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Short communication

18650 Li-ion cells with reference electrode and in situ characterization of electrodes

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Abstract

At Sandia National Laboratories, we have built 18650 Li-ion cells with Li reference electrode for in situ characterization of electrodes including impedance and other electrochemical properties. At a 200 mA (∼C/5 rate) discharge, the cell gave ∼900 mAh. Impedance measurements indicate that the anode dominates the cell impedance. For example, at 0 °C, the anode and cathode impedances at 10 mHz were around 149 and 53 mΩ, respectively, and the total cell impedance at 10 mHz was ∼203 mΩ. The three-electrode configuration also permits measurement of individual electrode voltages during charge and discharge. During discharge, while the cell voltage drops from 4.1 to 3 V, the cathode and the anode voltages change from 4.1 to 3.7 and from ∼0 to 0.7 V, respectively. During charge, the cathode and anode voltages trace back to their initial values before discharging. The voltage swing for the anode is higher than that for the cathode. This also indicates that the impedance for the anode is higher than for the cathode. Pulse measurements on the cells indicate the voltage drop of the full-cell is equal to the sum of the anode and cathode voltage drops for a 2 A discharge pulse.

Keywords: Li-ion cells; Charge/discharge curves; Cell impedance

1. Introduction

Although Sony Corporation [1] introduced into commercial market 18650 Li-ion cells in the early 1990s, new materials are still being investigated around the world with a view to improving delivered capacity [2], low temperature performance [3], thermal abuse and safety [4]. The 18650 size cell is believed to be more representative of real-world cell performance characteristics and abuse response than smaller test cells often used for material evaluation. For example, in the "FreedomCAR" project sponsored by the US DOE [5] aimed at developing Li-ion batteries for electric vehicle (EV) and hybrid electric vehicle (HEV) applications 18650 size cells are tested for performance evaluation and safety. The principal aim of this effort is to evaluate new materials and to develop mechanistic understanding of the performance and degradation characteristics of the cell chemistry under a variety of use conditions. This necessitates the development of a technique that permits measurement of individual electrode properties in a non-destructive way. Although new materials with improved properties are continuing to be investigated, there is no published information available on the in situ characterization of the material properties of the electrodes and the electrolytes in an 18650 configuration for an unequivocal assessment of the changes in the electrodes' properties that occur in a full-cell during use.

Sandia has developed capability to build 18650 Li-ion cells specifically for the in situ determination of material property. In addition, we have developed the capability to fabricate cells containing a reference electrode (three-electrode cell). The three-electrode configuration allows in situ measurement of the impedance, voltage drops, etc., of the cathode and anode under a variety of use conditions and in turn correlate impedance rise with performance degradation. This capability is unique and to our knowledge no data has been published in the literature on 18650 Li-ion cells with a

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reference electrode as an integral part of the cell. In this study, we measured the impedance and other electrochemical performance characteristics of the full-cell and that of the anode and cathode and showed that the full-cell characteristics can be represented by the sum of the performance characteristics of the anode and cathode.

2. Experimental

18650 cells were fabricated using Hohsen equipment. A non-aqueous electrolyte solution consisting of ethylene carbonate (EC), ethyl methyl carbonate (EMC) 3:7 wt% and 1.2 M $LiPF_6$ as the electrolyte salt was used in this study. A Celgard 2325 was used as separator in this study. Double-sided cathode (thickness: ∼4 mil) and anode (thickness: ∼3 mil) electrodes were used in our study. The compositions of the cathode and anode were:

- Cathode: $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (84 wt%); acetylene black (4 wt%); graphite (4 wt%) and PVDF (8 wt%).
- Anode: GDR carbon (90 wt%) and PVDF (10 wt%). GDR is a natural carbon coated with a thin layer of carbon.

The cathode and anode dimensions were 50 mm × 815 mm and 54 mm × 840 mm, respectively. These electrodes were made for this program by Quallion. The electrodes were cut to size and baked out at 100 °C in vacuum before rolling them together. About 4.2 ml of electrolyte was added followed by crimping the cell in inert atmosphere. The cells are cathode limited.

