

Study of electrochemical performance of Li-ion batteries based on simultaneous measurement of a three-electrode system

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Abstract—In this paper, the electrochemical performance of the cathode and the anode of the three-electrode Li-ion batteries (LIBs) was measured and studied. During the process of the charge and discharge for three-electrode LIBs, the voltage of the cathode and the anode can be simultaneously collected. The incremental capacity curves show that the intercalation and de-intercalation occur both in the cathode and the anode. From the electrochemical impedance spectra, it is known that the electrochemical behavior of full cell depends on both cathode and the anode. The Li ion diffusion on the surface of the cathode dominates the full cell performance at low-frequency range, and electrochemical impedance of the anode dominates at the medium to high frequency.

Keywords— *Li-ion batteries; three-electrode system; simultaneous measurement; electrochemistry*

I INTRODUCTION

With the electric vehicles (EVs) growing up in popularity these days, Li ion batteries (LIBs) as the core component is of crucial importance to electric vehicles, especially their efficient operation and safety. While aging of LIBs is still a challenge in commercial applications, and the process of aging is complicated. The capacity loss and the power fading are not just resulted from single cause, but from various

processes (such as the depth of discharge, speed of charge or discharge, operating temperature and mechanical stress) and their interactions[1]. Also the aging mechanisms occurring at anodes and cathodes differ remarkably.

Generally, some instantaneous information, such as state of charge (SOC) quantifying the usable energy at the present cycle and state of health (SOH) indicating the remaining performance of the battery[2] is provided to evaluate the current state of LIBs in operation. The SOC or SOH is often estimated using the open circuit voltage (OCV) [2] or coulombic counting[3]. The SOC or SOH of LIBs can also be evaluated using electrochemical impedances. The traditional measurement of OCV and impedances is carried out directly using commercial batteries, two-electrode system including cathodes and anodes. So the measured OCV and impedances are based on the full LIBs, and also the modeling of SOH or SOC is based on the full battery. However, the charge/discharge process and the aging mechanisms between the cathode and the anode of LIBs are different from each other[4, 5], the reactions and contributions from the cathode and anode cannot be clearly distinguished when measuring the OCV or impedance of the full cell.

In order to study electrochemical behavior of the single electrode (cathode and anode) after various aging processes, conventionally half-cells using cathode or anode as the working electrode and Li metals as a counter electrode and a reference electrode are reassembled. But this half-cell system only focuses on the working electrode (the cathode or the anode) without consideration of the effect and contribution from the other electrode. Furthermore, working conditions of reassembled half-cells using the cathode or the anode after aging tests differ from that of the full cell, for example, the electrolyte may change after aging tests, the cathode or the anode may suffer impact of oxygen and water when it is taken out from full-cells.

In this paper, three-electrode LIBs are assembled with adding a Li metal as a reference electrode, the cathodes and anodes are from fully discharged commercial LIBs (Sony 18650VCT4). The voltages (vs. Li metal) and impedance of the cathode and the anode can be collected separately and simultaneously, without taking electrode out of batteries. The three-electrode system is validated by comparing its charge/discharge data with the datasheet of commercial LIBs. After, the incremental capacity (IC) and electrochemical impedances from cathode and anode were investigated in this three-electrode cell.

II EXPERIMENTAL

a) Fabrication of three-electrode LIBs

The cathode (LiCoO₂) and the anode (graphitized microbeads) were from fully discharged commercial batteries (Sony 18650VCT4, capacity of 2 Ah), and materials on one side of electrodes were removed with acetone. Then cathode and anode (diameter of 1.8 cm²) was obtained after incised with stamp cutter (EL-CELL). Lithium metal is used as a reference electrode in the three-electrode system. Glass fiber with thickness of 1.55 mm (EL-CELL) and 1 M LiFP₆ in EC/DMC (1:1 by vol.) were used as separator and electrolyte correspondingly. Both the disassembly of commercial batteries and the reassembly of three-electrode LIBs are carried out in glove box with oxygen and water lower than 1 ppm. The three-electrode LIBs were kept standing for 5 hours to let the electrolyte sufficiently permeated into electrode materials before electrochemical measurement.

b) Simultaneous measurement of electrochemical behavior on electrodes of three-electrode LIBs

After standing for 5 hours, the three-electrode cell was charged and discharged using constant current-constant voltage (CC-CV) method, with upper and lower cut-off voltage of 4.2 V and 2.5 V correspondingly, according to the specification of commercial batteries (Sony 18650VCT4). The voltage on the cathode and anode (vs. Li metal) and the voltage of the full cell was collected simultaneously. Electrochemical impedance spectroscopy (EIS) was carried out using AC stimulation with the amplitude of 5 mV and frequencies ranged from 1 MHz to 0.01 Hz. The impedances of cathode and anode were measured after galvanostatic charge and discharge at different temperatures.

