

Cycle Life Modeling of Advanced Technology  
Development Program Gen 1 Lithium Ion Cells  
Randy B. Wright  
Chester G. Motloch  
Idaho National Engineering and Environmental  
Laboratory  
PO Box 1625, Idaho Falls, ID 83415-3830

The U.S. DOE Office of Advanced Automotive Technologies is engaged in the study of high-power 18650-size lithium ion cells through the Advanced Technology Development (ATD) Program to address technical barrier limiting the development of batteries for hybrid electric vehicles (1). National laboratory participants include INEEL, ANL, SNL, LBNL, and BNL. The chemistry for Phase I, dubbed Gen 1, has been chosen by ANL to baseline the cells. The cells were built to ATD specification by a commercial vendor. The cathodes were 84 wt%  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  with graphite and carbon black added for electrical conductivity. The anode was a blend of SFG-6 and MCMB-6 carbons. The electrolyte was 1.0 M  $\text{LiPF}_6$  in 1:1 EC/DEC. PVDF binder was used in the fabrication of both electrodes. The anode current collector was copper foil; aluminum foil was used for the cathode current collector. Celgard supplied the separator (polyethylene).

The cells had a rated capacity of 0.9 Ah at a C/1 discharge rate with a voltage range of 3 V to 4.1 V. The test matrix included four temperatures (40, 50, 60, and 70°C) and two states-of-charge (60 and 80% SOC), and three life cycle profiles (3%, 6%, and 9% SOC swing). The cells also underwent characterization at the beginning of testing and periodic reference performance tests at 25°C to compare their performance after cycling to the baseline (2).

The test results indicate that both the discharge and regen resistance increased in a nonlinear manner as a function of the test time and decreased with temperature. (Although tests were performed at 60 and 80% SOC, only the 60% SOC data has been analyzed to date.) Other observations are:

- (1) The discharge resistances are greater than the regen resistances at all of the test temperatures of 40, 50, 60, and 70°C.
- (2) The 70°C discharge and regen resistance data did not always follow the general trend of the rest of the data in that the resistance at this temperature was slightly greater than that at 60°C. This observation appears to indicate that a new physical/chemical process is occurring that causes an anomalous increase in the resistance. The exact nature of these processes is not presently known.
- (3) At each of the four test temperatures, the magnitude of the discharge and regen resistance was in the following order: delta 6% SOC > delta 3% SOC > delta 9% SOC. No explanation is currently known for this observation. (Other research groups within the ATD Program are currently conducting physical/chemical studies on the test cells that may provide insight into this observation.)

A model was developed to account for the time, temperature, SOC, and  $\Delta\%$  SOC of the batteries during the cycle life test. The functional form of the model is given by:

$$R(t, T, \text{SOC}, \Delta\% \text{ SOC}) = a\{\exp[b/T]\}t^{1/2} + c\{\exp[d/T]\}$$

where a, b, c, and d are parameters that are a function of SOC and  $\Delta\%$  SOC. However, due to the lack of analyzed test data at other than 60% SOC, the exact SOC dependence has not been determined yet. Also, b and d are related to activation energies  $E_b$  and  $E_d$  such that  $b = E_b/R$  and  $d = E_d/R$ , and where R is the gas constant.

The square root of time dependence can be accounted for by either a one-dimensional diffusion type of mechanism, presumably of the lithium ions, or by a parabolic growth mechanism for the growth of a thin film solid electrolyte interface (SEI) layer on the anode and/or cathode. The diffusion type of mechanism would arise from the lithium ions diffusing into/out of the electrodes, through the electrolyte, through the separator, or through the SEI that is present on the surface of the electrode materials. The growth of a thin film mechanism could be related to the growth of a SEI layer on the anode and/or cathode as a function of test time. The increased thickness of the SEI film would increase the resistance of the cell due to an increased hindrance of the transport of lithium ions through the SEI layer to subsequently be intercalated/de-intercalated into the active electrode material. The best physical/chemical model appears at present to be the growth of the SEI layer.

Figure 1 shows a representative comparison of test results to the model at 60% SOC. The model fit is excellent except for the 70°C data as discussed above. Leakage current and differential capacitance analyses were also performed. A complete discussion of the results is given in Reference 3.

This is an account of work performed for the U.S. Department of Energy under DOE Idaho Operations Office Contract DE-AC07-99ID13727.

## References

1. Advanced Technology Development, 1999 Annual Progress Report, U.S. DOE, OAAT, March 2000.
2. C. G. Motloch, J. P. Christophersen, et al., "Performance and Life Evaluations of Generation 2 Advanced Technology Development Lithium Ion Cells," Electrochemical Society 199<sup>th</sup> Meeting, Washington DC, March 25-29, 2001.
3. R. B. Wright and C.G. Motloch, "Cycle Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries," DOE/ID-10845, March 2001.

