Energy Storage Technologies

Use of Acoustic Emissions for Understanding Degradation in Anode Materials for Lithium Ion Batteries

Background

Volume changes during cycling are typical of intercalation compounds in batteries. Related stress and strain can cause mechanical degradation. The role of mechanical degradation in capacity fade is under debate. A fundamental understanding of the accumulation of point defects, crack initiation, crack growth, and particle fracture and sliding is needed to understand their roles in capacity fade. An understanding of those mechanisms in different intercalation compounds can be used to develop "fatigue-like" models to create better lifetime predictions and guidance for microstructure design of advanced electrodes.

Technology

Acoustic emission (AE) spectroscopy is used to detect, sort, and classify mechanical events such as crack initiation, crack growth, particle or coating fracturing, and particle loosening and sliding during cycling. We plan to use additional characterization methods such as x-ray diffraction, Raman spectroscopy, and various microscopy techniques in situ to link acoustic signatures to "real" events. This will allow for a deeper fundamental understanding of those mechanisms and their contributions to capacity fade. In a later stage of the project, "fatigue-like" models will be developed that can predict cycle life and guide advanced microstructure development for improved mechanical performance (Figure 1).

Status

Initially, carbon electrodes were studied. Future studies will include a variety of other electrode materials. Several classes of events were identified from the AE data. Type 1 emissions may result from crack initiation or propagation in the solid-electrolyte interphase (SEI) layer that develops on and around individual mesocarbon microbead (MCMB) particles. Other authors have associated emissions similar to Type 2 with gas formation. Because CO_2 is a by-product of SEI formation, the formation of CO_2 bubbles is a likely cause of this emission type. A Type 3 emission is characteristically very similar to a Type 2, but with a less-defined waveform and frequency peak

Figure 1: An x-ray diffractometer is used to evaluate how battery materials change during charges and discharges.

Benefits

- *Establish methodology for detection and monitoring of mechanical degradation in lithium ion batteries.*
- *Develop understanding of the relationship between mechanical degradation and capacity fade.*
- *Develop guidance for future battery materials and structure developments.*

average and duration. The cause of this event type is unclear, but it may result from either shifting of the MCMB particles past one another as they expand and contract or tearing of the composite film.

Events were manually sorted into class types and were put in a scatter plot to establish grouping trends. The values of an event's duration, amplitude, and frequency centroid parameters proved particularly important in discriminating between different event types. Amplitude was very useful in filtering electromagnetic interference events that showed very regular emission amplitudes. The duration, amplitude, and frequency centroid proved to be statistically different between Type 1, 2, and 3 emissions based on Student's t-tests with 95% confidence. Figure 2 shows a scatter plot matrix of these three parameters.

A scanning electron microscope (SEM) image of the cycled electrode showed the presence of a fractured SEI layer (see Figure 3). The formation of these cracks is the most likely source of Type 1 events. SEM images of the electrodes in cross section showed a 28% increase in thickness, from 25 to 32 μm, as a result of cycling. This may indicate a loosening of the composite film as cycling proceeds, which may allow for an increased amount of particle shifting and hence the observed increase in Type 3 emissions as cycling proceeds.

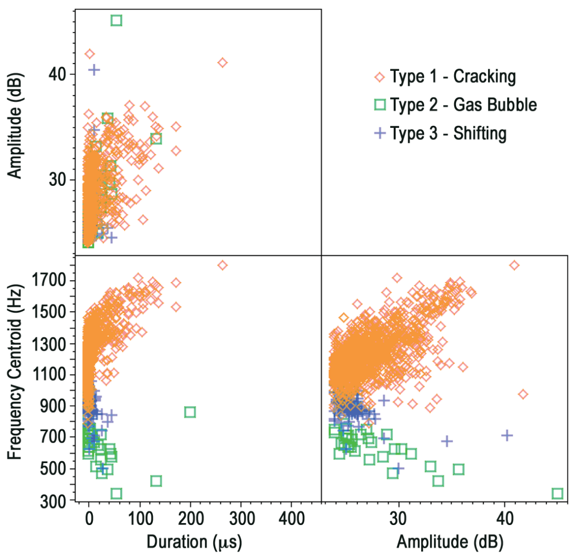

Figure 2: Scatter plot of duration, amplitude, and frequency centroid showing grouping of emissions useful for identifying event types.

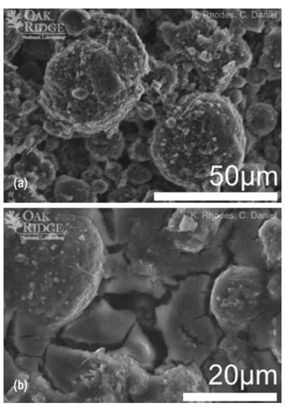

Figure 3: Scanning electron micrograph of (a) a fresh MCMB electrode and (b) the electrode after cycling, showing a fractured SEI layer.

Parts of this research were performed at the High Temperature Materials Laboratory, a National User Facility sponsored by the U.S. Department of Energy, located at ORNL.

Contacts

Claus Daniel
Oak Ridge National Laboratory
(865) 241-9521
danielc@ornl.gov

David Howell
Team Leader
Hybrid Electric Systems Subprogram
U.S. Department of Energy
(202) 586-3148
david.howell@ee.doe.gov

A Strong Energy Portfolio for a Strong America

Energy efficiency and clean, renewable energy will mean a stronger economy, a cleaner environment, and greater energy independence for America. Working with a wide array of state, community, industry, and university partners, the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy invests in a diverse portfolio of energy technologies.