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Journal of Power Sources 139 (2005) 295–303

JOURNAL OF POWER SOURCES

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Differential voltage analyses of high-power, lithium-ion cells
1. Technique and application[☆]

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Received 28 June 2004; accepted 20 July 2004
Available online 16 September 2004

Abstract

The *C*/25 discharge data from 18650-size cells containing $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$ cathode and graphite anode laminates were analyzed through the use of the differential voltage, d*V*/d*Q*, curves. Using half-cell data, the peaks in the d*V*/d*Q* curve of the full cell data were assigned. Analysis of the relative peak shifts allowed for the determination of the source of capacity fade. For cells formed and aged at 45 °C for 40 weeks (capacity fade = 7.5%), the analysis indicated negligible loss of accessible material at the anode and at the cathode. Capacity loss of the cell could be accounted for, largely, by side reactions at the anode. This type of analysis can be used when the introduction of a reference electrode is difficult or impractical.

Keywords: Differential voltage; Reference electrode; Lithium ion; Battery

1. Introduction

Lithium-ion batteries have attracted much interest since the initial report in the early 1990s [1]. These batteries usually consist of a lithiated metal oxide positive electrode (cathode), such as $LiCoO_2$, $LiMn_2O_4$, or $LiNiO_2$, a carbon negative electrode (anode) and a lithium salt dissolved in an organic electrolyte. Lithium-ion batteries have found many uses in consumer electronics. Such batteries are also being considered for use in automotive applications by the U.S. Department of Energy and automobile manufacturer-supported Freedom Cooperative Automotive Research (FreedomCAR) Program.

These secondary batteries operate by intercalating/de-intercalating lithium-ions in both the cathode and anode. The potential of the cell is defined by the difference in the lithium electrochemical potential between the two electrodes. Both the anode and cathode of graphite-based, Li-ion cells have potential profiles versus a lithium metal reference that vary with the amount of lithium in each electrode. Graphite intercalation is typically a first-order phase transition and consists of many potential plateaus as lithium enters or leaves the structure. Intercalation in the cathode of choice, layered oxides, exhibits typically higher-order phase transitions, in which the potential changes gradually with lithium content. Thus, the lithium content in an electrode is not only a measure of its state of charge (SOC) or discharge, but also a measure of the voltage of the electrode versus a reference electrode. Without a reference electrode, however, the cell voltage is a measure of the difference of the potentials of the cathode and anode. It does not tell the lithium content or SOC of either electrode.

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doi:10.1016/j.jpowsour.2004.07.021

Intercalation compounds similar to those used in the lithium-ion cell have been studied by many electrochemical techniques, such as electrochemical voltage (or potential) spectroscopy (EVS) [2–36] and galvanostatic intermittent titration [37]. A typical EVS cell consists of an intercalation compound, such as TiS_2 [2,3] or TaS_2 [4], and a counter electrode with a flat voltage profile, like lithium or sodium metal. The EVS technique uses small, discrete voltage steps while monitoring cell current. When the current reaches a low, limiting value, the cell potential is close to its equilibrium value and the voltage versus lithium content can be calculated [2,3]. EVS has been extended to a continuous voltage sweep using a very low sweep rate, $10\,\mu V\,s^{-1}$ [5,11]. Data from these measurements were used to calculate differential capacity curves (dQ/dV, approximated as $\Delta x/\Delta V$, where Δx is the number of moles or Ah of metal intercalated in a given step and ΔV is a discrete voltage change). These curves have been used to elucidate phase transitions and infer information about the mechanism of the intercalation/de-intercalation of materials into the host lattice [12–36,38].

As described above, most of the information on electrode performance is derived from well-defined electrochemical systems, in which the counter electrode maintains constant voltage during reduction and oxidation. Data from actual lithium-ion batteries can be more complex than those from, for instance, Li/TiS_2 cells. Very little information about the performance of individual lithium-ion electrodes in actual batteries is available in the literature where both electrodes' potential varies with lithium content. The full cell discharge and charge voltage versus capacity data contains thermodynamic information from both electrodes.

To separate the electrode information, one can use either dQ/dV or dV/dQ. The main difference between the two derivatives is that the peaks in the dV/dQ curve represent phase transitions, whereas the peaks in the dQ/dV curve represent phase equilibria. Graphically speaking, the approximation of dQ/dV by $\Delta x/\Delta V$, ΔV can be zero for a given Δx (e.g., in a two-phase equilibrium region); the result is division by zero, a common problem in plotting dQ/dV of graphite versus Li. dV/dQ does not have this problem since Δx, and hence, dQ, is always non-zero. The derivative of voltage with respect to capacity, dV/dQ, is well suited for graphical analysis of battery data, since the voltage of a cell can be written as

$$V_{\text{cell}} = V_{\text{cathode}} - V_{\text{anode}}$$

$(dV/dQ)_{\text{cell}}$ can be written as

$$\left(\frac{dV}{dQ}\right)_{\text{cell}} = \left(\frac{dV}{dQ}\right)_{\text{cathode}} - \left(\frac{dV}{dQ}\right)_{\text{anode}}.$$

That is, the contributions from the anode and cathode electrodes add linearly. This contrasts to the way the contributions add when using dQ/dV,

$$\left(\frac{dQ}{dV}\right)_{\text{cell}} = \frac{1}{(dV/dQ)_{\text{cathode}} - (dV/dQ)_{\text{anode}}}$$

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)	4.9 mg cm^{-2} loading density
84 wt.% $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$	35 μm-thick coating/side
8 mg cm^{-2} loading density	18 μm-thick Cu current collector
35 μm-thick coating/side	
30 μm-thick Al current collector	
Electrolyte	Separator
1.2 M $LiPF_6$ in EC/EMC (3:7 by wt.)	25 μm-thick Celgard 2325 separator

Previously, we described the results from calendar life testing at Argonne National Laboratory (ANL) under the U.S. Department of Energy's (DOE's) Advanced Technology Development (ATD) Program [39]. Here, 0.8 Ah high-power lithium-ion cells were tested using the procedures given in the PNGV Battery Test Manual [40]; in these tests, the calendar life tests were conducted at a fixed SOC. As part of the calendar life testing conducted under the ATD Program, reference performance tests (RPTs) were performed after every 4 weeks of testing. These tests are used to measure the performance of the battery with time. As part of these tests low-constant-current ($C/25$ rate) full charge and discharge tests were conducted to measure the amount of accessible capacity and to determine the relationship between cell potential and capacity under quasi-equilibrium conditions. Since these cells were designed for high-rate applications, the resulting charge and discharge curves contain electrode phase information with a minimum amount of kinetic artifacts and are well suited for further analyses.

Preferably, reference electrodes should be used to identify which electrode produced which part of the discharge curve as well as the source of change in a battery system as it ages. However, introducing a reference electrode into a sealed battery represents a challenge. In the present paper, we show the utility of the dV/dQ curves to identify electrode sources of capacity fade either by side reactions or loss of accessible active material.

2. Experimental

2.1. 18650-sized cells

Detailed information regarding the cell construction and the testing regime is given in [39]. The cell chemistry is given in Table 1. The cells have an average active area of 846.3 cm^2. Eleven weld-sealed 18650-sized cells were fabricated to ANL's specifications for this work. The cells underwent formation cycles at the manufacturer before delivery to