

Synthesis of CuZn Alloy Films through Electrodeposition

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Abstract—Porous copper current collectors have been shown to be an effective method for reducing dendrite growth in lithium-metal anodes. Thicker and more porous copper films are desirable due to their ability to store more lithium while successfully inhibiting dendrite growth. In order to optimize the synthesis of porous copper films, Cu-Zn (brass) alloys were deposited on a copper foil substrate and electrochemically dealloyed to create porous copper structures. The effects of polyethylene glycol (PEG) in the presence of chloride ions and agitation of the electrolyte on the phase and morphology of the resulting films were investigated. The addition of PEG was found to increase the electrode potential during electrodeposition. Agitation of the electrolyte lead to a substantial decrease in electrode potential and resulted in a thick (~26 μm) and highly porous (~81%) film. Samples with both PEG additive and agitation were then tested under various electrolyte compositions and deposition conditions to optimize the deposition process.

I. INTRODUCTION

Lithium-metal anode batteries are an increasingly promising alternative to the industry-standard lithium ion batteries due to the higher theoretical capacity and more negative electrochemical potential of lithium metal, allowing the manufacturing of batteries with a higher specific capacity. A major limitation on the performance of lithium-metal batteries is the growth of lithium metal dendrites during repeated charging and discharging [1]. When exposed lithium experiences a buildup of critical charge density, lithium dendrites deposit onto the anode, which can reduce the amount of electrochemically active lithium in the cell or cause potentially dangerous short-circuits. Depositing lithium into a porous copper current collector has been shown to be an effective method of improving the cycling performance of lithium-metal batteries.[2] By increasing the electrochemically active surface area, total current density across the cell is reduced, reducing the likelihood of critical charge density buildup and thus lithium dendrite growth. However, depositing too much lithium into the current collector will result in a flat lithium surface, negating its effectiveness. As such, increasing the thickness and porosity of the current collector is desirable to increase the amount of lithium that can be effectively present in the anode. However, synthesis of current collectors through the electrodeposition of pure copper has only yielded high-porosity films at low thicknesses (~5 μm), suggesting that new methods must be used to improve on this technology.

II. METHODS

A. Static Bath Experiments

To synthesize CuZn alloy films, a baseline electrolyte was formed from 0.03 M CuSO_4 (99.9%, Sigma-Aldrich), 0.50 M ZnSO_4 , (99.9% Sigma-Aldrich), and 0.25 M trisodium citrate (99.9%, Sigma-Aldrich). 40 mL of this electrolyte was produced in a 150 mL beaker. A Cu foil working electrode with surface area 2.25 cm^2 and Pt counter electrode were inserted into the electrolyte and connected to a LAND battery testing system. For static bath depositions, the samples were held under galvanostatic conditions (5 mA/cm^2) for 1 hour to electroplate the alloy onto the copper substrate. A 0.8 M solution of PEG 200 (99.9% Sigma-Aldrich), 0.2 M solution of PEG 600 (99.9% Sigma-Aldrich) and 45 mM/0.2 M solutions of NaCl were produced for use as additives to the electrolyte. The range of concentrations for PEG and Cl⁻ were found to produce results on the morphology and electrochemical profile of Cu depositions in [3] and [4] (Thin Solid Films 546 2013, J Electrochem 2014).

TABLE I: Static Bath Experiments

Experiment	Bath Additives
1	None
2	200 ppm PEG 200
3	200 ppm PEG 200 + 2 ppm Cl ⁻
4	200 ppm PEG 200 + 4 ppm Cl ⁻
5	200 ppm PEG 600 + 4 ppm Cl ⁻
6	200 ppm PEG 600 + 1 mM Cl ⁻

B. Agitated Bath Experiments

80 mL of electrolyte solution were prepared, consisting of the treatment group concentrations of metal salts, 0.25 M sodium citrate, 1 mM PEG 600, and 4 ppm Cl⁻. Samples were agitated by a ~300 rpm magnetic stirrer under the deposition conditions in Table II. A sample was produced for every combination of electrolyte composition and deposition condition. The goal of the electrolyte compositions was to observe the effects of changes in weight% composition of the bath on the resulting composition and morphology of the deposited alloys. Composition 3 was tested in order to determine if the morphologies observed in Composition 1 could be replicated without using zinc. Treatments B and C were used to produce thinner films for potential small angle x-ray analysis, as well as observing the morphological effects of lower current density and deposition time.

