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Journal of Power Sources 150 (2005) 182–186
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

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

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Received 17 February 2005; received in revised form 28 February 2005; accepted 28 February 2005
Available online 3 June 2005

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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0378-7753/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.jpowsour.2005.02.024

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 $V_{p\text{–}p}$ 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.

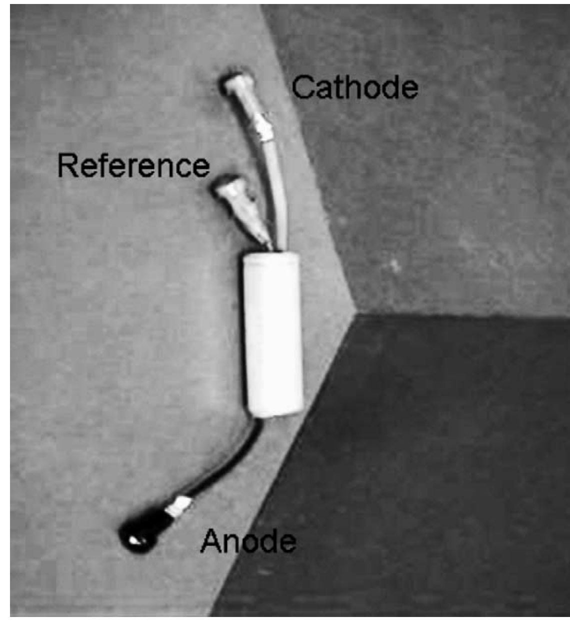

Photo 1. Photograph of a three-electrode18650 cell built and tested at Sandia National Laboratories.

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,

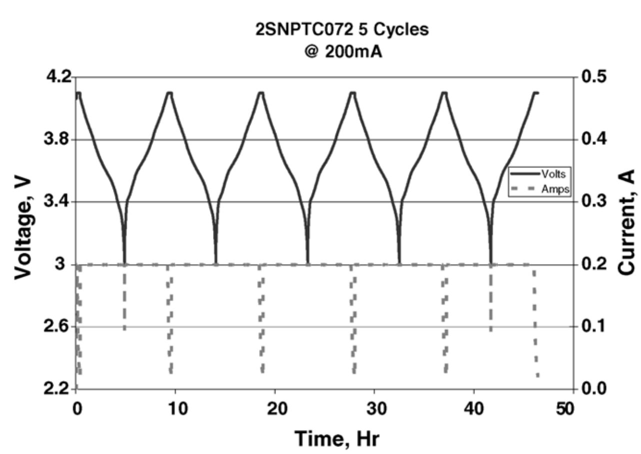

Fig. 1. Charge/discharge curves for the Li-ion cell built at Sandia. Data collected at room temperature ∼20 °C.

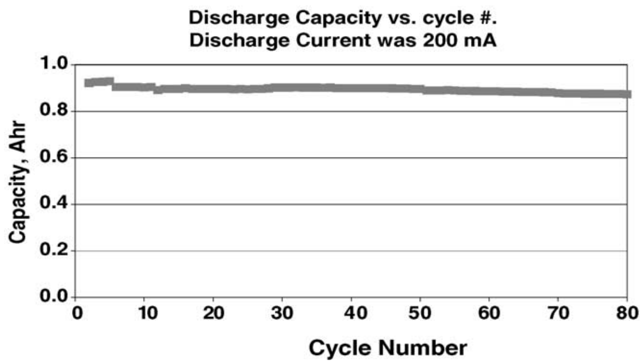

Fig. 2. Charge/discharge capacities vs. cycle #. Data collected at room temperature ∼20 °C.

the individual voltages of the cathode and anode electrodes were also measured in situ using the reference electrode. The voltage traces for the individual electrodes are plotted versus time along with that of the full-cell voltage in Fig. 3. The three-electrode configuration offers a window to look through at the voltage behavior of the two electrodes. This is only feasible with a reference electrode in place. The plots clearly show that during discharge, the cathode voltage decreases from 4.1 to between 3.8 and 3.7 V and the anode voltage increases from −0.05 to between 0.7 and 0.8 V. The voltage for the anode varies at roughly double the rate for the cathode. Further, the cathode is being cycled in a narrow voltage regime, which means the cathode has more capacity left within it untapped. As mentioned before these cells are cathode limited. In addition, the cathode is being under utilized due to the smaller voltage swing of the cathode (i.e., larger voltage swing of the anode). The 900 mAh observed capacity might be lower than what the cell can actually deliver. The larger voltage swing of the anode implies larger anode impedance.

