte in a 10 cm diameter dish was used). Furthermore, RDE rotation speeds used herein are in the 500–7000 rpm range, which ensure rapid mixing of the injected PEI. In separate experiments, a 1 mL volume of blue dye injected into the electrolyte visually confirmed that the dye mixed instantly, i.e., mixing time was less than 1 s at RDE rotation speeds of 3000 rpm. At all rotation speeds used below, the system mixing time was negligibly small in comparison to the current (or potential) response time.
4.2 PEI Injection Studies under Potentiostatic Conditions

As discussed in the experimental procedure above, RDE setup was used to conduct additive (PEI) injection experiments from which the transport and adsorption properties of PEI could be extracted. RDE enables well-defined hydrodynamic conditions, so that the diffusion boundary layer thickness ($\delta$) near the RDE surface is precisely determined. Eq. 4.1 illustrates the dependence of the boundary layer thickness ($\delta$) on angular rotation rate ($\omega$) of the RDE:

$$\delta = 1.61 D^{1/3} \omega^{-1/2} \nu^{1/6}$$  \[4.1\]

where $\nu$ is the kinematic viscosity of the electrolyte and $D$ is the diffusion coefficient of the transported species.

The RDE setup described in Figure 4.1 is first used at a fixed rotation rate of 2000 rpm to electrodeposit Zn potentiostatically at $-1.39$ V vs. Hg|HgO. This applied potential corresponds to an activation overpotential ($\eta_a$) of $-25$ mV, corresponding to an average current density of $-8$ mA/cm$^2$ prior to PEI injection. This current density corresponds to a Wagner number (as discussed in section 2.2.1 of Chapter 2), $Wa = 4.2$, indicating uniform current distribution on the RDE. After plating Zn for 60 s, 1 mL of PEI-containing electrolyte was injected. The concentration of the PEI in the injected solution was varied in order to produce bulk electrolyte concentrations of PEI in the range 0.1–200 ppm upon injection into the cell. Current response upon injection for two PEI concentrations (0.1 and 1 ppm) is shown in Figure 4.2. Injection of both PEI concentrations results in a gradual decrease in the measured current due to PEI adsorption.
on the Zn electrode surface. However, injection of 1 ppm PEI produces a significantly faster response compared to 0.1 ppm. Specifically, the time constant, *i.e.*, time required for the current to decrease and for the system to establish a new steady-state current, is \(~20\) s for the higher PEI concentration and \(~400\) s for the lower PEI concentration.

![Current response](image)

**Figure 4.2.** Current response after injection of PEI measured on a RDE held potentiostatically at \(-1.39\) V vs. Hg|HgO. Current response to 1 ppm PEI injection is shown in *blue*. Current response to 0.1 ppm PEI injection is shown in *red*. It is assumed that the PEI adsorbs on the electrode surface and blocks sites that otherwise would be available for Zn electrodeposition.\(^8\) In such a site-blocking mechanism, the average current density (current per total electrode area) is related to the PEI surface coverage (\(\theta\)) according to Eq. 4.2.

80
\[ i_{PEI} = i_{NoAdd} (1 - \theta) \]  \[4.2\]

where \( i_{PEI} \) is the current density in the presence of adsorbed PEI, \( i_{NoAdd} \) is the current density in the absence of adsorbed PEI, and \((1 - \theta)\) represents the fraction of the electrode surface that is not occupied by PEI and thus available for Zn electrodeposition. Rearranging Eq. 4.2 yields Eq. 4.3:

\[ \theta = 1 - \frac{i_{PEI}}{i_{NoAdd}} \]  \[4.3\]

Since \( i_{PEI} \) and \( i_{NoAdd} \) are available from the injection experiments (Figure 4.2), the steady-state PEI surface coverage \( (\theta_{SS}) \) may be computed. The steady-state PEI surface coverage depends on the PEI concentration, and is shown in Figure 4.3. It is observed that the steady-state PEI surface coverage reaches a value close to unity when the PEI concentration in the bulk electrolyte is higher than 0.1 ppm. This indicates that PEI almost completely saturates the Zn electrode surface at bulk concentrations above 0.1 ppm. This behavior is discussed below in the framework of the classical Langmuir adsorption isotherm.\(^78\)
Figure 4.3. Steady state PEI surface coverage on the Zn electrode surface as a function of the bulk PEI concentration. Tests were conducted potentiostatically at –1.39 V vs. Hg|HgO on a RDE at 2000 rpm. Injection tests provided $i_{PEI}$ and $i_{NoAdd}$, from which the steady-state PEI surface coverage is calculated using Eq. 4.3. Data points are shown in red diamonds; dashed blue lines connect each data point.

The Langmuir adsorption isotherm relates the PEI surface coverage ($\theta_{SS}$) to its bulk concentration ($C$) as shown in Eq. 4.4.

$$\theta = \frac{K_{eq} C}{1 + K_{eq} C} \quad [4.4]$$

In Eq. 4.4, $K_{eq}$ is the equilibrium constant, defined in Eq. 4.5 as:
where \( k_{ads} \) is the adsorption rate constant and \( k_{des} \) is the desorption rate constant. As seen in Figure 4.3, in a wide PEI concentration range of 0.1–200 ppm, the PEI surface coverage is essentially concentration-independent and very close to 1. Thus, from Eq. 4.4, it follows that the PEI equilibrium constant must be in agreement with: \( K_{eq}C >> 1 \). This in turn implies that the PEI adsorption rate is very large in comparison to the desorption rate: \( k_{ads}C \gg k_{des} \), an observation that will be applied in the model development in section 4.4 below.

### 4.3 PEI Injection Studies under Galvanostatic Conditions

Figure 4.4 shows the response of the electrode potential upon injection of PEI at a constant current density of \(-5\ mA/cm^2\). The injected PEI, when mixed uniformly with the bulk electrolyte, corresponds to a concentration of 1 ppm. PEI injection experiments were performed at various RDE rotation rates from 500–7000 rpm. These rotation speeds correspond to limiting current densities that are higher in magnitude than the applied current density of \(-5\ mA/cm^2\) implying minimal diffusion limitations on zincate ions.

Figure 4.4 shows electrode potential response after PEI injection at four RDE rotation speeds: 500, 1000, 1500, and 2000 rpm. It is observed that immediately upon injection of PEI, the electrode potential drifts cathodically from \(-1.385\ V\) vs. Hg|HgO and reaches a new steady-state electrode potential of \(-1.428\ V\) over a period of \(~175\ s\). The rate at which the electrode potential changes is a function of the RDE rotation speed.
The higher the RDE rotation speed, the faster is the initial response of the electrode potential following PEI injection.

Figure 4.4. Electrode potential response during PEI injection. Zn was electrodeposited at a constant current density of –5 mA/cm^2 on RDE at various rotation rates. For clarity, data at only four rotation speeds is shown: 500 rpm (blue), 1000 rpm (red), 1500 rpm (green), and 2000 rpm (purple).