A Maccor tester Model # Series 4000 was used for charge/discharge cycling and pulsing. The charging and discharging of the cells were done at 200 mA between 4.1 and 3.0 V. These are only the full-cell values and the individual electrodes voltage values are given in the Section 3. A high-speed Tektronix oscilloscope Model # TDS 5140 was used for fast data acquisition of the anode and cathode voltage drops at 8 μS per point. A Model 273A potentiostat (EG&G PAR) equipped with a 1255 Solatron frequency response analyzer and controlled with a M398 impedance software was used for impedance measurement. Impedance data were collected between 10 kHz and 10 mHz at a $V_{p–p}$ of 5 mV. A picture of the three-electrode 18650 Li-ion cell that was fabricated at Sandia and used in our study is shown below (see Photo 1). The charge/discharge cycling was conducted at room temperature. However, the impedance and pulse measurements were carried out at three different temperatures (25, 0 and −20 °C). The cell temperature during impedance and pulse measurements was controlled with a Tenney Environmental Chamber.

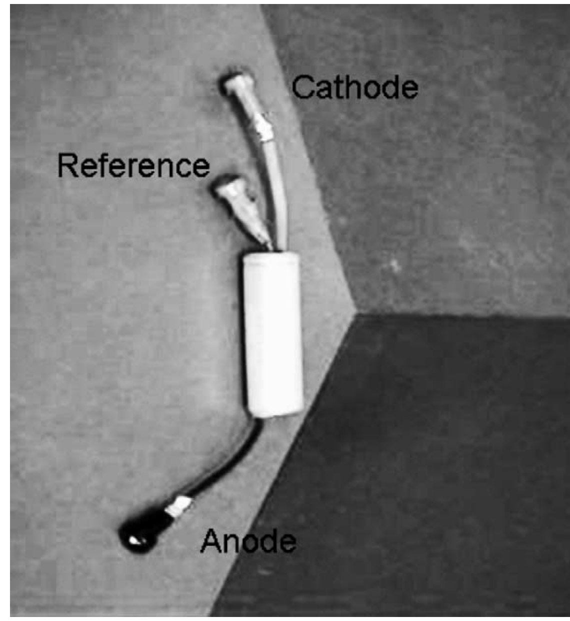

Photo 1. Photograph of a three-electrode18650 cell built and tested at Sandia National Laboratories.

3. Results and discussion

3.1. Cycling

Fig. 1 gives charge/discharge curves for the first few cycles for the full-cell. The traces are reproducible, implying that the cells did not undergo any tangible degradation in performance. Fig. 2 shows both charge and discharge capacities (for 75 cycles) versus cycle # at room temperature. The discharge capacity is not only very nearly constant with cycling, but the charge and discharge capacities are very nearly equal.

This observation implies that the Li^+ intercalation/deintercalation reaction is highly reversible [6]. Commercial cells exhibit similar behavior. During cell cycling,

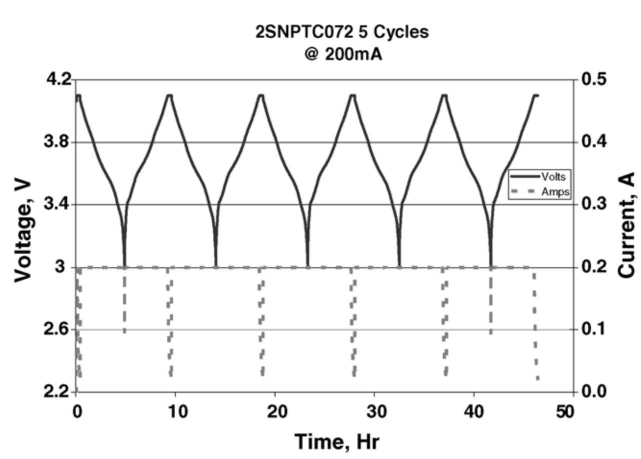

Fig. 1. Charge/discharge curves for the Li-ion cell built at Sandia. Data collected at room temperature ∼20 °C.