Electrochemical Modeling of Lithium-Ion Cells

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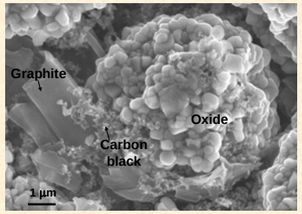
CAUTION
HIGH EQUATION DENSITY

Introduction

Various analytical diagnostic tools are being used to study a high-power lithium-ion battery technology for hybrid electric vehicle applications under the Department of Energy's Advanced Technology Development Program. Also under this program, a series of electrochemical studies are being conducted to examine the performance and aging characteristics of these batteries. Results indicate that the positive electrode is the main contributor to the cell's overall electrochemical performance degradation during aging. This modeling effort is directed toward associating changes that are seen in the positive electrode's post-test analytical diagnostic studies with the electrode's electrochemical performance degradation observed during testing.

Positive Electrode's Composite Structure



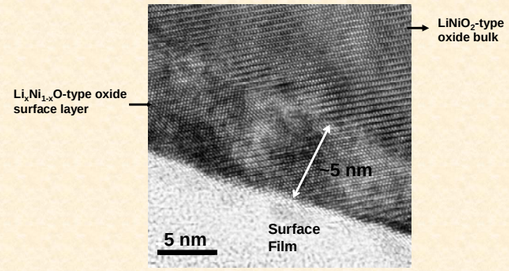
Challenge

The positive electrode under study has a composite structure of a layered nickel oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) active material powder, carbon black and graphite powder additives for distributing current, and a PVDF polymer binder, all on an aluminum current collector. The porous composite positive electrode is flooded with a non-aqueous electrolyte ($LiPF_6$ dissolved in a mixture of EC and EMC). A Celgard microporous membrane, also flooded with electrolyte, is used as the separator between the positive and negative electrodes. Current enters the positive electrode as lithium ions through the electrolyte and leaves as electrons through the current collector. The model must be able to relate the interaction of all the many microscopic physiochemical phenomena occurring in the electrode to macroscopically measured variables such as electrode voltage and current.

Argonne's Approach

The approach taken in this effort is to develop a model based on the analytical diagnostic studies, establish the model parameters, and conduct parametric studies with the model. The parametric studies are conducted to gain confidence with the model, examine degradation mechanisms, and analyze cell limitations. The general methodology for the electrochemical model follows the work of Professor Newman at Berkeley. Concentrated solution theory is used to describe the transport of salt in the electrolyte. Volume-averaged transport equations account for the composite electrode geometry. Electrode kinetics, thermodynamics, and diffusion of lithium in the oxide active particles are also included. The detailed theoretical description of the oxide active material/electrolyte interface, commonly referred to as the solid electrolyte interface or SEI, is based on post-test analytical diagnostic studies. The SEI region is assumed to be a film on the oxide and an oxide layer at the surface of the oxide. The film on the oxide is taken to be an ill-defined mixture of organic and inorganic material through which lithium ions from the electrolyte must diffuse and/or migrate across to react electrochemically at the surface of the oxide. The lithium is then assumed to diffuse through the oxide surface layer and into the bulk oxide material in the particle. A double layer capacity is added in parallel with the Butler-Volmer kinetic expression. A localized electronic resistance between the current carrying carbon and the oxide interface can be added, and a secondary film capacitance can also be included.

High-Resolution TEM Image of Solid Electrolyte Interface



Active Material Impedance Expressions

$$Z_s = \left(\frac{-K_s \frac{dU_b}{dc_{sb}}}{z_+ F\sqrt{D_{si}\, j\omega}}\right)\left(\frac{1+K_s\sqrt{\frac{D_{sb}}{D_{si}}}\tanh\left(\delta_b\sqrt{\frac{j\omega}{D_{sb}}}\right)\tanh\left(\delta_i\sqrt{\frac{j\omega}{D_{si}}}\right)}{K_s\sqrt{\frac{D_{sb}}{D_{si}}}\tanh\left(\delta_b\sqrt{\frac{j\omega}{D_{sb}}}\right)+\tanh\left(\delta_i\sqrt{\frac{j\omega}{D_{si}}}\right)}\right)$$

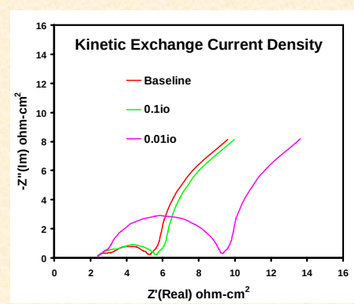
$$Z_f = \frac{\delta_f}{\kappa_f} + \left(\frac{-s_+ RT\delta_f}{nF^2 c_+^0 D_+ z_+}\right)\frac{\tanh\left(\sqrt{\frac{j\omega\delta_f^2}{4D_+}}\right)}{\left(\sqrt{\frac{j\omega\delta_f^2}{4D_+}}\right)}$$

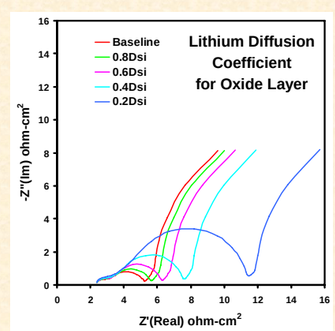
Electrolyte Concentrated Solution Transport Equations

$$i_2 = -\frac{\kappa\varepsilon}{\tau}\frac{\partial\Phi_2}{\partial x} - \nu RT\frac{\kappa\varepsilon}{F\tau}\left(\frac{s_+}{n\nu_+}+\frac{t_+^o}{z_+\nu_+}\right)\left(1+\frac{\partial \ln f_\pm}{\partial \ln c}\right)\frac{1}{c}\frac{\partial c}{\partial x}$$

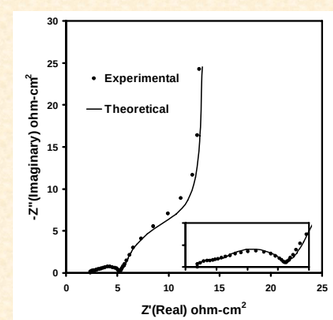
$$\varepsilon\frac{\partial c}{\partial t} = \frac{\varepsilon}{\tau}\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{1}{z_+\nu_+ F}\frac{\partial\left[\left(1-c\bar{V}_e\right)\left(1-t_+^o\right)i_2\right]}{\partial x}$$

Sample Parametric Studies Conducted to Examine Changes in the Positive Electrode Impedance with Interfacial Parameters





Comparison of Electrochemical Model and Experiment for the Positive Electrode AC Impedance (100 kHz-1 mHz)



Conclusions

In using the electrochemical model to examine aging effects associated with the positive electrode, three possible sources for the observed interfacial impedance increase were identified. First, changes in the electrolyte/oxide interfacial structure and/or properties could have a significant impact on the interfacial impedance. This is likely the primary source of the interfacial impedance increase. Further, the size of the parameter changes needed to account for the impedance increase suggests that there is a general degradation of the interfacial properties. Second, a loss of positive electrode capacity, particularly isolation of the finer oxide particles would also cause the interfacial impedance to increase. Loss of electrode capacity can at best only be a minor contributor to the positive electrode's interfacial impedance. Finally, a large increase in the resistance between the electronically conducting carbon matrix and oxide active material could result in an increase in the positive electrode interfacial impedance, provided the carbon matrix has a significant double layer capacitance associated with it.

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