The measured electrode potentials (as shown in Figure 4.4) are comprised of the zincate thermodynamic reduction potential ($E_{Zn}$), the activation overpotential ($\eta_a$), the concentration overpotential ($\eta_c$), and the ohmic overpotential ($\eta_\Omega$). Thus, before PEI injection, the measured electrode potential is shown in Eq. 4.6:

$$V_{NoAdd} = E_{Zn} + \eta_{a,NoAdd} + \eta_c + \eta_\Omega$$  \[4.6\]
While the activation overpotential is a function of the additive concentration (or surface coverage), the concentration and ohmic overpotentials are a function mainly of the applied current and the electrolyte conductivity and thus remain constant in a galvanostatic PEI injection experiment. [Note: The presence of PEI in the electrolyte or on the electrode surface was confirmed not to affect the electrolyte conductivity or the limiting current to the RDE.] Accordingly, after PEI injection into the electrolyte, Eq. 4.7 can be written:

\[ V_{PEI} = E_{Zn} + \eta_{a,PEI} + \eta_c + \eta_\Omega \]  

Since \( E_{Zn}, \eta_c, \) and \( \eta_\Omega \) are constant, subtracting Eq. 4.6 from Eq. 4.7 yields Eq. 4.8:

\[ V_{PEI} - V_{NoAdd} = \eta_{a,PEI} - \eta_{a,NoAdd} = \Delta \eta_a \]

The time-dependent activation overpotential change (\( \Delta \eta_a \)) for PEI injection at four RDE rotation speeds is shown in Figure 4.5.
4.4 Transient Diffusion-Adsorption Model for Simulating the Effect of PEI Injection

Assuming Tafel kinetics, the activation overpotential before PEI injection is related to the current density by Eq. 4.9:

$$\eta_{a, NoAdd} = -\frac{RT}{\alpha_e F} \ln\left(\frac{|i|}{i_0}\right)$$

[4.9]
where \( R \) is the universal gas constant, \( T \) is temperature, \( F \) is Faraday’s constant, \( \alpha_c \) is the charge transfer coefficient, and \( i_0 \) is the exchange current density. In the presence of PEI, the activation overpotential is given by Eq. 4.10:

\[
\eta_{a,\text{PEI}} = -\frac{RT}{\alpha_c F} \ln\left(\frac{|i|}{i_0 (1 - \theta)}\right) \quad [4.10]
\]

where \( \theta \) is the PEI surface coverage. Subtracting Eq. 4.9 from Eq. 4.10 yields the following relationship for galvanostatic operation, as shown in Eq. 4.11:

\[
\Delta \eta_a = \frac{RT}{\alpha_c F} \ln(1 - \theta) \quad [4.11]
\]

Eq. 4.11 relates the activation overpotential change (\( \Delta \eta_a \)) to the PEI surface coverage (\( \theta \)). For small values of \( \theta \), one may approximate \( \ln(1 - \theta) \) to \( -\theta \). This reduces Eq. 4.11 to that shown Eq. 4.12:

\[
\Delta \eta_a = -\frac{RT}{\alpha_c F} \theta \quad [4.12]
\]

Eq. 4.12 indicates that the activation overpotential change, for small PEI surface coverage, is proportional to the PEI surface coverage.

The PEI surface coverage (\( \theta \)) is governed by mass balance. While PEI is transported to the electrode surface at a rate proportional to its diffusion flux, PEI adsorbs
on the electrode surface at a rate assumed to be governed by first-order adsorption kinetics. A schematic illustrating the mass balance of PEI at the electrode surface is shown in Figure 4.6.

Figure 4.6. Schematic illustrating mass balance of PEI at the electrode surface. PEI is transported to the electrode at a rate proportional to its diffusion flux and is adsorbed on the electrode surface at a rate governed by first order adsorption kinetics.

At steady state, the PEI diffusion and adsorption fluxes are equal, which gives Eq. 4.13:

\[
D_{PEI} \frac{dC}{dx} = k_{ads} C_e (1 - \theta)
\]  

[4.13]

where \(D_{PEI}\) is the diffusion coefficient of PEI, and \(C_e\) is the concentration of PEI at the electrode surface. Assuming a linear PEI concentration profile in the diffusion boundary layer (as shown schematically in Figure 4.6), yields Eq. 4.14.
where $C_b$ is the concentration of PEI in the bulk electrolyte. The establishment of a linear PEI concentration profile in the boundary layer following PEI injection into the bulk electrolyte takes time. However, this time is of the order of $\delta^2/D_{PEI}$. Assuming $D_{PEI} = 1.7 \times 10^{-6}$ cm$^2$/s (estimate extrapolated from data in Ref. 79) and $\delta = 12.8$ µm (at the lowest RDE rotation speed employed), one estimates the concentration relaxation time constant to be 0.96 s and thus negligibly small. This scaling estimate of the concentration relaxation time constant, which is also validated through numerical simulations in Appendix B, justifies the linear concentration approximation. Eq. 4.14 can be rearranged to provide the PEI concentration near the electrode ($C_e$), shown in Eq. 4.15:

$$D_{PEI} \frac{C_b - C_e}{\delta} = k_{ads} C_e (1 - \theta) \quad [4.14]$$

$$C_e = \frac{D_{PEI} C_b}{\delta k_{ads}} \begin{array}{c} \frac{1}{1 + \frac{D_{PEI}}{\delta k_{ads}} - \theta} \end{array} \quad [4.15]$$

The accumulation of PEI on the electrode surface is assumed to follow first-order adsorption kinetics, as shown according to Eq. 4.16:

$$\Gamma \frac{d\theta}{dt} = k_{ads} C_e (1 - \theta) \quad [4.16]$$
where $\Gamma$ is the saturation surface concentration of PEI. Inserting $C_e$ from Eq. 4.15 into Eq. 4.16 provides a differential equation that governs the mass accumulation of PEI on the electrode surface, shown as Eq. 4.17:

$$
\Gamma \frac{d\theta}{dt} = \frac{D_{PEI} C_b}{\delta} \frac{(1 - \theta)}{1 + \frac{D_{PEI}}{\delta k_{ads}} - \theta} \tag{4.17}
$$

To aid in solving Eq. 4.17, the time-invariant parameters of the equation are grouped into two variables defined in Eq. 4.18 and Eq. 4.19:

$$
A \equiv \frac{D_{PEI} C_b}{\delta} \tag{4.18}
$$

$$
B \equiv 1 + \frac{D_{PEI}}{\delta k_{ads}} \tag{4.19}
$$

Eq. 4.17 can thus be rewritten as Eq. 4.20:

$$
\Gamma \frac{d\theta}{dt} = \frac{A(1 - \theta)}{B - \theta} \tag{4.20}
$$

Eq. 4.20 can then be integrated along with the initial condition, as provided in Eq. 4.21:

$$
\int \frac{B - \theta}{1 - \theta} d\theta = \frac{A}{\Gamma} \int dt \quad \text{At } t = 0, \ \theta = 0 \tag{4.21}
$$
Consulting a table of integrals yields the following solution:

\[
\theta - (B - 1)ln(1 - \theta) = \frac{At}{\Gamma}
\]  \hspace{1cm} [4.22]

\(A\) and \(B\) are defined in Eq. 4.18 and Eq. 4.19. Both parameters incorporate the diffusion boundary layer thickness, \(\delta = 1.61D^{1/3}\omega^{-1/2}\nu^{1/6}\), (originally shown as Eq. 4.1 in section 4.2). Combining this with Eq. 4.22 and re-arranging provides:

\[
t = \left(\frac{1.61\Gamma\omega^{-1/2}\nu^{1/6}}{C_bD_{PEI}^{2/3}}\right)\theta + \left(\frac{-\Gamma}{C_bk_{ads}}\right)ln(1 - \theta)
\]  \hspace{1cm} [4.23]

which shows the time \((t)\) after PEI injection required to obtain a certain PEI surface coverage \((\theta)\). Note that the PEI surface coverage is linearly proportional to the activation overpotential change only when the small coverage approximation (typically \(\theta \leq 0.3\)) of Eq. 4.12 applies. Now, the time constant \((\tau)\) associated with the electrode potential change can arbitrarily be defined as the time required to reach a PEI surface coverage of \(\theta = 0.3\), which corresponds to an activation overpotential change of 30\%, \(i.e., \Delta\eta_a = -13\) mV in Figure 4.5. From Eq. 4.23, the time constant at 30\% coverage \((\tau_{\theta=0.3})\) is given as Eq. 4.24:

