Effect of Foreign Metal Ions on the Morphology and Redox Efficiency of Lithium Metal

Johanna K. Stark, Paul A. Kohl School of Chemical & Biomolecular Engineering Georgia Institute of Technology 311 Ferst Dr NW, Atlanta GA 30332-0100

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 codeposit with lithium from ionic liquids to form a nondendritic 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(trifluoromethansulfonyl)imide (QA-TFSI). Metals discussed will include sodium, potassium, magnesium and calcium.

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

- J. K. Stark, Y. Ding, and P. A. Kohl, "Dendrite-Free Electrodeposition and Reoxidation of Lithium-Sodium Alloy for Metal-Anode Battery," *Journal of The Electrochemical Society*, vol. 158, no. 10, pp. A1100–A1105, 2011.
- [2] J. K. Stark and P. A. Kohl, "Nucleation of Electrodeposited Lithium Metal: Dendritic Growth and the Effect of Co-deposited Sodium," *Journal of The Electrochemical Society*, 2013 (under review).
- [3] F. Ding, W. Xu, G. L. Graff, J. Zhang, M. Sushko, X. Chen, Y. Shao, M. H. Engelhard, Z. Nie, J. Xiao, X. Liu, P. V Sushko, J. Liu, and J.-G. Zhang, "Dendrite-Free Lithium Deposition via Self-Healing Electrostatic Shield Mechanism.," *Journal of the American Chemical Society*, Feb. 2013.