



# Suppressing Dendritic Growth during Alkaline Zinc Electrodeposition using Polyethylenimine Additive



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## ABSTRACT

Dendritic morphology evolution during zinc electrodeposition is a major roadblock in the development of rechargeable zinc anodes in alkaline zinc batteries. In the present work, we report the use of branched polyethylenimine (PEI, M.W. = 800 g/mol) as an effective electrolyte additive for suppressing dendrite formation during zinc electrodeposition from typical alkaline electrolytes used in secondary zinc batteries. Dendrite suppression is characterized as a function of the PEI concentration via 'live' observation of the dendrite propagation using an *in-situ* optical microscopy setup. Steady-state and transient electrochemical polarization measurements on a rotating disk electrode, combined with electrochemical quartz crystal microgravimetry and *ex-situ* scanning electron microscopy, reveal the mechanism by which PEI suppresses dendrites, *i.e.*, PEI adsorption on the zinc surface leading to suppression of the zinc electrodeposition kinetics. Our work presents a comprehensive characterization of the role of polymeric additives, such as PEI, in suppressing dendritic growth during alkaline zinc electrodeposition.

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## 1. Introduction

Battery systems utilizing zinc (Zn) anodes hold great promise for future energy storage devices due to their high theoretical energy density, low toxicity, and the abundance of Zn [1]. While primary Zn batteries are used in numerous applications today, the development of rechargeable Zn battery technology has faced numerous technical hurdles. A major issue has been the evolution of dendritic Zn electrodeposition morphology at the anode during high-rate battery charging, which compromises both battery life and safety [2].

Since the 1960s, numerous efforts have focused on characterizing and suppressing dendritic growth during Zn electrodeposition. Diggle et al. developed early models for describing activation-controlled deposit growth at micro-scale dendrite tips [3], while Naybour et al. [4] characterized the crystal orientation of the electroformed Zn dendrites. Bockris et al. provided careful measurements of the kinetic parameters during Zn electrodeposition from an alkaline (zincate) electrolyte [5]. Investigations of Zn dendrite growth in acidic electrolytes have also been reported. Oren and Landau characterized Zn dendrite growth in acidic chloride electrolytes [6], Chen and Joré characterized

fractal-like morphologies during Zn electrodeposition from sulfate electrolytes [7], and Barkey and coworkers studied the formation of branched Zn aggregates also in sulfate electrolytes [8,9].

Many early attempts to control the Zn electrodeposition morphology focused on optimization of the applied current or potential waveform. Arouete et al. experimented with pulsed-current electrodeposition for surface smoothing [10]. Despic and Popov showed Zn dendrite suppression using high-frequency square-wave potential pulses [11]. The effect of pulsing on surface smoothing may be understood through the modeling work of Ibl [12].

Suppression of roughness or dendrite evolution during Zn electrodeposition may also be achieved through the use of ppm-levels of additives in the plating electrolyte [13–20]. Recently, we reported the use of polyethylene glycol (PEG) additive for suppressing Zn dendrites during electrodeposition from halide-containing acidic electrolytes [21]. Several studies reporting the use of additives to control the Zn deposit quality and appearance are noted [22–25]. Additives in these studies include polyvinyl alcohols [22,23], polyamines [24], and carbonyl compounds [25]. Bass et al. documented additives relevant to alkaline Zn battery applications [26]. These include surfactants, ammonium salts, lead ions ( $\text{Pb}^{2+}$ ), bismuth compounds, and metal oxides [27–36]. Additives for suppressing hydrogen evolution and preventing battery self-discharge include weak acids [37], surfactants [38], organics [39], and metal oxides [40]. While

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several promising additive candidates have been identified in prior work, a systematic study of the mechanism through which these additives suppress Zn dendrites is still lacking.

In the present paper, we focus on polyethylenimine (PEI) as an additive to suppress Zn dendrites during alkaline Zn electrodeposition. Our work is motivated by the fact that PEI is a widely studied polarizer during copper (Cu) electrodeposition [41,42] and is also stable in alkaline media [43,44]. We demonstrate below, using a combination of electrochemical and surface microscopy techniques, that PEI strongly suppresses the formation of Zn dendrites. The dendrite suppression effect is PEI concentration-dependent, and is mechanistically linked to the adsorption of PEI at propagating dendrite tips, which leads to the suppression of the deposit growth rate at dendrite tips.