\[
\tau_{\theta=0.3} = \left(\frac{0.48\Gamma\nu^{1/6}}{C_bD_{PEI}^{2/3}}\right)\omega^{-1/2} + \left(\frac{0.36\Gamma}{C_bk_{ads}}\right)
\]  \hspace{1cm} [4.24]
Eq. 4.24 indicates that a plot of $\tau_{\theta=0.3}$ vs. $\omega^{-1/2}$ should yield a straight line with slope and intercept shown in Eq. 4.25 and Eq. 4.26, respectively:

$$\text{slope} = \frac{0.48\Gamma \nu^{1/6}}{C_b D_{PEI}^{2/3}} \quad [4.25]$$

$$\text{intercept} = \frac{0.36\Gamma}{C_b k_{ads}} \quad [4.26]$$

The time constants ($\tau_{\theta=0.3}$) corresponding to a 30% change in the activation overpotential upon PEI injection were determined from Figure 4.5. For a wide range of RDE rotation speeds (500–7000 rpm), the time constant $\tau_{\theta=0.3}$ was plotted as a function of the inverse square root of the RDE angular velocity ($\omega^{-1/2}$). This is shown in Figure 4.7 for PEI concentration of 1 ppm reached in the bulk electrolyte after injection.
Figure 4.7. Time constants extracted from electrode potential responses collected during galvanostatic PEI injection experiments on a RDE. PEI concentration was 1 ppm. Time constants are plotted as a function of the inverse square root of the RDE angular velocity, per Eq. 4.24.

Regression analysis on Figure 4.7 shows that the best linear fit to the data provides a $y$-intercept very close to zero (as seen in Figure 4.8). Since the intercept is equal to $0.36\Gamma/C_b k_{ads}$ (per Eq. 4.26), it can be interpreted that the adsorption rate constant ($k_{ads}$) of PEI is extremely large. This is qualitatively consistent with the observation that $k_{ads} \gg k_{des}$ made at the end of section 4.2. Furthermore, this observation agrees with the findings of Akolkar and Landau, who showed that polymeric plating additives such as polyethylene glycols exhibit fast surface-adsorption kinetics.\textsuperscript{71}
Figure 4.8. Linear best-fit to data in Figure 4.7 with intercept set to 0 provides relationship for time constant: $\tau_{\theta=0.3} = 132.70 \omega^{-1/2}$.

Having determined the slope to be 132.70 (Figure 4.8), one can now estimate the PEI diffusion coefficient ($D_{PEI}$) using Eq. 4.24. Using Eq. 4.24 requires knowledge of various PEI parameters, i.e., the PEI bulk concentration ($C_b = 1$ ppm), the electrolyte kinematic viscosity ($\nu = 0.0124$ cm$^2$/s), and the PEI saturation surface concentration ($\Gamma$). In the next section, the PEI saturation surface concentration is estimated, which is then used in Eq. 4.24 to estimate $D_{PEI}$ in section 4.6.

4.5 Estimation of the PEI Saturation Surface Concentration ($\Gamma$)

The PEI saturation surface concentration ($\Gamma$) is required for determining the diffusion coefficient of PEI ($D_{PEI}$) using Eq. 4.24. The PEI saturation surface
concentration is defined as the number of moles of PEI adsorbed per unit surface area of the Zn electrode at saturation coverage $\theta = 1$. To estimate $\Gamma$, the structure and size of a single PEI molecule is first examined, as seen in Figure 4.9.

![Branched structure of PEI used in this study.](image)

**Figure 4.9.** Branched structure of PEI used in this study.

Under the highly alkaline conditions of the electrolyte (pH $\approx$ 14.7), the amine groups of the PEI structure will be unprotonated and exist as NH$_2$. In an acidic environment, the end groups are more likely to exist in the protonated NH$_3^+$ form.$^{79,81}$ In an unprotonated state, there is little internal coulombic repulsion to force the molecule into an extended-chain conformation. Instead, the polymer exists as a tightly-coiled ball.$^{79,81}$

To determine the size of the tightly-coiled PEI sphere, PEI is first approximated as a linear chain with an equivalent molecular weight as the branched structure. The structure of linear PEI is shown in Figure 4.10. Because PEI will be coiled-up at high pH, little internal void space exists. Thus, the compact PEI sphere should have a size that depends primarily on the molecular weight and only to a second order on the degree of branching.
**Figure 4.10.** Linear representation for PEI with average M.W. = 800 g/mol containing approximately 18 repeating units. Schematic created in ChemDraw 3D.

To estimate the polymer size, the length and width of the linear molecule shown in Figure 4.10 was extracted from ChemDraw 3D using the space-fill approximation. Accordingly, the length ($L$) of a linear chain of 18 repeating units is 6.732 nm, and its width ($W$) is 0.384 nm. The volume of the molecule can then be determined by approximating the linear molecule as a rod of length, $L$, and diameter equivalent to its width ($W$), as seen in Eq. 4.27:

$$V_{rod} = \frac{\pi}{4} W^2 L$$ \[4.27\]

Equating this total volume ($V_{rod}$) to that if PEI were a compact, single, tightly-coiled sphere ($V_{sphere}$) yields Eq. 4.28:

$$V_{sphere} = \frac{4\pi}{3} r^3 = \frac{\pi}{4} W^2 L$$ \[4.28\]

Thus, the PEI radius ($r$) is given by Eq. 4.29:
Using the values for $L$ and $W$ obtained from ChemDraw 3D, the average PEI radius ($r$) was calculated to be 0.57 nm, or a PEI diameter of $d = 1.14$ nm.

Now, it is assumed that there is no substantial change in the size of a PEI molecule upon its adsorption onto the Zn electrode surface. This assumption is supported by the work of Hostetler and Swanson whose calculations from their experimental data show minimal differences in the average PEI diameter when in solution and upon adsorption onto silica gel.\textsuperscript{78} Work by Dick and Ham\textsuperscript{85} and Lawrence and Conway\textsuperscript{86} also suggests that due to the branching structure of PEI and level of counterion binding at high pH, PEI likely resembles an impenetrable sphere both in solution and when immobilized on a surface. Second, it is assumed that PEI adsorbs on the electrode surface in a square-packing orientation as seen in Figure 4.11, in which each PEI occupies an area equal to the square of its diameter ($d^2$).

\begin{equation}
    r = \sqrt[3]{\frac{3}{16} W^2 L} \tag{4.29}
\end{equation}

\textbf{Figure 4.11.} Schematic representation of the square-packing arrangement of PEI spheres adsorbed on the electrode surface.
The PEI saturation surface concentration can be expressed as Eq. 4.30:

\[
\Gamma = \frac{1}{d^2 N_A} \tag{4.30}
\]

where \(N_A\) is Avogadro’s Number \((6.022 \times 10^{-23} \text{ molecules/mole})\). Inputting \(d = 1.14 \text{ nm}\) into Eq. 4.30 yields the PEI surface saturation concentration as \(\Gamma = 1.28 \times 10^{-10} \text{ mol/cm}^2\). This PEI saturation surface concentration is within range of that anticipated based on surface concentrations of other polymers. For polyethylene glycol, average M.W. = 4000 g/mol (PEG-4000), typical saturation surface concentrations of \(0.6 \times 10^{-10} \text{ mol/cm}^2\) have been reported. Since PEG-4000 is a larger polymer than the PEI used here, it is expected that the PEG saturation surface concentration is a smaller value of the two. A smaller molecule common to many electroplating systems, bis-sodium sulfopropyl-disulfide (SPS), has a saturation surface concentration\(^8\) of \(8 \times 10^{-10} \text{ mol/cm}^2\). Since SPS is a smaller molecule than PEI of M.W. = 800, it is expected that the SPS saturation surface concentration is the larger value of the two.

