High Concentration Supporting Electrolytes for Enabling Stable Zinc Electrodeposition

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Abstract:

Zinc metal is an excellent choice for metal based secondary batteries not only because of its high abundance and low toxicity, but also due to its high anodic redox potential and energy density when compared with cells that use nickel and lead anodes. Furthermore, aqueous electrolytes can be used, thus minimizing the risk of thermal runaway or explosion. A common problem faced in such batteries is the formation of dendrites, needle-like structures, which can pierce separators and produce sudden short circuits. In this work, the electrodeposition of zinc metal was visualized using an in-house built electrochemical setup with a base electrolyte of zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) dissolved in water. Results discussed in this report show that aqueous electrolytes containing higher concentrations of zinc salts and zinc cells operated at lower current densities exhibit significant less tendency to dendrite formation. Additionally, an enhanced stability at a current density as high as 1000 mA/cm^2 was obtained using high concentration of zinc sulfate solutions and sodium-salts as supporting electrolytes.

Summary of Research:

Zinc metal batteries are in development as a new generation of battery systems which can achieve high energy densities to power full electric vehicles [1]. Zinc metal is an excellent choice for the anode in secondary batteries not only because of its high natural abundance and low toxicity, but also due to its high anodic redox potential and energy density when compared with the commonly used nickel and lead anodes [2]. Furthermore, because the cells can be operated in aqueous electrolytes, this minimizes the risk of thermal runaway or fires. A common problem faced in such batteries is the formation of dendrites, needle-like structures, which can pierce separators and produce sudden short circuits [1,2].

The purpose of this project was to investigate how conditions in the electrolyte influence dendrite formation during zinc electrodeposition. Electrolyte salt concentration, current density and a secondary/ supporting electrolyte salt additive were studied in order to determine their respective relationship with dendrite formation. Electrodeposition was visualized in an in-house built electrochemical cell which consisted of a glass slide, zinc metal (99.994%, Alfa Aesar), which acted as the electrodes, and copper strips. The electrode separation distance of each cell was maintained constant at 1 cm apart. Each electrodeposition experiment was filmed for one hour under an optical microscope (Olympus BX51) at a constant current density. Each electrolyte solution was prepared using zinc sulfate heptahydrate, $ZnSO_4 \cdot 7H_2O$ (J.T. Baker), and sodium sulfate, Na_2SO_4 (Macron Fine Chemicals), dissolved in deionized water at different molarities. Impedance spectroscopy was also done in order to calculate the conductivity and interface resistivity of each electrolyte solution.

Results and Conclusions:

