Differential voltage analyses of high-power lithium-ion cells
2. Applications

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Abstract

We characterized high-power lithium-ion cells in terms of performance and cycle- and calendar life at 45 °C. Among other parameters, we measured the C/25 capacity every 4 weeks during the test. Differentiation of the C/25 voltage versus capacity data with respect to capacity yielded dV/dQ curves. Analysis of Q_0 dV/dQ curves has shown that capacity fade in high-power lithium-ion cells can be complex. From the analysis, the anode material in a significant fraction of the cells showed two types of capacity loss. The loss of accessible material tended to happen early in cell life, either during formation or during the first 4 weeks of testing. Most likely this was caused by a physical rather than chemical process. After 4 weeks, the principal cause of capacity loss was side reactions.
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1. Introduction

Lithium-ion batteries are considered ideal where applications require high specific or volumetric energy or power densities. High-power lithium-ion batteries are also being considered for use in automotive applications by the U.S. Department of Energy-supported Freedom Cooperative Automotive Research, FreedomCAR, Partnership. The batteries usually consist of a lithiated metal oxide positive (cathode), such as $LiCoO_2$, $LiMn_2O_4$, or $LiNiO_2$, a carbon negative (anode) and a lithium salt dissolved in an organic electrolyte.

Two national laboratories, Argonne National Laboratory (ANL) and Idaho National Engineering and Environmental Laboratory (INEEL), collaborated to understand the causes of resistance rise and capacity and power fade in lithium-ion batteries [1]. This work showed that the C/25 capacity was

proportional to $t^{1/2}$. The trend in the resistance and power data also depended on $t^{1/2}$.

Some of the C/25 data were presented in an earlier paper [2] to describe and demonstrate the use of differential voltage (dV/dQ) curves to elucidate some of the fade mechanisms in lithium-ion batteries. The dV/dQ curves permitted easy graphical analysis, whereas using differential capacity curves (dQ/dV) was more problematic. Phenominologically speaking, the peaks in the dV/dQ curves are from phase transitions, whereas the peaks in the dQ/dV curves are from phase equilibria. At phase equilibria, two or more coexisting phases with different lithium concentrations have the same lithium chemical potential. Thus, $dV = 0$ at phase equilibria and the value of dQ/dV is undefined. On the other hand, with a constant current discharge (or charge) to generate the data, dQ is always nonzero.

The peaks in the dV/dQ curves were assigned to the cathode, the anode, or their sum by comparison to half-cell data. The paper showed how to apply the dV/dQ techniques to un-

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derstand a simple case. We showed that the capacity fade is primarily due to side reactions at the anode. In the work that follows, we will continue the discussion and show how to use d*V*/d*Q* curves in a more complicated case where there is evidence of complex phenomena occurring at the anode. These phenomena were observed in both the calendar- and cycle-life experiments.

2. Experimental

2.1. 18650-sized cells

Detailed information regarding cell construction is given in [1]. The testing regime is described in [1–4]. The cell chemistry is given in Table 1. The average active area was 846.3 cm^2 and the nominal C/1 capacity was 0.8 Ah. Twenty-six weld-sealed, 18650-sized cells were fabricated to ANL's specifications for this work. The cells underwent formation cycles before delivery to ANL and INEEL. After characterization at 25 °C, one cell was removed from testing at both ANL and INEEL. This left only 10 cells at ANL (calendar life) and 14 at INEEL (cycle life) for testing at 45 °C.

The cells were characterized in terms of their charge and discharge C/25 capacities before the tests began. After 4 weeks at temperature, the cells were cooled to 25 °C and reference performance tests (RPTs) were performed. The RPTs consisted of portions of the characterization tests, including the C/25 tests. The cells were then heated to the soak temperature. The process was repeated until the power fade at the 300 Wh line was greater than 50%. See [3,4] for more information regarding the test procedures and test plan.

Table 1
Cell chemistry

Cathode electrode
  8 wt.% PVDF binder (Kureha KF-1100)
  4 wt.% SFG-6 graphite (Timical)
  4 wt.% carbon black (Chevron)
  84 wt.% LiNi$_{0.8}$Co$_{0.1}$Al$_{0.1}$O$_2$
  8 mg/cm^2 loading density
  35 μm thick coating/side
  30 μm thick Al current collector

Anode electrode
  8 wt.% PVDF binder (Kureha #C)
  92 wt.% MAG-10 (Hitachi)
  4.9 mg/cm^2 loading density
  35 μm thick coating/side
  18 μm thick Cu current collector

Electrolyte
  1.2 M LiPF$_6$ in EC/EMC (3:7 by weight)

Separator
  25 μm thick Celgard 2325 separator

Table 2
Distribution of number of peaks in cell population

No. of peaks	Count	Percent of population
1	18	75
2	6	25
Total	24	

2.2. Half cells

Half-cell construction from fresh and aged 18650 materials was described previously [2,5]. The half cells were charged and discharged at the C/25 rate. The charge and discharge voltages were measured and recorded every 30 s. This yielded about 2500–4800 data points for analyses.

2.3. Data reduction and calculations

As described earlier [2], the C/25 charge and discharge data for the cells from each test population as well as the half cells were noisy due to the very slow charge/discharge rates. Mathematical filtering was used to average out the noise and accentuate the peaks. The filtering was performed using Microsoft Excel and consisted of calculating the percentage depth-of-discharge (%DOD) for each point based on the experimental data and then using the FORECAST function to interpolate the cell capacity and voltage at evenly spaced %DOD intervals. Typically, 0.5% DOD intervals were used, yielding 200 points for subsequent manipulation and plotting. $-Q_0$ d*V*/d*Q* was calculated as $-Q_0 \times \Delta V / \Delta(\text{Ah})$, where Q_0 is the measured C/25 capacity of the cells (in Ah), $\Delta(\text{Ah})$ the change in the capacity of a cell in a given interval and ΔV the change in cell voltage as a result of $\Delta(\text{Ah})$. The Q_0 factor served to normalize the derivatives based on cell capacity. Further smoothing of $-Q_0$ d*V*/d*Q* was accomplished by using a 5-point moving average. Plots of $-Q_0$ d*V*/d*Q* versus capacity density (mAh/cm^2) were then analyzed for trends.

In the half-cell work, full-cell potentials were calculated by subtracting the anode potential from that of the cathode. Similarly, the full-cell derivatives were calculated as the differences between those of the cathode and the anode. For the electrode slippage calculation, the electrode alignments relative to each other were shifted from left to right in terms of which section of the total electrode capacity was actually used in the cell. The cell capacity was defined as that between the voltage limits of 4.1 and 3.0 V.

Before comparing the 18650- and half-cell data, the 18650-cell data was shifted relative to the data from the anode half cell. The active area was also decreased. This aligned the voltage versus capacity discharge curves of the two types of cells. Once the adjustments were made, they were not changed.