### 4.6 Determination of the PEI Diffusion Coefficient

In section 4.4, it was established (in Eq. 4.25) that a plot of \(\tau_{\theta=0.3} \text{ vs. } \omega^{-1/2}\) should yield a straight line with the following slope:
\[ \text{slope} = \frac{0.48 \Gamma \nu^{1/6}}{C_b D_{PEI}^{2/3}} \]

Rearranging this provides an equation for the diffusion coefficient, as seen in Eq. 4.31:

\[ D_{PEI} = \left( \frac{0.48 \Gamma \nu^{1/6}}{\text{slope} \cdot C_b} \right)^{3/2} \]  \[\text{[4.31]}\]

In Figure 4.8, the slope was determined to be 132.70. Knowing the PEI bulk concentration, \((C_b = 1 \text{ ppm} = 1.46 \times 10^{-9} \text{ mol/cm}^3)\), the electrolyte kinematic viscosity \((\nu = 0.0124 \text{ cm}^2/\text{s})\), and the PEI saturation surface concentration \((\Gamma = 1.28 \times 10^{-10} \text{ mol/cm}^2)\), the PEI diffusion coefficient \((D_{PEI})\) was estimated to be \(1.87 \times 10^{-6} \text{ cm}^2/\text{s}\). The PEI diffusion coefficient agrees reasonably with the work of Hostetler and Swanson,\textsuperscript{78–79} who measured PEI diffusion coefficients using the ‘free-diffusion’ technique described at the start of this chapter. Extrapolating their data to PEI of M.W. = 800 results in a diffusion coefficient of \(1.7 \times 10^{-6} \text{ cm}^2/\text{s}\), very close to the value of \(1.87 \times 10^{-6} \text{ cm}^2/\text{s}\) measured herein.

In the determination of \(D_{PEI}\) above, it was apparent that the adsorption rate constant \(k_{ads}\) is very large because the \textgamma-intercept in Figure 4.8 is close to zero. Theoretical curves representing \(\tau_{\theta=0.3} \text{ vs. } \omega^{-1/2}\) plotted using Eq. 4.9 for various values of \(k_{ads}\) are shown in Figure 4.12. As observed, \(k_{ads} = 0.1 \text{ cm/s}\) or higher reasonably fits the experimental data, which indicates that the PEI adsorption rate constant is \(k_{ads} \geq 0.1 \text{ cm/s}\).
Figure 4.12. PEI surface adsorption time constant as a function of RDE rotation speed: experimental data (blue diamonds), analytical model predictions using Eq. 4.24 (solid lines). Various values of $k_{ads}$ were used in the analytical model.

To determine the rate-limiting process associated with PEI adsorption onto the electrode surface (i.e., diffusion vs. surface-limited adsorption), the diffusion-limited rate constant ($k_D$) is compared to the surface adsorption-limited rate constant ($k_{ads}$). Accordingly:

1) When $k_D = \frac{D_{PEI}}{\delta} \ll k_{ads}$ → PEI is diffusion-limited.

2) When $k_D = \frac{D_{PEI}}{\delta} \gg k_{ads}$ → PEI is surface adsorption-limited.

For the range of RDE rotation speeds employed (500–7000 rpm), $\delta$ varies from 3–13 μm, corresponding to $k_D = 0.001–0.005$ cm/s, which is significantly lower than the surface-
limited adsorption rate constant of $k_{\text{ads}} \geq 0.1 \text{ cm/s}$. This clearly shows that PEI adsorption, under the conditions studied herein, is limited by the transport (diffusion) of PEI towards the electrode surface.

4.7 Conclusions

Using a combination of experimental electroanalytical techniques and transport-kinetics modeling, this chapter analyzed the diffusion and surface-adsorption processes associated with the additive PEI during Zn electrodeposition. At typical PEI concentrations (in the ppm range) required for Zn dendrite suppression, it was shown that PEI adsorption on the Zn electrode surface is limited by its diffusional transport. PEI diffusion coefficient ($D_{\text{PEI}}$) was determined to be $1.87 \times 10^{-6} \text{ cm}^2/\text{s}$ and PEI adsorption rate constant was estimated to be $k_{\text{ads}} \geq 0.1 \text{ cm/s}$. This approach, while applied to PEI during Zn electrodeposition, is general and thus applicable to characterization of additives in other electrodeposition systems.
CHAPTER 5. Conclusions and Future Work

5.1 Summary and Conclusions

Optical microscopy, scanning electron microscopy, and surface profilometry characterization of Zn electrodeposits formed in the presence of the electrolyte additive polyethylenimine (PEI) confirms that PEI effectively suppresses the dendritic morphology and surface roughness evolution during Zn electrodeposition from alkaline electrolytes. PEI functions effectively as dendrite suppressor in the concentration range 10–100 ppm. Dendrite suppression is more effective at higher PEI concentrations. PEI is also effective in suppressing roughness evolution during charge-discharge cycling. Thus, PEI is a promising electrolyte additive for enabling high energy density rechargeable Zn-air batteries.

The mechanism for Zn dendrite suppression by PEI was studied. PEI adsorbs on the Zn electrode surface and suppresses the Zn electrodeposition kinetics. Specifically, adsorbed PEI lowers the Zn plating exchange current density \( i_0 \). Higher PEI concentrations in the electrolyte provides lower exchange current densities, thereby resulting in higher dendrite suppression efficacies. At current densities corresponding to typical Zn-air battery charging rates, PEI does not substantially affect the Zn deposition current efficiency.

Additive injection studies coupled with transport-kinetics modeling provided insights into the diffusion and surface-adsorption properties of PEI during Zn electrodeposition. At typical PEI concentrations required for Zn dendrite suppression, PEI adsorption on the Zn electrode surface is limited by its diffusional transport and not
by its surface adsorption kinetics. For branched PEI, M.W. = 800 g/mol in an alkaline electrolyte, the diffusion coefficient ($D_{PEI}$) was measured to be $1.87 \times 10^{-6}$ cm$^2$/s and the PEI adsorption rate constant was estimated to be $k_{ads} \geq 0.1$ cm/s.

### 5.2 Outlook and Future Work

Zn-air batteries are one of the most promising candidates to replace the state-of-the-art rechargeable Li-ion batteries.\(^7\) Attempts at solving the key issue at the Zn anode, \textit{i.e.}, eliminating Zn dendrites, are reported in the present thesis. Implementing these findings into a Zn-air battery will require identifying optimal PEI concentration to achieve sufficient cycling life while minimizing voltaic efficiency losses. Studies on the long term stability of PEI are also necessary. In addition to addressing these, several other technical hurdles still exist in realizing rechargeable Zn-air battery technology. For example, at the porous carbon cathode, the oxygen evolution reaction during charging and the oxygen reduction reaction during discharging exhibit sluggish kinetics. Because of the high overpotentials associated with these reactions, rechargeable Zn-air batteries exhibit low round-trip energy efficiencies below 60%.\(^7\) Bifunctional, non-noble metal catalysts show promise in catalyzing these reactions; however, their stability under cycling conditions is typically poor.\(^4\) Furthermore, Zn-air cells are highly sensitive to carbon dioxide (CO$_2$), as CO$_2$ reacts with the KOH-based electrolyte to form precipitates of carbonate. These precipitates passivate and de-activate the porous cathode.\(^7\) Development of cycleable cathode technology is thus proposed as a major task in future efforts.
While the target market for Zn-air batteries includes electric vehicles and portable electronics, one promising grid-scale energy storage device that also utilizes Zn-metal anodes is the Zn-Halogen flow battery. The Zn-Halogen flow battery utilizes acidic halide electrolytes \textit{(e.g.,} ZnCl\textsubscript{2}, ZnBr\textsubscript{2})\textit{). Zn dendrite formation at the anode during Zn-Halogen battery charging is a major issue\textsuperscript{1-2}. Electrolyte additives may provide Zn dendrite suppression enabling rechargeable Zn-Halogen batteries. Appendix A provides feasibility of utilizing the electrolyte additive polyethylene glycol (PEG, M.W. = 200 g/mol) for Zn dendrite suppression\textsuperscript{14}. Suggested future directions for this research are fundamental investigations to characterize how additives such and PEG and PEI affect the voltaic and energy efficiency in a Zn-Halogen battery.