TABLE II: Design of Agitated Bath Experiments
A. ELECTROLYTE COMPOSITIONS

Treatment Number	Composition
1	0.03 M CuSO ₄ , 0.50 M ZnSO ₄
2	0.03 M CuSO ₄
3	0.015 M CuSO ₄ , 0.515 M ZnSO ₄

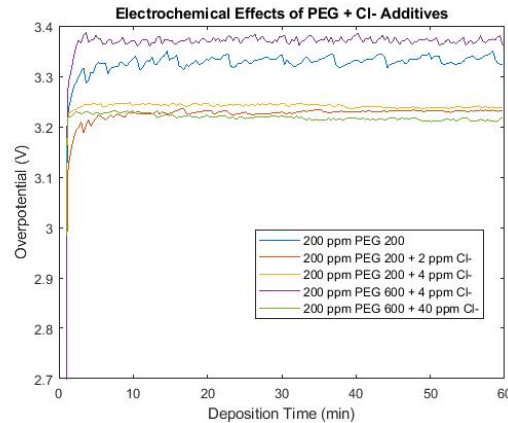
B. DEPOSITION CONDITIONS

Treatment	Condition (current density, time)
A	5 mA/cm ² , 1 hour
B	2.5 mA/cm ² , 1 hour
C	5 mA/cm ² , 30 min

III. RESULTS AND DISCUSSION

A. Effects of PEG Addition

The addition of PEG to the electrolyte bath resulted in an increase in electrode overpotential in comparison to the baseline electrolyte composition. The increase in overpotential was consistent for the duration of the deposition, suggesting that PEG can suppress CuZn deposition as well as Cu deposition. The addition of Cl⁻ ions to the electrolyte led to a minor decrease in overpotential and reduced the magnitude of fluctuations in potential during the deposition. Increasing the molecular weight of PEG to 600 had a corresponding increase in electrode potential as well, which is consistent with the experimental data in [4].

Figure 1: Effects of PEG and Cl⁻ addition on the electrochemical profile of deposition.

Samples synthesized in the static bath were analyzed through x-ray diffraction (XRD). For static bath depositions, CuZn alloys were primarily deposited in 2 phases. The peaks observed in XRD analysis correspond with the characteristic peaks for Cu₅Zn₈ and CuZn₅. The addition of PEG and Cl⁻ did not change the phases deposited, but the differences in relative peak intensity suggest that the additives may affect the overall composition of the deposited film.

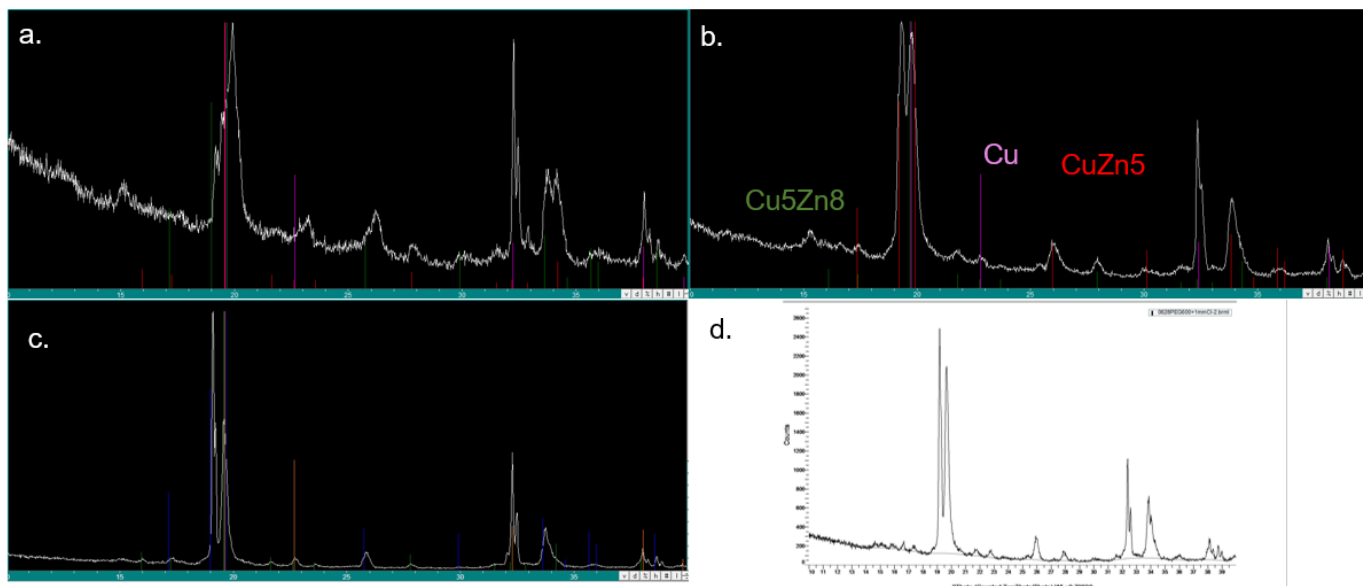


Figure 2: XRD spectra for a. PEG 200 + 2 ppm Cl⁻ b. PEG 200 + 4 ppm Cl⁻ c. PEG 600 + 4 ppm Cl⁻ d. PEG 600 + 40 ppm Cl⁻. The characteristic peaks are the same in each sample.

Observation of alloy morphology through SEM analysis also suggests the presence of two phases in the deposited films. Two distinct secondary structures were observed in the SEM images, with good homogeneity throughout the samples. Though the particle structure is largely unchanged with the addition of PEG and Cl⁻, the size distribution and relative abundance of each phase may vary with additives. A sample prepared using composition 5 (addition of 200 ppm PEG 600 + 4 ppm Cl⁻) was dealloyed under a constant voltage of 0.4 V for 4 hours and exhibited a porosity of 56% at a thickness of 9.5 μm .