The anode voltage at full charge is at −0.05 V versus Li reference although the measurements were made at ∼20 °C. This could possibly be coming from either Li electrode plating on carbon (anode) surface, leading to capacity degradation or impedance effect. However, within the limited number of charge/discharge cycles reported here we did not see any capacity degradation in the cell. We also did not see any unusual features in the impedance behavior that might suggest Li plating. We are currently investigating the Li plating phenomenon more carefully for applications such as "cold-cranking".

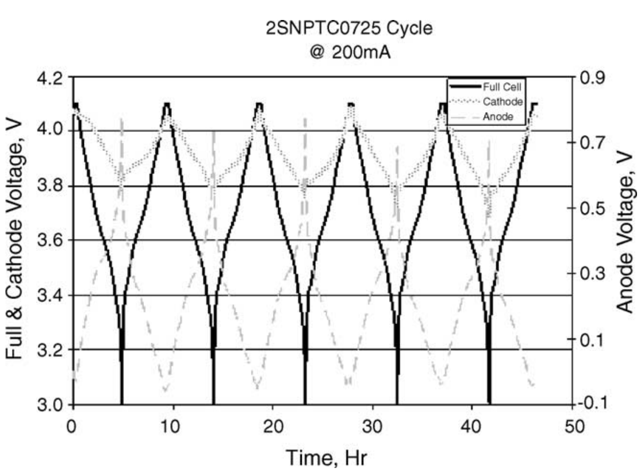

Fig. 3. Voltage behavior of the anode and cathode along with that of the full-cell vs. time in hours. Data collected at room temperature ∼20 °C.

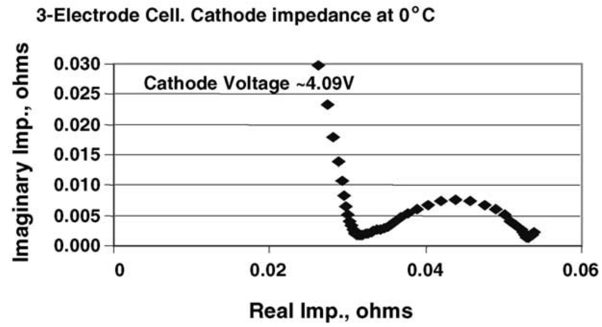

Fig. 4. Impedance of the cathode at 0 °C.

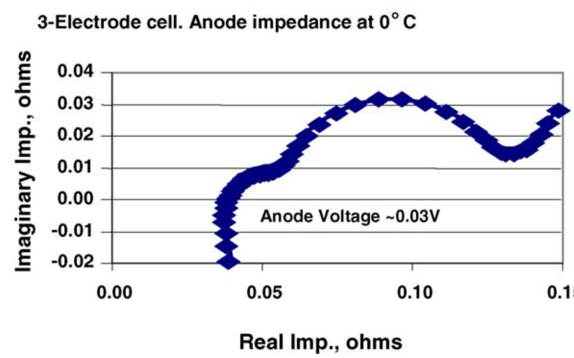

Fig. 5. Impedance of the anode at 0 °C.

3.2. Cell impedance

Cell impedance was measured at three temperatures (25, 0 and −20 °C) at different cell voltages. Figs. 4–6 show

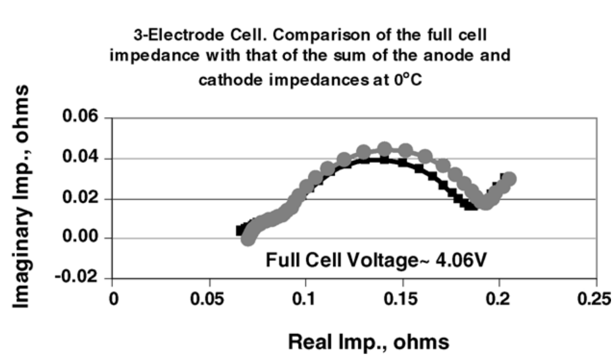

Fig. 6. Impedance of the full-cell at 0 °C.

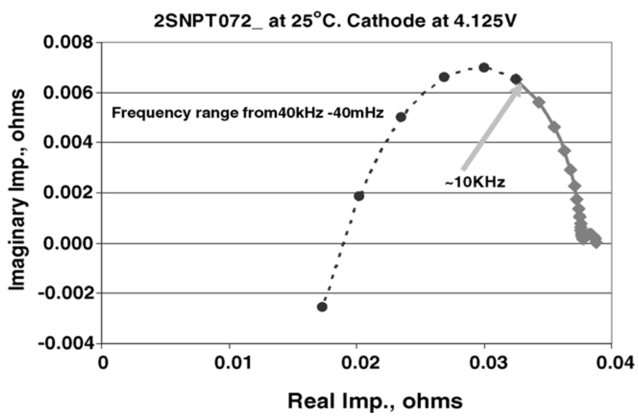

Fig. 7. Cathode impedance from 40 kHz to 40 mHz at 25 °C.