The effect of concentration, current density and the use of a secondary salt additive were studied in order to assess their respective influence on Zn dendrite formation. As shown in Figures 1 and 2, using higher concentrations of zinc salts in the electrolyte solution limits dendrite formation significantly. Also using lower current densities and sodium sulfate as a secondary salt additive have the same effect as well. As shown in Figure 3, a stable electrodeposition was obtained using a current density as high as 1000 mA/cm^2. This was done using a mix electrolyte solution of zinc sulfate heptahydrate at 1.70M and sodium sulfate at 0.80M.
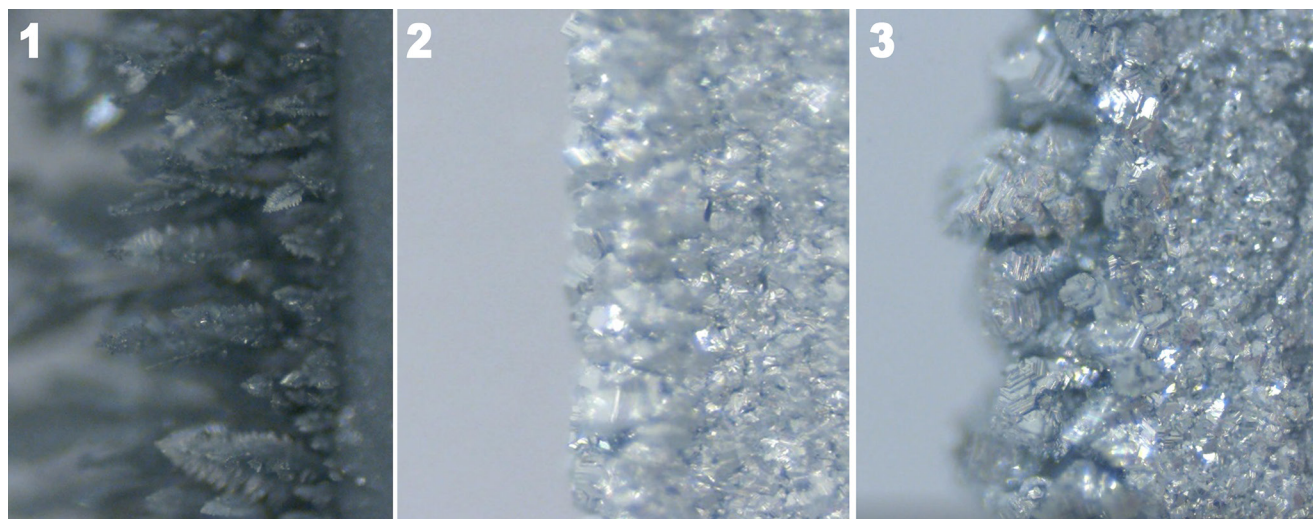
Figure 1, left: Electrodeposition of zinc sulfate heptahydrate at a concentration of 0.10M and a current density of 400 mA/cm² after one hour. Figure 2, middle: Electrodeposition of zinc sulfate heptahydrate at a concentration of 2.00M and a current density of 400 mA/cm² after one hour. Figure 3, right: Electrodeposition of a mix electrolyte solution of zinc sulfate heptahydrate at a concentration of 1.70M and sodium sulfate at a concentration of 0.80M at a current density of 1000 mA/cm² after one hour.

As a result of zinc achieving a stable deposition at a current density of 1000 mA/cm², indicates that zinc metal batteries are an excellent choice for further development to increase energy density, battery life and increase further applications.

Impedance spectroscopy was used to characterize the effect of the salts on ion transport in bulk electrolytes and at the interfaces between electrodes and electrolytes. Electrolyte concentration displays a linear effect on conductivity, where higher concentrations showed higher conductivity, as shown on Figure 4.
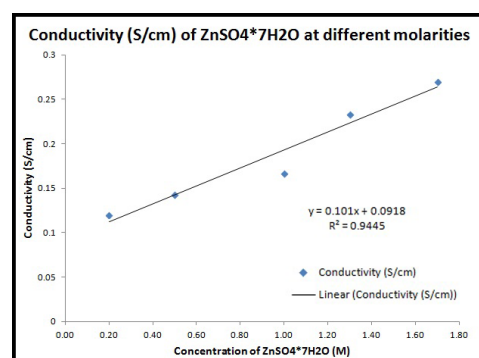
On the contrary, using higher concentrations of zinc have a tendency of increasing interfacial resistance. Also, the interfacial resistance using the supporting electrolyte had the same tendency as before, where higher concentrations showed higher interfacial resistance. Therefore, it can be concluded that the sodium was participating in the electrodeposition process.

Figure 4: Linear regression of conductivity (S/cm) versus molarity of zinc sulfate heptahydrate.

Future Work:

Due to sodium participating in the electrodeposition process, silica nanoparticles and ionic liquids will be used as stable salt additives in order to study how it affects dendrite formation. The growth rate of each electrodeposition will be calculated using a Matlab code. Also, the transferance number of zinc in solutions will be determined as well.

Acknowledgements:

References:

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[2] Sun, K. E. K.; Hoang, T. K. A.; Nam, T.; Doan, L.; Yu, Y.; Zhu, X.; Tian, Y.; Chen, P. ACS Appl. Mater. Interfaces. 2017, 9, 9681.9687.