SYSTEMATIC INVESTIGATION OF MORPHOLOGICAL TRANSITIONS ON LITHIUM METAL ANODES

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INTRODUCTION

The goal of this project is to make metallic lithium the last and best anode for lithium batteries. This material offers several advantages over the graphitic negative electrode materials currently in use. However, problems with safety and efficiency during prolonged battery operation block its implementation into advanced lithium batteries for hybrid electric vehicles. It is well known that changes in lithium metal surface chemistry and morphology that occur during cycling of the battery lead to dendritic/mossy growth and that these high surface area structures exhibit enhanced reactivity which is the direct cause of instability and significant reduction of the life of the battery [1]. Extensive studies of the chemical and physical changes in cells containing metallic lithium anodes had been performed. However, the vast majority of these studies have focused on the bulk or macroscopic properties and morphologies of the cell components using mostly post-mortem analysis [2], and in spite of the wealth of information gained so far, efforts to inhibit dendritic growth in these metallic electrodes have met with modest success [3].

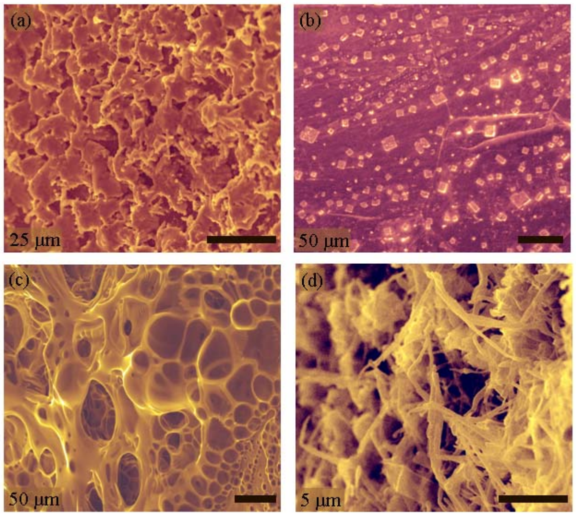

Figure 1: False-color SEM images showing the time and cycle-dependent changes in the surface morphology of the SEI layer: (a) 20 sec, (b) 5 min, (c) 1 cycle, (d) 150 cycles.

METHODS AND RESULTS

In this work, we focus on the micro- and nano-scale changes that occur on the surface of metallic lithium previous to cycling (i.e. formation of Solid-Electrolyte Interface or SEI layer, upon contact with solvent-electrolyte system), at different cycle lengths, and after failure of the battery. We have discovered that previous thin-film models of the SEI on metallic lithium anodes can only adequately describe it at macroscopic lengths scales (above ~ 100 microns) and that at lengths scales below 50 microns complex tridimensional patterns and morphological transitions can be observed at different cycling periods and conditions. And example of this phenomenon is illustrated in Figure 1. In this figure we show how the morphology of the surface of a lithium electrode changes with immersion time in an electrolyte system commonly used in lithium batteries (a-b), and after cycling in a coin cell at two different cycling lengths (c-d). A marked difference in surface structure can be observed for both the un-cycled and cycled electrodes, with wire-like dendritic growth becoming the final morphology. We use Scanning Electron Microscopy (SEM) and electrochemical methods to systematically study these morphological transitions with the goal of determining the precise onset conditions for dendritic growth, and how it relates to dynamic changes in the cell's chemical environment. In this manner, cell chemistries that could effectively quench the detrimental changes in the surface of the lithium electrode could be developed, which may yield significant improvement in battery performance and stability and enable its safe usage in hybrid electric vehicles.

REFERENCES

1. (a) T. Tatsuma, M. Taguchi, M. Iwaku, T. Sotomura, and N. Oyama, *J. Electroanal. Chem.* **472**, 142 (1999), (b) C. Brissot, M. Rosso, J.-N. Chazalviel, and S. Lascaud, *J. Electrochem. Soc.* **146**, 4393 (1999), (c) D. Aurbach, E. Zinigrad, H. Teller, and P. Dan, *J. Electrochem. Soc.* **147**, 1274 (2000).
2. (a) G. Gachot, S. Grugeon, M. Armand, S. Pilard, P. Guenot, J.M. Tarascon, S. Laruelle, *J. Power Sources* **178**, 409 (2008), (b) C. Naudin, J.L. Bruneel, M. Chami, B. Desbat, J. Grondin, J.C. Lassegues, L. Servant, *J. Power Sources* **124**, 518 (2003).
3. (a) D. Aurbach, E. Zinigrad, H. Teller, Y. Cohen, G. Salitra, H. Yamin, P. Dan, and E. Elster, *J. Electrochem. Soc.* **149**, A1267 (2002), (b) X.W. Zhang, Y. Li, S.A. Khan, P.S. Fedkiw, *J. Electrochem. Soc.* **151**, A1257 (2004).