While this thesis focused on developing PEI additive for use in aqueous electrolytes, the additive-characterization techniques and methodologies developed for studying surface morphology evolution are applicable to organic electrolytes used in other battery systems. As mentioned in the introduction, Li-Air is a promising next-generation high energy density battery technology\textsuperscript{8}. Li-Air batteries also suffer from significant Li dendrite formation at the anode during charging. While the mechanisms associated with Li dendrite growth may be different than those in the Zn system (due to the presence of surface films, \textit{i.e.,} the solid-electrolyte interphase on Li electrodes in organic solvents\textsuperscript{88}), the techniques applied in this thesis can be extended for analyzing surface roughness evolution during Li electrodeposition and quantifying the diffusion-adsorption properties of surface-film-forming additives that suppress Li dendrites.
APPENDIX A. Suppressing Dendritic Growth during Zinc Electrodeposition from an Acidic Electrolyte using Polyethylene Glycol as an Electrolyte Additive for Zinc-Halogen Flow Batteries

A.1. Introduction and Motivation

Increasing utilization of the world’s renewable resources (e.g., wind and solar) will require advancements to large-scale energy storage technologies. A promising grid-scale storage technology is the Zn-Halogen flow battery, which utilizes a Zn-metal anode. At the anode, Zn is electrodeposited during charging and undergoes dissolution during discharging via the reaction\(^{10}\) in Eq. A.1:

\[
Zn^{2+}_{(aq)} + 2e^{-}_{\text{charge}} \rightleftharpoons Zn^{0}_{(solid)} \quad (E_0 = -0.76 \, V \text{ vs. SHE}) \quad [A.1]
\]

In a Zn-Bromine flow battery, the cathode reaction is shown in Eq. A.2.

\[
Br_2 (l) + 2e^{-}_{\text{charge}} \rightleftharpoons 2Br^{-}_{(aq)} \quad (E_0 = +1.09 \, V \text{ vs. SHE}) \quad [A.2]
\]

These two half-reactions yield a thermodynamic cell potential of 1.85 V. The high output cell voltage along with a voltaic efficiency exceeding 85% makes the Zn-Bromine flow battery a promising alternative for future grid-scale energy storage.\(^3\)

A major limitation prohibiting wide-spread commercialization of Zn-Halogen flow batteries is Zn dendrite formation on the battery anode. When charging the battery at
high rates, metallic Zn deposited at the anode develops dendritic morphology. Dendrites degrade battery cyclability, round-trip efficiency, and life.\textsuperscript{3}

A popular technique for controlling surface morphology in electrodeposition is the use of ppm levels of plating additives. Suppressing, leveling, brightening, and surface film-forming additives have been widely employed.\textsuperscript{37,89–90} In the context of Zn, numerous investigators have studied the effect of additives such as sodium lauryl sulfate, tartaric acid, and Triton X-100.\textsuperscript{27–32,39,91–93} However, these studies have been primarily aimed at understanding the effect of the aforementioned additives on the electrodeposited crystal structure.\textsuperscript{29,32,92–93} No quantitative correlations relating the effects of additives on the Zn dendrite growth rates were provided. In recent studies, the synergistic roles of additives such as benzoic acid, polymeric ethers, and amines in controlling surface roughness and hydrogen co-evolution during Zn electrodeposition were investigated.\textsuperscript{30,91,94} While these studies provided valuable insight into the additives’ adsorption mechanisms, no direct quantification of the dendrite suppression efficacy of these additives was elucidated.

In this chapter, polyethylene glycol (PEG, M.W. = 200 g/mol) additive is investigated for use in suppressing dendrites formed during Zn electrodeposition from halide-containing electrolytes. The choice of M.W. = 200 for PEG is based on its stability and resistance to breakdown during the prolonged operation of a Zn battery. Using in situ optical microscopy, the growth of Zn dendrites was monitored, enabling quantitative characterization of the dendrite suppression efficacy of PEG. Electrode polarization measurements during Zn electrodeposition on a rotating disc electrode in the presence of PEG elucidated the role of PEG in suppressing electrodeposition kinetics. These kinetic parameters, when incorporated into a simple electrochemical model of activation-
controlled dendrite growth, provide dendrite suppression efficacies that are in reasonable agreement with experiments.

A.2. Experimental Procedure

A.2.1 Materials

Electrodeposition of Zn was studied from aqueous electrolytes containing zinc chloride (ZnCl₂) or zinc bromide (ZnBr₂). Both salts were purchased from ACROS and used as received. The additive polyethylene glycol (PEG, average M.W. = 200 g/mol) was acquired from Sigma-Aldrich and was also used as received. Millipore-spec (18.2 MΩ) deionized water was used to prepare all aqueous electrolytes. Prior to preparing the electrolytes, high purity argon was vigorously bubbled through the deionized water for one hour to remove dissolved oxygen. Electrolyte conductivity was measured using an Oakton PC2700 meter with an accompanying conductivity probe.

A.2.2 Methods

The setup used to track dendrite growth during Zn plating consisted of an electrochemical cell with a three-electrode configuration. A shallow glass dish contained the electrolyte, which was either 0.1 M ZnCl₂ or 0.1 M ZnBr₂ with various concentrations (0, 100, 1000 or 10000 ppm) of PEG additive. The working electrode was the exposed tip of a No. 18 AWG PVC-insulated copper wire. Prior to each experiment, the exposed copper surface of the wire was first polished with a 600 grit sand paper and then plated for 30 minutes at −10 mA/cm² to form a thin (~8 μm) and smooth layer of Zn. A platinum wire (Encompass) was used as the counter electrode and a Ag/AgCl electrode filled with
3 M KCl saturated with AgCl (Radiometer Analytical) served as the reference electrode. The tip of the wire electrode at which Zn was electrodeposited was monitored during Zn plating by a National 410 stereo optical microscope placed directly above the horizontally aligned wire electrode. The optical microscope was attached to a digital camera for image recording. The three electrodes were connected to a Solartron model 1287A potentiostat with automated data acquisition.

Electrode polarization during Zn electrodeposition in the presence of PEG was characterized on a rotating disc electrode (Pine Research Instrumentation). The platinum surface of the disc electrode was plated with a thin (~3 μm) layer of Zn prior to each measurement. Rotation speed of the disc electrode was maintained at 300 rpm.

A.3. Results and Discussion

A.3.1 Dendrite Suppression in a ZnCl₂ Electrolyte

The aforementioned in situ optical microscopy setup was used to characterize Zn dendrite suppression by PEG. The working electrode (Zn-coated wire) was held at a constant potential and the growth of dendrites was tracked as a function of time. Two electrode potentials ($V_{app}$) were tested: –1.25 V and –1.30 V (vs. Ag|AgCl).

