

Lithium Plating in the Presence of Alkali and Alkaline Earth Cations

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A lithium metal anode is an intriguing possibility for secondary batteries because it represents the maximum achievable energy density for a lithium-based anode, 3861 mAh/g instead of 329 mAh/g for commercial graphite anodes. However, the formation of lithium dendrites is one factor preventing the implementation of lithium metal anode batteries because their growth can short-circuit the battery and lead undesired thermal effects.

Recently, we have shown that sodium will co-deposit with lithium from ionic liquids to form a non-dendritic deposit [1], [2]. Work has also been published on an electrostatic shield mechanism, where the deposition potential of an additional metal ion is shifted to negative that of lithium by dissolving very low concentrations[3].

Both cases show that alkali metal ions can affect the morphology of deposited lithium. This study will present a survey of the effects of alkali and alkaline earth metal ions on the morphology of lithium metal deposited from a quaternary ammonium ionic liquid, butyltrimethylammonium bis(trifluoromethanesulfonyl)imide (QA-TFSI). Metals discussed will include sodium, potassium, magnesium and calcium.

A detailed study on the nucleation and early morphology has been completed for the sodium case. In QA-TFSI, lithium dendrites appear immediately upon nucleation. Addition of a small amount of sodium changed the nucleation geometry of the deposited metal to a rounded beads, rather than cylindrical dendrites. Analysis of current-time transients showed significant deviations from conventional geometry based growth models due to the effect of the solid electrolyte interface (SEI) layer. The model was adapted to better explain the behavior observed from electrochemical, SEM, and SIMS data.

The concentration of the metal ions has an effect on both the deposit morphology and the redox efficiency of the system. According to the Nernst equation, it is

possible to shift the reduction potential of the second metal ion, which may affect the ions efficacy in reducing dendrites; however it is not possible to reduce all metal ions from TFSI salts so the importance of this potential shift is unclear.

Despite claims that dendrites are a major cause of lithium metal cycling inefficiency, adding metal ions for the prevention of dendrites did not yield higher coulombic efficiency. In most cases, while adding metal ions positively affected the morphology, the cycling efficiency decreased slightly. This could be due to irreversible reduction of some metal ions.

References

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