Effect of Additives on Dendritic Growth During Zinc Electrodeposition

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Dendritic growth is commonly observed in metal electrodeposition, especially when operating under mass transport control.[1,2] Dendritic growth in energy storage devices is highly undesirable as it results in capacity loss and compromises safety. Zinc dendrites in particular are of concern, as they can form in zinc-halogen flow batteries during charging at high rates.[3]

In this work, we focus on the use of several electrolyte additives to arrest zinc dendritic growth. To study the effect of these additives, we have developed an electrochemical cell for in-situ microscopy of zinc electrodeposition. We focus here on two specific additives: polyethylene glycol (PEG, M.W. = 4000) and thiourea.

Polarization curves were obtained from a 0.1 M $ZnCl_2$ electrolyte, both with and without additives, as shown in Figure 1. As observed from the polarization curves, these additives produce mild to moderate polarization during zinc deposition, suggesting that the additives adsorb on the electrode surface and modify the electrodeposition kinetics. Adsorption is essential for an additive to function as an effective dendrite suppressor.

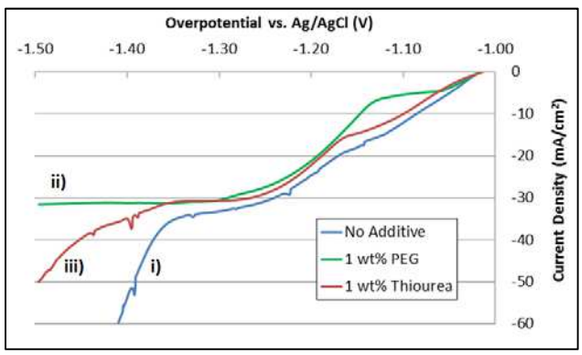

Figure 1. Polarization curves on a zinc-coated wire electrode in 0.1 M $ZnCl_2$ containing: i.) No additive, ii.) 1 wt% PEG, iii.) 1 wt% thiourea.

Using in-situ microscopy, we captured dendritic growth on the tip of a wire electrode. The polyvinyl chloride (PVC)-coated copper wire (1.024 mm inner diameter) was first pre-plated with a thin layer of zinc, then used as the working electrode in the electrochemical cell. A constant potential of -1.25 V vs. Ag/AgCl was applied to the wire electrode. At this operating potential, dendritic growth is expected to be prevalent. Chronoamperometry plots are shown in Figure 2. As indicated by an increase in the magnitude of the current, the electrode in the additive-free electrolyte begins developing dendrites around ~100s. However, neither the electrolyte with PEG nor that with thiourea develops dendrites, as indicated by a relatively constant current. This provides evidence that both PEG and thiourea arrest dendrites during zinc plating.

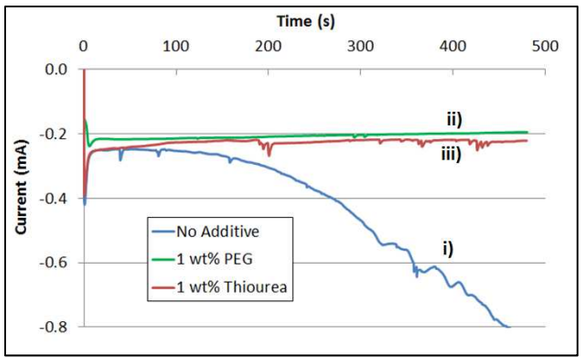

Figure 2. Potentiostatic plating at an overpotential = -1.25 V vs. Ag/AgCl on PVC-coated wire in 0.1 M $ZnCl_2$ containing: i.) No additive, ii.) 1 wt% PEG, iii.) 1 wt% thiourea.

Visual inspection of the wire electrodes (from the microscope-mounted camera) after the potentiostatic plating tests from Figure 2 confirms dendrite suppression by additives. Figure 3 shows the deposit morphology for each of the three baths. The additive-free electrode in panel a) has significant dendrite growth, whereas the electrodes in b) with 1 wt% PEG and c) with 1 wt% thiourea are smooth and dendrite-free. Thus, both PEG and thiourea strongly suppress zinc dendritic growth.

Figure 3. Comparison of wire electrodes after plating in 0.1 M $ZnCl_2$ for 8 minutes at -1.25 V vs. Ag/AgCl. a) No additive, b) 1 wt% PEG, c) 1 wt% thiourea.

In the present talk, we will outline the effect of additive molecular weight and concentration on its dendrite suppression strength. Additionally, we link our observations to a comprehensive mathematical model for additive-assisted dendrite suppression (extending a previously developed model for lithium electrodeposition).[4]

References:

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