After 8 minutes of plating at $V_{app} = -1.25$ V, microscopy revealed rapid development of dendritic morphology at the wire electrode in the absence of PEG (panel (a) of Figure A.1). Needle-like dendrites several hundred microns in length were visible. At $V_{app} = -1.30$ V as well, dendritic electrodeposition was evident (panel (e) of Figure A.1). Dendrites grew faster at –1.30 V as compared to –1.25 V.
Figure A.1. Optical microscopy of Zn dendrites protruding from the tip of PVC-coated wire electrode at which Zn is electrodeposited potentiostatically for 8 minutes. Electrolyte contains 0.1 M ZnCl$_2$ with various concentrations of PEG: 0 ppm ((a) and (e)), 100 ppm ((b) and (f)), 1000 ppm ((c) and (g)), and 10000 ppm ((d) and (h)). Two operating voltages are compared: $-1.25$ V vs. Ag|AgCl ((a)–(d)) and $-1.30$ V vs. Ag|AgCl ((e)–(h)).

Addition of 100 ppm of PEG to the electrolyte suppressed dendrite formation marginally (panels (b) and (f) of Figure A.1). Fractal-like aggregates were still visible at both electrode potentials indicating that 100 ppm of PEG additive is insufficient for eliminating dendritic morphology. However, substantial suppression of dendrite growth was obtained at PEG concentrations of 1000 and 10000 ppm. At these PEG concentrations, deposits did not exhibit the classical dendritic morphology. On the contrary, deposits were more compact, indicating effective suppression of dendritic
morphology. At 10000 ppm of PEG, dendrites were completely eliminated at –1.25 V and significantly suppressed at –1.30 V.

To ensure that the addition of PEG to the ZnCl₂ electrolyte did not accelerate side reactions (such as hydrogen co-evolution) that may degrade the current efficiency of Zn electrodeposition, Zn was electrodeposited galvanostatically (at –5 mA/cm²) from the aforementioned electrolyte onto a Zn-seeded substrate in the presence and absence of PEG. Electrodeposit weight gain was measured and converted into current efficiency by applying Faraday’s law. The current efficiency in all tested cases (in the presence and absence of PEG) exceeded 95% indicating no detrimental effects of PEG on the Zn deposition current efficiency. This confirms that PEG suppresses Zn dendrites while maintaining an overall high efficiency of Zn plating.

Figure A.2 shows chronoamperometry plots corresponding to the dendrite growth studies reported in Figure A.1. Chronoamperometry plots are shown only for the applied potential of –1.25 V since the general trends were similar at the applied potential of –1.30 V. Upon application of the potential, the Zn deposition current decayed from –0.41 mA (at time ~0 s) to –0.24 mA over an 8 s period. The steady state current of –0.24 mA was relatively insensitive to the applied potential, thus representing deposition of Zn close to the system limiting current. This was also confirmed by polarization scans on the wire electrode, which showed that the Zn limiting current at the wire electrode was ~ –0.247 mA. As seen in Figure A.2, after the first transient period (~8 s), the current remained constant for a period of about 100 s. During this period, no Zn dendrites were observed on the wire electrode (as determined via microscopy). However, after this period, the current gradually increased (in magnitude). The rate of current increase depended on the
concentration of PEG in the electrolyte (Figure A.2). The most rapid increase in current was recorded in the absence of PEG. Dendritic morphology concurrently developed on the wire electrode, which suggests that the current increase is attributed to the surface area increase during dendritic deposition. The rate of current increase (and thus surface area increase) was suppressed in the presence of PEG with 100 ppm and 1000 ppm PEG showing lower rate of rise. At 10000 ppm PEG, the current did not increase measurably, remaining nearly constant for about 8 min. This confirms the near complete suppression of morphology evolution due to Zn dendrites. These electrochemical trends complement the in situ growth studies (Figure A.1) in validating the concentration-dependence of the Zn dendrite suppression by PEG additive.

**Figure A.2.** Chronoamperometric trends during potentiostatic plating at –1.25 V vs. Ag/AgCl from a 0.1 M ZnCl₂ electrolyte.
A.3.2 Dendrite Suppression in a ZnBr₂ Electrolyte

In Zn-Bromine flow batteries, aqueous solutions of ZnBr₂ are employed as electrolytes.¹ To demonstrate that the PEG additive functions as an effective dendrite suppressor during Zn deposition from a ZnBr₂ system, experiments were conducted using the same in situ microscopy setup employed above for studies with ZnCl₂, but replacing the ZnCl₂ electrolyte with a 0.1 M ZnBr₂ electrolyte. A sample data set (collected at $V_{app} = -1.25 \text{ V vs. Ag|AgCl}$) is shown in Figure A.3. Panel (a) of Figure A.3 shows dendritic morphology evolution during Zn deposition in the absence of PEG. Panel (b) of Figure A.3 confirms the complete suppression and elimination of dendrites in the presence of 10000 ppm of PEG in the ZnBr₂ electrolyte. This demonstrates the flexibility of applying PEG as an effective dendrite suppressor in bromide-based electrolytes.

![Figure A.3](image_url)

**Figure A.3.** Optical microscopy of Zn dendrites protruding from the tip of a PVC-coated wire electrode at which Zn is electrodeposited potentiostatically. Electrolyte contains 0.1 M ZnBr₂ without PEG (a) and with 10000 ppm of PEG (b). Electrode potential is $-1.25 \text{ V vs. Ag|AgCl}$. Images confirm that PEG suppresses Zn dendrites in a ZnBr₂ electrolyte.

A.3.3 Model of Zn Dendrite Suppression by PEG

In this section, a model is proposed for the suppression of Zn dendrites by PEG. Model parameters are determined through electrochemical polarization measurements on
a rotating disc electrode. Dendrite suppression efficacy of PEG predicted by the model is compared with experimental observations reported in the previous section.

At an applied potential, $V_{\text{app}}$, a voltage balance at the dendrite tip (as shown in Figure A.4) provides Eq. A.3:

$$V_{\text{app}} - E_{Zn} = \eta_a + \eta_\Omega + \eta_c + \eta_s$$  \[A.3\]

In Eq. A.3, $E_{Zn}$ is the reduction potential of Zn (measured to be –1.0 V vs. Ag|AgCl), $\eta_a$ is the activation overpotential, $\eta_\Omega$ is the ohmic overpotential, $\eta_c$ is the concentration overpotential and $\eta_s$ is the surface curvature overpotential.

**Figure A.4.** Schematic representation of the various overpotentials that develop at a Zn dendrite tip. It is shown (see text) that the ohmic overpotential ($\eta_\Omega$), the concentration overpotential ($\eta_c$), and the surface curvature overpotential ($\eta_s$) are negligible at the tip of a dendrite. The analysis concludes that the activation overpotential ($\eta_a$) is the dominant overpotential at the dendrite tip.

In analogy to the model by Diggle et al.,\textsuperscript{12} it is assumed that dendrites in the Zn electrodeposition system studied here grow purely under activation control. To validate this hypothesis, the magnitude of each overpotential was examined relative to the total overpotential in the system. For experiments conducted at $V_{\text{app}} = –1.25$ V, the reduction
potential for Zn, \((E_{Zn} = -1.0 \text{ V vs Ag|AgCl})\) was subtracted to obtain the net overpotential, –250 mV. The contribution of the ohmic overpotential (shown in Eq. A.4) to the net overpotential is:

\[ \eta_{\Omega} = \frac{il}{\kappa} \]  

[A.4]

In Eq. A.4, \(i\) is the dendrite tip current density, \(l\) is the characteristic length scale over which the ohmic potential drop develops, and \(\kappa\) is the electrolyte conductivity. The dendrite tip growth rate measured from experiments is about 40 \(\mu\text{m/min}\), which corresponds to a current density, \(i \approx -1.5 \text{ A/cm}^2\). The characteristic length (\(l\)) can be taken as the dendrite tip radius in analogy to a micro-electrode.\(^{95}\) Typical dendrite tip sizes are typically 0.5 \(\mu\text{m}\) as reported by Diggle \textit{et al.}\(^{12}\) With a measured electrolyte conductivity of 17.7 mS/cm, \(\eta_{\Omega}\) is estimated to be only –4 mV and thus negligible in comparison to the net overpotential at the dendrite tip (–250 mV).

