IMPLICATIONS OF DIFFERENTIAL CAPACITY FOR THE ANALYSIS OF LI-ION BATTERY PERFORMANCE AND LIFE EVALUATIONS

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The U.S. Department of Energy (DOE) Office of Advanced Automotive Technology (OAAT) initiated the Advanced Technology Development (ATD) Program in 1998 [1] to address the outstanding barriers that limit the commercialization of high-power lithium-ion batteries, specifically for hybrid electric vehicle applications. As part of the program, 18650-size cells were designed and manufactured (the present cells are the 2nd Generation cells, i.e., Gen2) and are being aged using standardized calendar- and cycle-life tests [2]. The Baseline cells were fabricated using carbon anodes with binders. The cathodes consisted of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ with binders. The electrolyte was composed of 1.2 M $LiPF_6$ in EC/EMC (20:80 wt.%). Variant C cells have also been produced and are the same as the Baseline cells except that they used 10% Al-doped $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$ as the cathode material.

After initial characterization tests, and every four weeks thereafter, the cells are periodically subjected to reference performance tests (RPT's) to quantify capacity and power fade rates. The RPT's consist of a $C_1/1$ static capacity test, a low-current Hybrid Pulse Power Characterization Test, a $C_1/25$ static capacity test, and an Electrochemical Impedance Spectroscopy study [2,3]. The cells being tested at the INEEL are undergoing life-cycle testing at 25°C and 45°C. Argonne National Laboratory is studying the calendar-life aging of the cells at 45°C and 55°C.

A new measure of cell degradation under evaluation by the ATD Program is the differential capacity, Q_{diff} [4-6]. It is given by $Q_{diff} = (1/Q)[d(Ah)/dV)]$, where d(Ah)/dV is the derivative of the amount of charge added (charge cycle) or charge removed (discharge cycle) with respect to the cell voltage. Q is the cell average characterization $C_1/25$ charge capacity. The differential capacity can be plotted as a function of the cell voltage or the state-of-charge (SOC). The peaks of the resulting curves are thought to be related to specific lithium intercalation sites within the anode and/or cathode [4-6]. Figure 1 shows the $C_1/25$ constant-current discharge voltage as a function of charge removed for a representative Baseline cell being cycle-life tested at 45°C. The $C_1/25$ data are shown for characterization and for 4-week test intervals up to 28-weeks. The capacity of the cell at characterization was ~1.08 Ah, which decreased with cycle-life aging to ~0.94 Ah after 28-weeks. There is also a noticeable change in the shape of the voltage decay curves as the cell ages. The differential capacity curves for the $C_1/25$ discharge and charge data for the same cell used in Figure 1 are shown in Figure 2. In Figure 2, there are three principle peaks in the differential capacity that occur at ~10 to 12% SOC, ~40 to 42% SOC, and ~80% SOC. The exact nature of these sites where the lithium is intercalated is not presently known. The peak heights in the differential capacity curve are observed to decrease with aging indicating that the number of available sites for lithium occupancy at these voltages (or SOCs) is decreasing with aging.

Results for the Variant C cells are similar with some notable differences such as the rate of capacity fade (and power fade), and the rate change of the peak heights and peak positions in the differential capacity curves with aging

The concept of differential capacity provides information regarding those SOC and voltage values where the cell capacity is changing the most due to aging. This information should be of interest to diagnostic evaluation studies and for the development of physical/chemical models of the cell degradation processes occurring for these ATD cells, as well as for Li-ion batteries in general. The $C_1/25$ (and the $C_1/1$) capacity has been found to be related to the power capabilities of the cells, which has also been observed to decrease with aging. The 45°C aged cells performance decreased more rapidly than the 25°C aged cells. Similarities between the differential capacity, and concepts such as differential energy and differential power were also observed and will be discussed in the paper.

References

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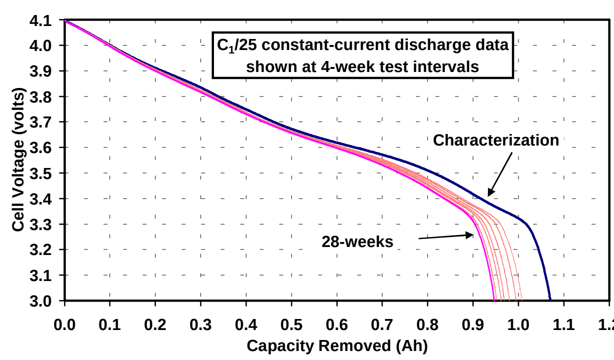

Figure 1. $C_1/25$ constant-current discharge voltage as a function of charge removed for a Baseline cell undergoing cycle-life testing (characterization through 28-weeks) at 45°C

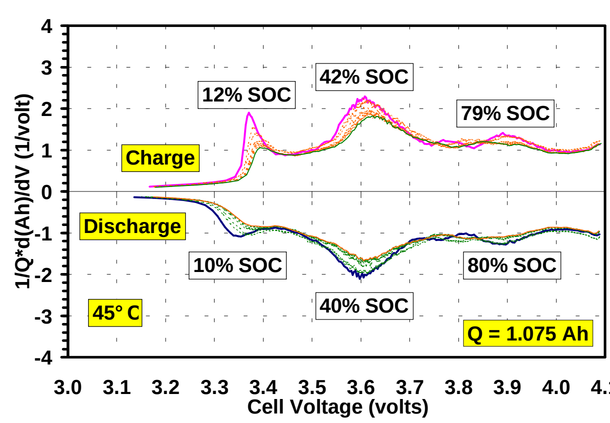

Figure 2. Differential capacity curves for the $C_1/25$ constant-current charge (and discharge) tests for characterization through 28-weeks for the Baseline cell used in Figure 1.