

Failure Mechanism Diagnosis of Lithium Ion Batteries

Ping Liu, Kevin Kirby, and Elena Sherman
HRL Laboratories, LLC, Malibu, CA 90265

There have been intensive studies on failure mechanisms of lithium-ion batteries in recent years, most notably for automotive applications [1]. In general, the loss of capacity is associated with one or several of the following factors: loss of active lithium, loss of cathode or anode active materials, and increase of cell resistance. For long term applications of lithium-ion batteries, it is important to both qualitatively and quantitatively identify the relative contributions of these factors so that their service life can be reasonably modeled and predicted.

In this presentation, we employ electrochemical impedance spectroscopy (EIS) to characterize cells that have been aged at high temperatures and subsequently cycled at various depths of discharge. The cells characterized are manufactured by Saft and have nominal capacities of 40 Ah. It has been found that capacity degradation increases significantly with increasing depth of discharge (DOD) while the loss of rate capability is minimal. Figure 1 shows that the C/32 capacity loss at 80% DOD is 17% while at 60% DOD it is 6%. The values for C/2 are 20% and 7%, respectively. It is evident that the overall capacity loss is dominated by material loss rather than kinetic loss which may include internal resistance increase.

Figure 2 displays the EIS spectra of the cell cycled at 80% DOD. The evolution of the spectra during the life of the cell indicates a great increase in resistance during storage and a significant decrease during subsequent cycling. A possible explanation is that the solid electrolyte interface (SEI) layer on the anode experiences significant growth during aging but is subsequently disrupted during cycling due to the volume modulation associated with lithium insertion and removal. Recent work indicates that similar process may also take place on the cathode [2]. We also monitor the evolution of capacitance components of the impedance spectra. The capacitance does not change during the storage period but increases greatly during cycling. Since capacitance is often proportional to electrode surface area, our results are indicative of major microstructural changes on the electrodes, most likely roughening of electrode surface and fracturing of active material particles. These changes may in turn lead to cathode or anode material loss due to electrical isolation of particles. They may also lead to further active lithium loss due to the increasing area that needs to be protected by the SEI layer. Both these material losses can result in further capacity loss.

We have analyzed the effect of DOD on the evolution of EIS spectra. Internal resistance is found to be higher at low DODs, consistent with our proposal that the disruption of SEI layer is more profound at higher DODs. Microstructural changes as indicated by increased capacitances increase with DOD, also consistent with greater structural changes in materials associated with higher DODs.

In summary, our analyses show that material loss rather than resistance increase is mainly responsible for the capacity degradation of these lithium-ion cells. We have also identified capacitance of the cells as an important indicator of the microstructural changes of the electrodes during cycling.

References

- [1] Joongpyo Shim, Kathryn A. Striebel, J. Power Sources **122**, 188 (2003).
[2] D. Aurbach, J. S. Gnanaraj, W. Geissler, and M. Schmidt, J. Electrochem. Soc., **151**, A23 (2004).

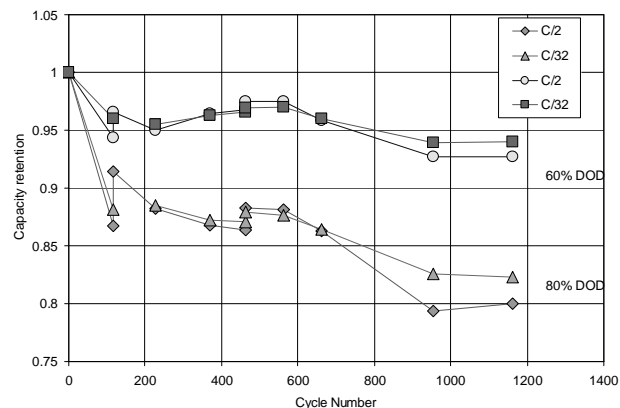


Figure 1 Capacity retention at C/2 and C/32 rates after cells were aged at 60°C and an open circuit voltage of 3.8 V for 137 days. The cells were discharged to 60 and 80% DOD, respectively.

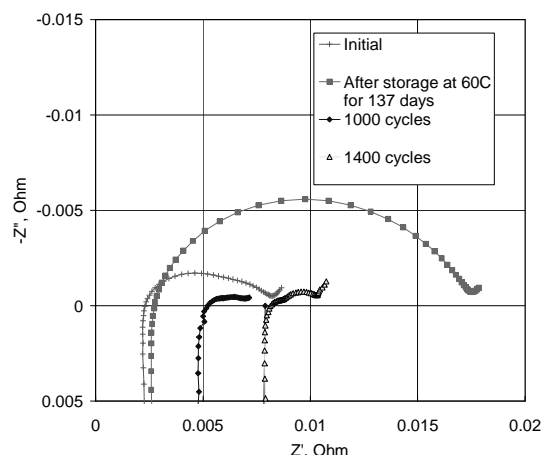


Figure 2. Nyquist plots of the cell cycled at 80% DOD.