The concentration overpotential is next examined, seen in Eq. A.5:

\[ \eta_c = \frac{RT}{nF} \ln \left(1 - \frac{|i|}{i_L}\right) \]  

[A.5]

In Eq. A.5, \(R\) is the universal gas constant (8.314 \(\text{J/mol K}\)), \(T\) is the temperature (298 K), \(n\) is the number of electrons transferred \((n = 2)\) during the electrodeposition reaction, \(F\) is Faraday’s constant, and \(i_L\) is the magnitude of the limiting current density at the dendrite
tip. For ‘spherical’ 3D diffusion to a dendrite tip, the limiting current density is given in Eq. A.6:

\[ i_L = \frac{nFD C_b}{(1-t_+)^2} \quad \text{[A.6]} \]

Taking the diffusion coefficient \((D)\) to be \(7.03 \times 10^{-6} \text{ cm}^2/\text{s}\) (Ref. 96), the transport number \((t_+)\) to be 0.41 (calculated based on reported ionic conductivities\(^{96}\)), and the dendrite tip radius \(r\) to be 0.5 \(\mu\)m\(^{12}\) the magnitude of the limiting current density \(i_L\) is estimated to be \(\sim 4.6 \text{ A/cm}^2\) at \(C_b = 0.1 \text{ M}\). Inputting this value of \(i_L\) in Eq. A.5, the concentration overpotential \((\eta_c)\) is calculated to be \(-5 \text{ mV}\) and thus negligible with respect to the net overpotential of \(-250 \text{ mV}\). Next, the surface curvature overpotential is calculated (via the relationship used by Barton and Bockris\(^{15}\)) in Eq. A.7:

\[ \eta_s = -\frac{2\gamma K}{nF} \quad \text{[A.7]} \]

In Eq. A.7, \(\gamma\) is the surface tension at the electrode-electrolyte interface (\(7.9 \times 10^{-5} \text{ J/cm}^2\) for Zn\(^{97}\), and \(K\) is the molar volume of Zn (9.2 \(\text{ cm}^3/\text{mol}\)). From Eq. A.7, the surface curvature overpotential for a Zn dendrite with \(r = 0.5 \mu\)m is \(-0.2 \text{ mV}\), and thus also negligible.

From the above discussion, it is clear that the ohmic overpotential \((\eta_\Omega \approx -4 \text{ mV})\), concentration overpotential \((\eta_c \approx -5 \text{ mV})\) and the surface curvature overpotential \((\eta_s \approx -0.2 \text{ mV})\) are all negligible in comparison to the total electrode overpotential of \(-250 \text{ mV}\).
Thus, the activation overpotential ($\eta_a$) is the dominant overpotential at the dendrite tip. This confirms that the dendrite tip grows purely under activation control. Thus, assuming Tafel kinetics yields Eq. A.8:

$$V_{app} - E_{Zn} \approx \eta_a = -\frac{RT}{\alpha_c F} \ln \left( \frac{i}{i_0} \right)$$  \hspace{1cm} [A.8]

In Eq. A.8, $\alpha_c$ and $i_0$ represent the cathodic charge transfer coefficient and the exchange current density, respectively. These kinetic constants correlate the activation overpotential at the dendrite tip ($\eta_a$) to the current density ($i$) at which the dendrite grows. The dendrite growth rate ($\dot{h}$) is then obtained by applying Faraday’s law, as seen in Eq. A.9:

$$\dot{h} = \frac{M |i|}{nF \rho}$$  \hspace{1cm} [A.9]

In Eq. A.9, $M$ is the molecular weight of Zn (65.38 g/mol), and $\rho$ is its density (7.14 g/cm$^3$). Combining Eq. A.8 and Eq. A.9 yields Eq. A.10:

$$\dot{h} \approx \frac{Mi_o}{nF \rho} \exp \left\{ -\frac{\alpha_c F}{RT} \left( V_{app} - E_{Zn} \right) \right\}$$ \hspace{1cm} [A.10]

Eq. A.10 can be used to correlate the Zn dendrite growth rate to the system kinetic constants ($\alpha_c$ and $i_0$). Eq. A.10 also reveals that the dendrite growth rate increases exponentially with the applied potential. While kinetic parameters for Zn
electrodeposition in the absence of additives have been reported, no systematic study on the PEG-concentration dependent Zn electrodeposition kinetics is available. The effect of PEG on Zn electrodeposition kinetics is reported below.

**A.3.4 Effect of PEG on Zn Electrodeposition Kinetics**

In this section, electrode polarization during Zn electrodeposition on a Zn-coated rotating disc electrode (at 300 rpm) was studied from a 0.1 M ZnCl$_2$ electrolyte. Tafel plots, shown as the magnitude of the activation overpotential, $|\eta_a|$, vs. the natural log of the magnitude of the current density, $\ln(|i|)$, can be seen in Figure A.5. In these Tafel plots, the activation overpotential was obtained after subtracting the IR (ohmic) and concentration overpotentials from the measured total overpotential. Newman’s analytical solution for ohmic resistance of a disc electrode was used for IR correction, and Eq. A.5 (with $i_L$ provided by the Levich Equation) was used to correct for concentration polarization. The effect of PEG concentration on the electrode polarization is evident from Figure A.5. The electrode polarization increases monotonically with PEG concentration, indicating that PEG adsorbs on the electrode surface and polarizes the electrode during Zn deposition.
Figure A.5. Tafel plots for Zn electrodeposition obtained on a rotating disc electrode at 300 rpm. Plots show that PEG additive suppresses Zn electrodeposition kinetics by lowering the exchange current density (Table A.1). PEG does not affect the Tafel slope during Zn plating.

This is analogous to the electrode polarization observed during copper electrodeposition in the presence of PEG additive.\textsuperscript{71–72} Figure A.5 shows that the slope of the $\ln(|i|)$ vs. $|\eta_a|$ curve, which relates to the Tafel slope, remains unaltered in the presence of PEG. This indicates that PEG does not affect the cathodic transfer coefficient during Zn electrodeposition. From Figure A.5, the cathodic transfer coefficient was computed to be: $\alpha_c = 0.79$. PEG substantially alters the $y$-intercept of the $\ln(|i|)$ vs. $|\eta_a|$ curve, indicating a significant lowering of the exchange current density ($i_0$) of Zn plating. The values for the exchange current density were computed from Figure A.5 and are listed in Table A.1. The exchange current density is lowered by almost an order of magnitude by the addition of 10000 ppm of PEG to the electrolyte.
Table A.1. Kinetic parameters for Zn electrodeposition in the presence of PEG additive, indicating that PEG predominantly affects the exchange current density during Zn electrodeposition. Electrolyte contains 0.1 M ZnCl₂. The cathodic transfer coefficient is: \( \alpha_c = 0.79 \).

<table>
<thead>
<tr>
<th>PEG Concentration (ppm)</th>
<th>Exchange Current Density ( (i_0, \text{mA/cm}^2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.82</td>
</tr>
<tr>
<td>100</td>
<td>2.22</td>
</tr>
<tr>
<td>1000</td>
<td>1.30</td>
</tr>
<tr>
<td>10000</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The effect of PEG on \( i_0 \) (but not on \( \alpha_c \)) indicates that PEG suppresses deposition kinetics by adsorbing on the electrode surface and blocking sites available for Zn deposition.99–100 This manifests into a shift in the apparent exchange current density.