Nyquist plots of impedance for the cathode and anode and full-cell, respectively, at 0 °C. Additionally, Fig. 6 shows the impedance plot for the sum of the cathode and anode impedances taken from Figs. 4 and 5. The high frequency behavior of the cathode (tail going up) is not an artifact of the measurement but due to the limited high frequency range used in this study. Increasing the high frequency limit to 40 kHz shows a bending over of the curve to lower imaginary and real values as shown in Fig. 7 (dashed line). This measurement was carried out at 25 °C. We have been testing 18650 Li-ion cells for impedance in the FreedomCar program in the frequency regime 10 kHz to 10 mHz since at frequencies higher than 10 kHz the full-cell shows only inductive behavior, which does not have any chemical significance. For this reason, we continued with the same frequency regime in this study.

The full-cell impedance at 10 mHz is 203 mΩ and that of the cathode and anode are 53 and 149 mΩ, respectively. The sum of the anode and cathode impedances is ∼202 mΩ. These data clearly show that the full-cell impedance can be adequately represented by the sum of the electrode impedances. This observation lends proof to the in situ measurement technique as a viable method for probing the individual electrode properties non-invasively. Similar observations were made at other temperatures. Fig. 6 compares the full-cell impedance and the sum of the impedances of the cathode and anode. The plots are similar to each other again amplifying the validity of the three-electrode technique.

3.3. Voltage drop measurement

The voltage drops for the full-cell, cathode and anode were measured for a 2 A discharge pulse.

The anode and the cathode voltage drops were captured as described in the Section 2 using the oscilloscope. However, the cell voltage drop was captured in a Maccor tester. Fig. 8 shows the voltage drops for the full-cell and the sum of the cathode and anode calculated voltage drops. The voltage drops are comparable. Similar results were obtained at the other temperatures as well.

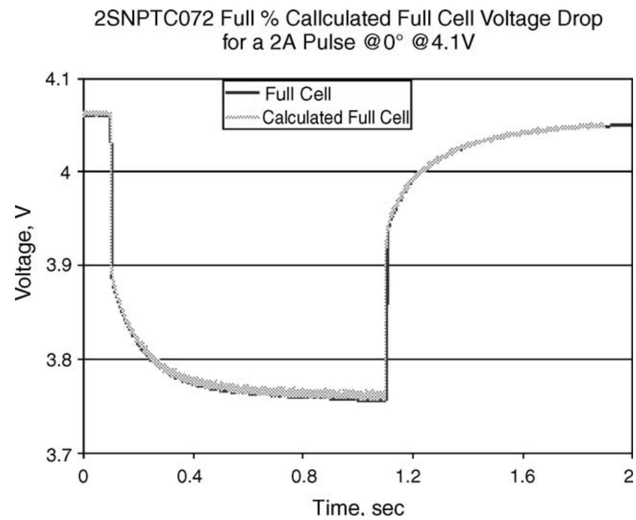

Fig. 8. Voltage drops comparison for the full-cell and the sum of the anode and cathode at 0 °C. The initial cell voltage was ∼4.1 V.

4. Conclusions

Sandia National Laboratories have successfully fabricated three-electrode 18650 Li-ion cells with the electrodes purchased from Quallion. The three-electrode configuration enabled us to monitor, in situ, the voltage and impedance characteristics of the electrodes in a non-destructive way. Such measurements clearly indicate that the impedance and voltage changes are higher for the anode than for the cathode. During charge/discharge the cathode voltage changes only by about 0.4 V while that of the anode, under the same condition, changes by ∼0.8 V. The voltage drop for a 2 A discharge pulse for the full-cell is identical to that of the sum of the voltage drops for the anode and cathode. These observations show that the three-electrode technique can be used gainfully in non-invasively probing the electrical characteristics of the individual electrodes.

Acknowledgements

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. This work was performed under the auspices of DOE FreedomCAR and Vehicle Technologies Office through the Advanced Technology Development (ATD) High Power Battery Development Program. The authors acknowledge Bryan Sanchez's help in making the cell and the electrochemical measurements.

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