Calendar 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's Office of Advanced Automotive Technologies initiated the Advanced Technology Development (ATD) Program in 1998 to help find solutions to technical barriers limiting the development of high-power lithium-ion batteries for hybrid electric vehicles. The intent of the testing portion of the ATD program is to characterize the performance and to determine the cycle life and calendar life behavior of lithium ion cells (1). A primary goal is to quantify power fade as a function of calendar time. Phase I (dubbed Gen 1) of the testing and data analyses have now been completed. Other aspects of the program are focusing on thermal abuse intolerance, development of diagnostics tools, advanced materials, and low-cost packaging (2). National laboratory participants include INEEL, ANL, SNL, LBNL, and BNL.

The 18650-size Gen 1 cells were built to ANL specifications by a commercial vendor. The cathodes were 84 wt% $LiNi_{0.8}Co_{0.2}O_2$ with graphite and carbon black. The anode was a blend of SFG-6 and MCMB-6 carbons. PVDF binder was used in the fabrication of both electrodes. The electrolyte was 1.0 M $LiPF_6$ in 1:1 EC/DEC. The anode current collector was copper foil, the cathode current collector was aluminum foil, and the separator was 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. Calendar life testing was conducted at elevated temperatures of 40, 50, 60, and 70^{o}C at 60 and 80% states-of-charge (SOC). Periodically, the cells also underwent a series of reference performance tests at 25°C to compare their performance after aging to the baseline.

The test results indicate the following trends:

(1) The discharge and regen resistance increased in a nonlinear manner as a function of the test time and SOC.
(2) The discharge and regen resistance decreased with temperature.
(3) The discharge resistances are greater than the regen resistances at all of the test temperatures of 40, 50, 60, and 70^{o}C.
(4) The rate of increase of the resistances is higher at 80% SOC than at 60% SOC.

However, notable exceptions to the second observation exist at higher temperatures. At 80% SOC, the 70^{o}C discharge and regen resistance data is slightly greater than the 60^{o}C resistance. At 60% SOC, the 60^{o}C discharge and regen resistance data is greater that at 50^{o}C resistance. Although the 70^{o}C data is lower than the 50^{o}C and 60^{o}C data, it may also be influenced at 60% SOC. This anomalous increase in the resistance appears to indicate that new physical/chemical processes are occurring. These observations also indicate that the SOC at which the test was conducted may influence the temperature at which the onset of these new processes occurs. The exact nature of these processes is not presently known.

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

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

where a, b, c, and d are parameters that are a function of SOC, and where 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 80% SOC. The model fit is excellent except for the 70°C data as discussed above. Leakage current and differential capacity analyses were also performed. A complete discussion of the results is given in Reference 3.

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References

1. C. G. Motloch, J. P. Christophersen, et al., "Performance and Life Evaluations of Generation 2 Advanced Technology Development Lithium Ion Cells," Electrochemical Society 199th Meeting, Washington DC, March 25-29, 2001.
2. Advanced Technology Development, 1999 Annual Progress Report, U.S. DOE, OAAT, March 2000.
3. R. B. Wright and C.G. Motloch, "Calendar Life Studies of Advanced Technology Development Program Gen 1 Lithium Ion Batteries," DOE/ID-10844, March 2001.

Figure 1. Calendar Life Discharge Resistance Data and Model Predictions for ATD Gen 1 Cells at 80% SOC