## 2. Experimental

### 2.1. Materials

Electrolyte components zinc oxide (ZnO, Fisher Scientific), potassium hydroxide (KOH, Fisher Scientific) and branched polyethylenimine additive (PEI, average M.W.=800, Aldrich Chemistry) were used as received. Per the MSDS provided by Sigma-Aldrich, the PEI additive solution has a pH~11 at 10g/L concentration. Millipore-spec (18.2M $\Omega$ ) deionized water was used to prepare all electrolytes. Prior to preparing the electrolytes, high purity argon was bubbled through the deionized water for 1 hour to remove dissolved oxygen.

### 2.2. 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 Zn wire (99.95% purity, purchased from Alfa-Aesar) was used as the counter electrode and Hg/HgO electrode filled with 4.0 M KOH (Koslow Scientific) served as the reference electrode. 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  $\sim 0.008$  cm<sup>2</sup>. Prior to each experiment, the wire electrode tip was sanded with 1000 grit sand paper, then polished using 5  $\mu$ m

alumina slurry. Scanning electron microscopy (SEM) using FEI Helios Nanolab 650 provided high-resolution *ex-situ* imaging of the Zn electrodeposits.

To study the effect of PEI on Zn electrodeposition kinetics, electrochemical polarization data was obtained on a 0.5 cm diameter rotating disc electrode (RDE), rotated at 1000 rpm. The copper RDE was galvanostatically pre-plated with a thin ( $\sim 1$   $\mu$ m) layer of Zn at 10 mA/cm<sup>2</sup> from an additive-free electrolyte prior to each polarization run. For polarization measurements, a Zn wire served as the counter electrode and Hg/HgO electrode served as the reference electrode. A Solartron model 1287A potentiostat/galvanostat with automated data acquisition was used for all electrochemical studies. Plating-stripping studies on a Cu RDE provided the faradaic efficiency of Zn electrodeposition in the presence and absence of PEI additive in the electrolyte.

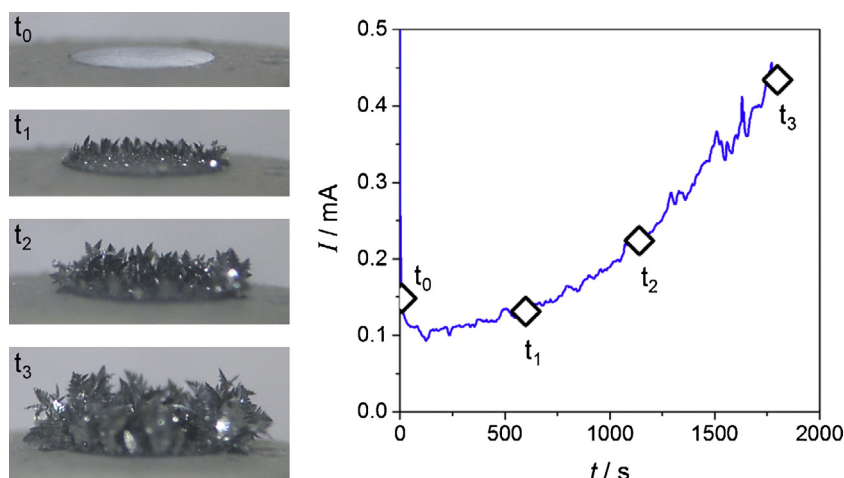
PEI adsorption on the Zn surface during electrodeposition was studied using a Stanford Research Systems QCM-200 quartz crystal microbalance with 5 MHz Fil-Tec gold-coated quartz crystals. Prior to each experiment, the gold crystal was gently rinsed in ethanol followed by deionized water, and then dried. The crystal was then galvanostatically pre-plated with a uniform layer of Zn ( $\sim 250$  nm) at 10 mA/cm<sup>2</sup> from an additive-free electrolyte under moderate agitation. Various quantities of PEI were injected into the electrolyte and the QCM frequency response during Zn electrodeposition was recorded.

In general, the wire electrode studies were conducted under diffusion-limited conditions (*i.e.*, at current densities approaching the limiting current density of the system) favoring Zn dendrite formation. In contrast, the RDE and QCM experiments were conducted under conditions of minimal diffusion limitations so as to probe the effect of PEI on the Zn electrodeposition kinetics without interference from surface roughness evolution.

## 3. Results and Discussion

### 3.1. Suppression of Zn dendrites using PEI additive

In this section, we report on the Zn dendrite suppression efficacy of PEI 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 base, 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



**Fig. 1.** Live tracking of Zn dendrite growth using optical microscopy (left), and corresponding chronoamperometry (right) indicating surface area increase due to dendritic morphology evolution. Zn is electrodeposited potentiostatically at  $-1.57$  V (vs. Hg/HgO) on a Zn-coated wire electrode for a period of 1800 s. Additive-free electrolyte contains 0.1 M ZnO+4.0 M KOH.

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