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MORPHOLOGICAL INSTABILITIES IN SOLID STATE LITHIUM BATTERIES: AN EXPERIMENTAL AND THEORETICAL INVESTIGATION

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Most customers are satisfied with their portable electronic appliances but dissatisfied with the limited life and power of the batteries, which drive the appliances. While battery performance has improved in recent years, it has not kept pace with the power demands of the devices and their users. In this regard, lithium metal batteries offer a competitive alternative to existing battery systems because of their improved energy density. Although rechargeable batteries using metallic lithium have been under development and some early stage commercialization for the last two decades, their widespread commercial use has been hindered by issues such as materials compatibility (a direct consequence of the high reactivity of lithium) and 'dendrite' (surface pattern) formation during cycling. Surface reconstruction as a result of the pattern formation often leads to premature failure of the battery system.

In the 1990's, researchers at Oak Ridge National Lab (ORNL) demonstrated break-through performance in a Li metal anode stability by inserting a thin inorganic membrane between the anode and the cathode. This thin (~2µ) Li ion conductor is a nitrogen modified vapor deposited lithium phosphate, called "LiPON". In the years since the original demonstration, numerous groups have shown that this solid Li/solid electrolyte interface is capable of tens of thousands of cycles, while the Li/liquid electrolyte cannot approach even hundreds of cycles.

While the high cycle-life success stands on its own, detailed SEM and TEM analysis has shown that stripping/deposition in this configuration results in non-uniformities of the Li metal surface, both at and beyond the interface. Two questions come to mind: how is a solid/solid interface maintained during cycling and how do inhomogeneities translate to positions distant from the interface. In an effort to probe these complex questions, we proposed several hypotheses and tested them mathematically. In this study we focus on one possibility.

The mathematical method that we have developed derives heavily from other morphological instability modeling efforts in the electrochemical literature [1-3]. However significant changes were made in the existing theories to better describe the lithium battery under investigation as well as to justify assumptions made in our hypothesis. The resulting governing equations were linearized and subsequently used in perturbation analysis in order to determine the system stability. The system response was parameterized against operating variables such as applied current density and material properties such as kinetic parameters, conductivity, interfacial energy etc.

Subsequently, model predictions were compared to experimental data, wherein the ORNL device was cycled for a few thousand times keeping the output voltage during discharge close to a constant value. The top surface of the battery was monitored as a function of time in the experiments. Comparisons were made with experimentally observed wavelength relatively uniform pattern which results on the surface and with the corresponding growth rate of the amplitude of the surface roughness. The model predictions were in good agreement with the experimental observations.

The ultimate goal of this project is to develop a stability map that shows conditions for 'stable' (acceptable number of cycles) battery operation. This model provides the user with a tool that can be used to predict the battery life of a given lithium-electrode-cathode combination subjected to specified operating parameters. This will further help target appropriate applications consistent with the battery capabilities as well as guide improvements, which can make it more competitive in other portable energy devices.

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