An Investigation of the Impedance Rise in High-Power Li-ion Cells

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The Advanced Technology Development Program (ATD) was established by the US Department of Energy to investigate key issues affecting the calendar and cycle life of high-power lithium-ion batteries. These issues include impedance rise and power fade.

For the purposes of this study, two different lots of 18650-sized cells (hereafter called Gen 1 and Gen 2) were built to our specifications containing commercially available chemistries. They were subjected to accelerated calendar and cycle life tests according to standards established by the Partnership for a New Generation of Vehicles (PNGV). The Gen 1 cells were life tested at three temperatures (40, 50 and 60°C) and two states of charge (SOC) (40 and 60%). The Gen 2 cells were life tested at 45 and 55°C and at 60% SOC.

As a part of PNGV testing, the cells were initially characterized by undergoing a series of performance tests, including the hybrid pulse power characterization[1] (HPPC). The cells were then aged at the desired temperatures for 4-week periods. At the end of 4 weeks, the cells were cooled to 25°C and the performance tests were repeated to determine how the power capability of the cells changed during the time at temperature.

Area-specific impedance and power values were calculated from the HPPC results for each Gen 1 and Gen 2 cell. From these results, the percent changes were averaged and plotted versus time. The Gen 1 calendar life cells were found to follow Arrhenius and $(\text{time})^{0.5}$ kinetics. A detailed discussion of the Gen 1 results appears in the literature.[2] Figure 1 shows the time dependencies of the Gen 2 calendar-life cells tested at 45 and 55°C. The Gen 2 calendar- and cycle-life cells at 45°C appear to follow $(\text{time})^{0.5}$ kinetics, which is ascribable to thin-film, SEI layer, formation. The calendar life cells at 55°C, however, appear to follow a different kinetic law, linear with time.

In order to understand some of the more basic reasons for these time dependences, the 60%-SOC HPPC data were modeled using the Lumped Parameter Model.[3] This model linearizes the pulse response characteristics in terms of ohmic and polarization resistances (R_o and R_p, respectively) and capacitances.

Using the Gen 1 and Gen 2 calendar life cell data, we found that R_o dominates in both cases. For the Gen 1 cells, the time dependence of R_o was $(\text{time})^{0.5}$. The time-dependence of R_p was more complex. At 40°C, R_p was linear with time; above 40°C, it depended on $(\text{time})^{0.5}$ at both 40 and 60% SOC storage conditions.

For the Gen 2 calendar life cells, temperature-dependence was also found. The time dependence of R_o and R_p for the Gen 2 calendar-life cells tested at 55 and 45°C are shown in Figs, 2 and 3, respectively. R_o was linear with time at 55°C and depended on $(\text{time})^{0.5}$ at 45°C. R_p was linear with time at 55°C and almost time-independent at 45°C. For the Gen 2 cycle life cells, R_o depended on $(\text{time})^{0.5}$ and R_p had a slight time dependence.

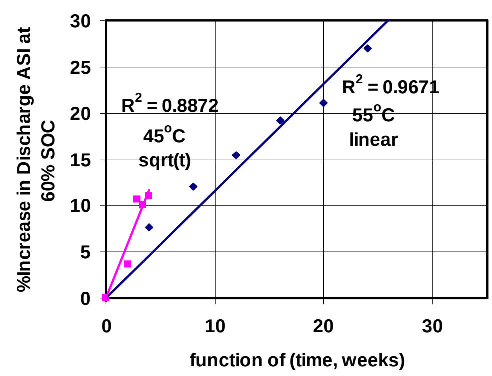

Fig. 1. Time-dependencies of Gen 2 calendar life cells at 45 and 55°C.

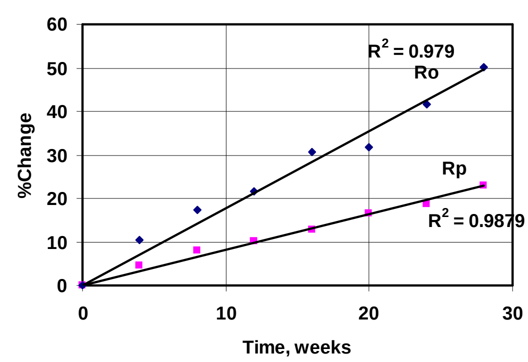

Fig. 2. Time dependencies of R_o and R_p for Gen 2 calendar life cells at 55°C.

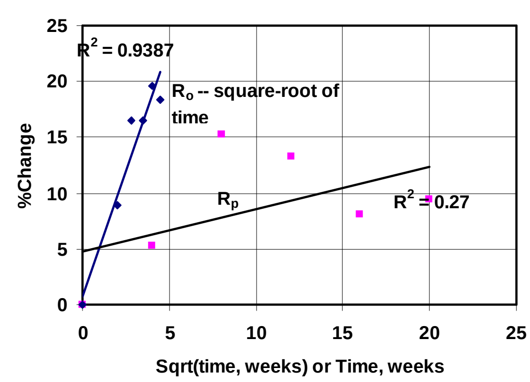

Fig. 3. Time dependencies of R_o and R_p for Gen 2 calendar life cells at 45°C.

[1] PNGV Test Manual, DOE/ID-10597, Rev. 2 (August 1999) and Rev. 3 (February 2001).
[2] I. Bloom, et al, *J. Power Sources*, 101 (2001) 238-247.
[3] PNGV Test Manual, Rev. 3, p. D-4.