Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Power Sources 157 (2006) 537–542
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Differential voltage analyses of high-power lithium-ion cells
3. Another anode phenomenon

Ira Bloom[a,*], Jon P. Christophersen[b], Daniel P. Abraham[a], Kevin L. Gering[b]

[a] *Electrochemical Technology Program, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439, USA*
[b] *Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA*

Received 15 June 2005; received in revised form 28 July 2005; accepted 29 July 2005

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 (d*V*/d*Q*) has been used to elucidate another type of side reaction at the anode. In cycle-life cells, with their higher capacity throughput, the analysis showed that one phase transition (a peak in the profile) was disappearing with time. In contrast, this effect was not seen in calendar-life cells.

Keywords: Battery; Differential voltage analysis; Lithium-ion; Aging

1. Introduction

Lithium-ion batteries represent the state-of-the art where a high specific- or volumetric-energy or power-density battery is required. These batteries usually consist of a lithiated transition metal oxide positive (cathode), a lithiated carbonaceous negative (anode), and a lithium salt dissolved in an organic solvent (electrolyte). High-power lithium-ion batteries are being considered for use in automotive applications by the U.S. Department of Energy (DOE)-supported Freedom Cooperative Automotive Research Partnership. The DOE established the Advanced Technology Development Program to help battery developers overcome key barriers to the automotive application. Among these are life, safety, cost, and low-temperature operation.

Two national laboratories, Argonne National Laboratory (ANL) and Idaho National Laboratory (INL), collaborated to understand some of the life-limiting phenomena: the causes of resistance rise and capacity and power fade in lithium-ion batteries [1]. This work showed that the *C*/25 capacity data and the beginning-of-life cell resistance and power data were well correlated with a square-root-of-time ($t^{1/2}$) dependence. This common dependence on $t^{1/2}$ suggests that one or more degradation mechanisms are affecting all cell performance parameters in a like manner.

Some of the *C*/25 data were presented in earlier papers [2,3] to describe and demonstrate the use of differential voltage (d*V*/d*Q*) curves to elucidate some of the locations and types of fade mechanisms in lithium-ion batteries. The d*V*/d*Q* curves permitted easy graphical analysis, whereas using differential capacity curves (d*Q*/d*V*) was more problematic. Phenominologically speaking, the peaks in the d*V*/d*Q* curves are from phase transitions, whereas the peaks in the d*Q*/d*V* curves are from pseudo-phase equilibria (i.e., very small polarization). Under these conditions, $dV = 0$ and the value of d*Q*/d*V* is undefined. On the other hand, with a constant current discharge (or charge) to generate the data, d*Q* is always nonzero.

The peaks in the d*V*/d*Q* curves were assigned to cathode, anode, or their sum by comparison to half-cell data. The earlier papers showed how to apply the d*V*/d*Q* techniques to understand two cases. In the first, we showed that the capacity fade could be primarily due to side reactions at the anode. In the second, we showed how to use d*V*/d*Q* curves in a

---

[*] Corresponding author. Tel.: +1 630 252 4516; fax: +1 630 972 4516.
E-mail address: bloom@cmt.anl.gov (I. Bloom).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.07.054

more complicated case in which there was evidence of complex physical as well as chemical phenomena occurring at the anode. These phenomena were observed in both the calendar- and cycle-life experiments.

In the work that follows, we continue the discussion, focusing on the aging of the anode. We show that, by using d*V*/d*Q* curves to analyze cell data, other, more subtle changes at the anode can be visualized. These changes were seen in all cycle-life cells, but were most noticeable in four of them.

2. Experimental

2.1. 18650-Sized cells

Detailed information regarding cell construction is given in Reference [1], and the testing regime is given in References [1,4,5]. 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. The four cells that are discussed below came from a population of 26 weld-sealed, 18650-sized cells. These cells were fabricated to ANL's specifications for this work. The cells underwent formation cycles before delivery. Fifteen of the 26 cells were delivered to INL, and 11 were delivered to ANL. After characterization at 25 °C, one cell was removed from testing at both sites. This left 14 cells at INL for cycle-life testing at 45 °C and 10 cells at ANL for calendar-life testing at 45 °C (see References [4,5] for more information regarding the test procedures and the test plan).