A.3.5 Dendrite Suppression Factor

In this study, dendrite suppression factor \( (\xi) \) is defined as the ratio of the dendrite growth rate observed in the presence of PEG to that observed in the absence of PEG, as seen in Eq. A.11:

\[
\xi = \frac{\dot{h}_{\text{PEG}}}{\dot{h}_{\text{PEG}=0}} \tag{A.11}
\]

A value of \( \xi \) well below unity suggests strong suppression of Zn dendrite growth by PEG, whereas \( \xi \) approaching unity suggests weak suppression of Zn dendrite growth. Estimates
of the dendrite propagation length were obtained from microscopy images shown in Figure A.1 by measuring the maximum distance from the electrode surface to which the Zn dendrites grew. These propagation lengths were then used in Eq. A.11 to yield the experimentally observed dendrite suppression factor. To calculate the theoretical dendrite suppression factor, the dendrite growth rate expression (Eq. A.10) was inserted into Eq. A.11. Recognizing that the cathodic transfer coefficient is unaffected by PEG (Figure A.5), Eq. A.11 reduces to that shown in Eq. A.12:

\[ \xi = \frac{i_{0,\text{PEG}}}{i_{0,\text{PEG}=0}} \]  

[A.12]

Thus, dendrite suppression by PEG is directly related to the lowering of the exchange current density during Zn electrodeposition. Dendrite suppression factors measured experimentally (by inserting measurements from Figure A.1 into Eq. A.11) and those estimated from theory (by applying Eq. A.12 with kinetic constants from Table A.1) are plotted in Figure A.6 as a function of the PEG concentration. Both theory and experiment show a monotonic decrease in \( \xi \) (i.e., an increase in the dendrite suppression efficacy) with an increase in the PEG concentration. Good agreement is seen between the experimentally observed suppression factor and that predicted by theory. This demonstrates the ability of the simple model (Eq. A.12) to serve as a predictive tool for determining the effectiveness of Zn dendrite suppression by PEG additive.
Figure A.6. Dendrite suppression factor ($\xi$) is plotted as a function of the PEG concentration. Increasing PEG concentration lowers the dendrite suppression factor indicating more effective dendrite suppression. Model (Eq. A.12, red diamonds) and experimental (measured from Figure A.1, black dashed line) dendrite suppression factors agree reasonably well over the entire PEG concentration range studied.

A.4. Conclusions

A combination of in situ optical microscopy, electrochemical polarization, and modeling was employed to study the suppression of dendrite growth during Zn electrodeposition from aqueous halide electrolytes containing PEG additive. The study led to the following key conclusions:

(i) Over a wide concentration range (100–10000 ppm), PEG suppresses dendritic growth during Zn electrodeposition. The degree of dendrite suppression depends on the PEG concentration; dendrite suppression is more effective at higher PEG concentrations.
(ii) Analysis shows that a spherical micro-scale Zn dendrite tip is released from mass transport and ohmic limitations, allowing the tip to grow rapidly under activation, *i.e.*, kinetic control. Thus, dendrite suppression can be achieved by using additives, such as PEG, which affect the exchange current density in Zn electrodeposition.

(iii) PEG suppresses Zn dendrites by lowering the plating exchange current density. The higher the PEG concentration, the lower the exchange current density and thus, the higher the dendrite suppression efficacy.

(iv) A simple model for activation controlled dendrite growth was developed to compute Zn dendrite suppression efficacies in the presence of PEG and compare them to experimental observations. Good agreement between model predictions and experimental observations was observed.
APPENDIX B. Numerical Simulation for PEI Diffusion-Adsorption Using COMSOL Multiphysics

Within the diffusion boundary layer, Fick’s second law of diffusion governs the PEI transport towards the electrode surface, as shown in Eq. B.1:

\[ D_{PEI} \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \]  

[B.1]

Eq. B.1 can be non-dimensionalized using the definitions shown in Eq. B.2, B.3, and B.4.

\[ \bar{C} = \frac{C}{C_b} \]  

[B.2]

\[ \bar{x} = \frac{x}{\delta} \]  

[B.3]

\[ \bar{t} = \frac{D_{PEI} t}{\delta^2} \]  

[B.4]

The dimensionless form the diffusion equation (Eq. B.1) can then be written as Eq. B.5:

\[ \frac{\partial^2 \bar{C}}{\partial \bar{x}^2} = \frac{\partial \bar{C}}{\partial \bar{t}} \]  

[B.5]

The accumulation of PEI on the electrode surface is assumed to follow first-order adsorption kinetics, as seen in Eq. B.6:
\[ \Gamma \frac{d\theta}{dt} = k_{ads} C_{x=0} (1 - \theta) \]  

[B.6]

Eq. B.6 can be non-dimensionalized to give Eq. B.7:

\[ \Gamma \frac{d\theta}{d\bar{t}} = \frac{k_{ads} \delta^2 C_{x=0} C_b}{D_{PEI}} (1 - \theta) \]  

[B.7]

At time \( t = 0 \), the initial condition is given in Eq. B.8:

\[ \bar{C} = 0 \quad \theta = 0 \]  

[B.8]

At the electrode surface \( (x = 0) \), the boundary condition of Eq. B.9 holds:

\[ \frac{d\bar{C}}{d\bar{x}} = \frac{k_{ads} \delta}{D_{PEI}} \bar{C} (1 - \theta) \]  

[B.9]

In the bulk electrolyte \( (x = \delta) \), the PEI concentration is given in Eq. B.10:

\[ \bar{C} = 1 \]  

[B.10]

The set of differential equations (Eq. B.5 and B.7) together with the initial and boundary conditions specified by Eq. B.8, B.9, and B.10 were numerically solved in COMSOL Multiphysics. The following parameter values were used in simulations: \( \delta = 13.2 \, \mu m \) (500 rpm), \( \nu = 0.0124 \, cm^2/s \), \( C_b = 1.46 \times 10^{-9} \, mol/cm^3 \) (1 ppm PEI), \( \Gamma = 1.28 \times 10^{-10} \, mol \, PEI/cm^2 \), \( D_{PEI} = 1.87 \times 10^{-6} \, cm^2/s \), \( k_{ads} = 0.1 \, cm/s \). Simulations provided the
concentration profile of PEI in the diffusion boundary layer as a function of time and the time-dependent PEI surface coverage on the electrode. Figure B.1 shows that the PEI concentration profile develops into a linear profile in a period of \(~0.3\) s. This concentration relaxation time is consistent with the scaling estimate of \(\frac{\delta^2}{D_{PEI}} = 0.93\) s used in deriving Eq. 4.14 which assumes that a linear PEI concentration gradient is established almost instantly.

![Time-dependent PEI concentration profile](image)

**Figure B.1.** Time-dependent PEI concentration profile inside boundary layer simulated numerically using *COMSOL Multiphysics*. Profile becomes linear in a period of \(~0.3\) s 

After this time, the PEI concentration profile remains linear but its gradient drops gradually as PEI adsorbs on the electrode surface, as seen in Figure B.2.
Figure B.2. Time-dependent PEI concentration profile inside boundary layer simulated numerically using *COMSOL Multiphysics*. Profile remains linear though gradient drops with time as PEI adsorbs on the electrode surface.

The PEI surface coverage predicted by the numerical simulations is compared with that modeled analytically (Eq. 4.23) in Figure B.3. Very good agreement between the two approaches is observed.
Figure B.3. Comparison of the PEI surface coverage predicted by the analytical model (Eq. 4.23, shown as blue dashed line) to that predicted using COMSOL Multiphysics simulations (solid green line). Excellent agreement between the two approaches is observed.
BIBLIOGRAPHY