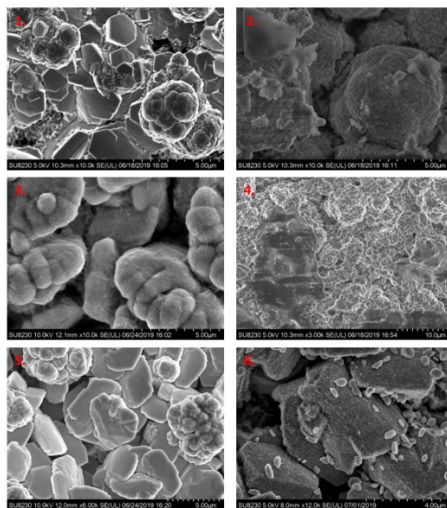


Figure 3: SEM images of samples corresponding to treatments in Table I.

B. Effects of Agitation

Samples prepared in 80 mL of composition 5 and agitated by a magnetic stirrer at about 300 rpm exhibited extremely high thickness ($\sim 26 \mu\text{m}$) and porosity ($\sim 81\%$). The mean electrode overpotential decreased significantly in comparison to static bath experiments under the same conditions ($\sim 675 \text{ mV}$). Furthermore, the composition and morphology of the agitated samples changed considerably, as the films consisted of almost entirely pure copper and produced porous, spherical secondary particles.

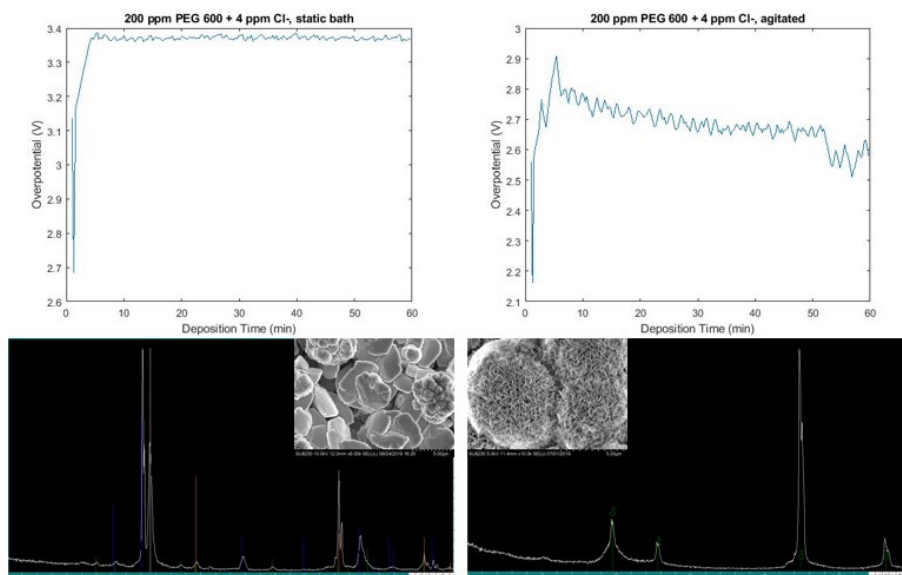


Figure 4: Comparison of electrochemical, SEM, and XRD data for static bath and agitated samples.

C. Optimization of Agitated Samples

In order to further optimize the thickness and porosity of the deposited copper samples, the concentration of metal ions in solution and deposition conditions, namely current density and deposition time, were varied across a series of samples. The design of this experiment is detailed in Table II. The original electrolyte composition and deposition conditions produced the most favorable results, though some experiments did not produce consistent data due to the foil electrode detaching from the beaker during deposition. Though the composition of the original porous film is mainly copper, films with similar properties were not replicated in the experiments using only copper sulfate in the electrolyte.

TABLE III. Thickness and Porosity of Deposited Films

Thickness (μm)	Treatment Conditions			
Bath Composition		A	B	C
	1	26.1	4.5	14.2
	2	11.5	5.5	4.5
	3	19.1	24.5	8.5
Porosity (%)	Treatment Conditions			
Bath Composition		A	B	C
	1	81.2	30	68.2
	2	37	--	--
	3	67.5	58	--

IV. CONCLUSION

Addition of PEG and Cl⁻ was shown to suppress the deposition of CuZn alloys. Alloys were predominantly deposited in two phases in varying ratios, with XRD peaks corresponding to Cu₅Zn₈ and CuZn₅ for all static bath experiments. Films deposited exhibited good homogeneity and thickness. Agitating electrolyte consisting of composition 5 during deposition produced a highly thick and porous pure copper film. The results of optimization of the deposition process suggest that the original metal ion composition and deposition conditions yielded the highest thickness and porosity of the treatments attempted. Although further experimentation and integration of lithium is needed to apply these films in battery applications, the results suggest that high-porosity copper films can be synthesized at higher thicknesses than pure copper depositions.

V. REFERENCES

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