The test procedures are defined in References [4,5]. Briefly, the calendar test consisted of potentiostating the cells at 60% SOC (3.741 V) at 25 °C, heating the cells to the test temperature, and, while remaining at the test temperature, performing the profile shown in Fig. 1 once per day. The cycle-life test consisted of using the profile given in Fig. 2 at 60% SOC at the test temperature.

The cells were characterized in terms of their charge and discharge *C*/25 (0.032-A rate) capacities before the tests began. After 4 weeks (or 33,600 cycles) 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 back to the test temperature. The process was repeated until the power fade at the 300-Wh line was greater than 50%. The test types differed in the amount of lithium capacity charged and discharged during a 4-week period. For the calendar-life cells, it was about 7 Ah, and about 735 Ah for the cycle-life cells.

Table 1
Cell chemistry

Cathode electrode	Anode electrode
8 wt.% PVDF binder (Kureha KF-1100)	8 wt.% PVDF binder (Kureha #C)
4 wt.% SFG-6 graphite (Timical)	92 wt.% MAG-10 (Hitachi)
4 wt.% carbon black (Chevron)	
84 wt.% $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$	4.9 mg/cm^2 loading density
8 mg/cm^2 loading density	35-μm-thick coating/side
35-μm-thick coating/side	18-μm-thick Cu current collector
30-μm-thick Al current collector	
Electrolyte	Separator
1.2 M $LiPF_6$ in EC/EMC (3:7, w/w)	25-μm-thick Celgard 2325 separator

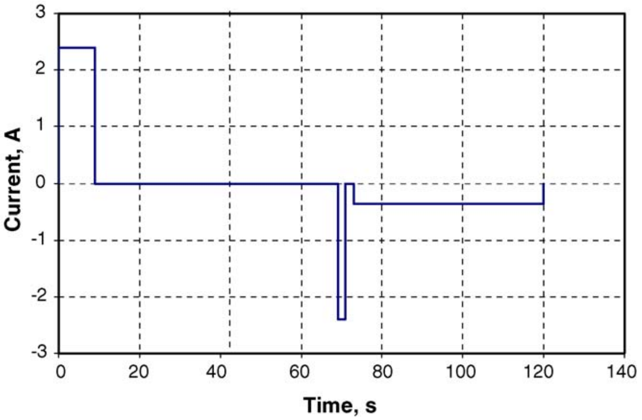

Fig. 1. Calendar-life test pulse profile. This profile was performed once per day. Positive current is discharge.

2.2. Half-cells

Half-cell construction from fresh and aged 18650 materials was described in prior papers [2,3]. 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 [2,3], the *C*/25 charge and discharge data from the cells from each test population, as

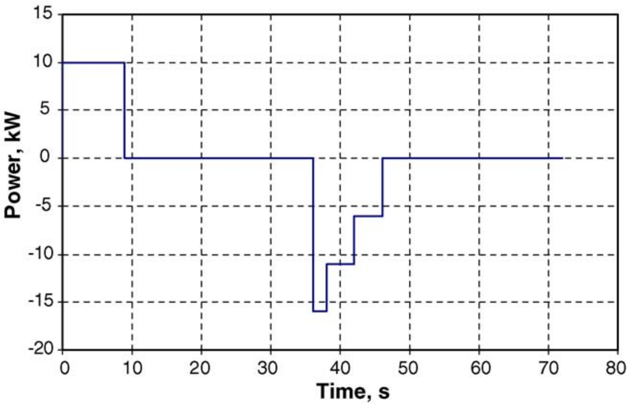

Fig. 2. 25-Wh profile used in cycle-life tests. The profile was scaled down by a factor of 651. Positive current is discharge.