III RESULTS AND DISCUSSION

a) Availability of the three-electrode cell

After standing for 5 hours, the voltage of the reassembled three-electrode cell was 2.4 V. The three-electrode cell was charged using constant current of 2 mA to 4.2 V, then the voltage of the cell was kept at 4.2 V using constant voltage until the current declined to 0.5 mA. After 1 h rest, the voltage of the cell was stable at 4.1 V, then discharged under constant current of 2 mA. Figure 1 shows the charge and discharge curve of the three-electrode cell using CC-CV method. Measured discharge capacity of the three-electrode cell was 5.05 mAh, which is consistent with the calculated capacity according to the datasheet of the commercial batteries (Sony 18650VCT4). Herein, the capacity of the three-electrode cell is 5.05 mAh when it is fully charged, and this reassembled three-electrode cell is validated.

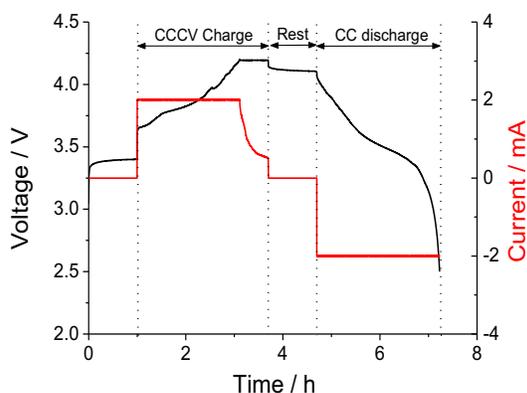


Figure 1. Voltage and current curves of three-electrode cell during CC-CV charge and CC discharge.

Continuous cycling of charge and discharge for the three-electrode cell using constant current of 2 mA was carried out. Figure 2 shows five cycles of charge-discharge curve of the three-electrode cell. The measured capacity slightly decreases with the increasing number of charge-discharge cycles. The following are potential reasons: the current applied in this study for charge and discharge caused the polarization; no constant-voltage process is applied during charge, so the cell can't be fully charged. Although the capacity of the three-electrode cell decreased slightly, the voltage and impedance of electrodes could still be collected.

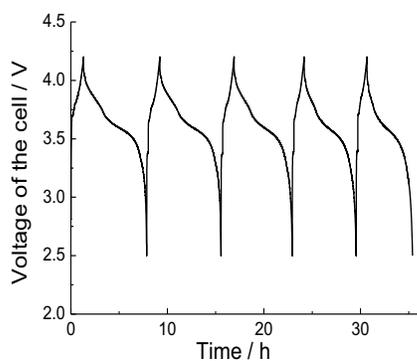


Figure 2. Continuous cycling of charge and discharge for the three-electrode cell using the constant current.

b) *Simultaneous measurement of electrochemical behavior on the cathode and the anode*

The voltage of the cathode (vs. Li^+/Li), the anode (vs. Li^+/Li) and the full cell were collected simultaneously. Figure 3 presents the charging and discharging profiles of the cell, the cathode and the anode, under constant current of 2 mA with upper and lower cut-off voltage of 4.2 V and 2.5V. During charging, the voltage of the three-electrode cell rises from 3.6 V to 4.2 V. Then the voltage of the cell declines and stabilize around 3.89V after 2 hours due to the polarization of the electrodes. Then the three-electrode cell was discharged to 2.5 V under constant current of 2 mA. The voltages of the cathode and the anode (vs. Li^+/Li) were collected simultaneously.

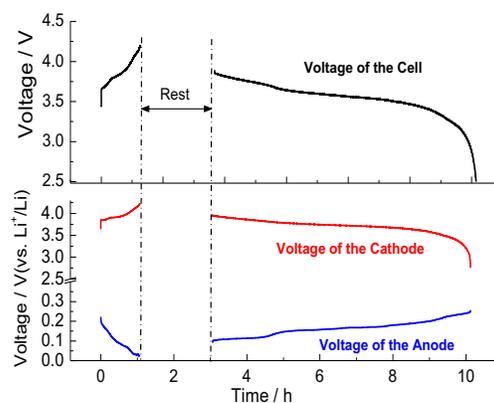


Figure 3. Charging and discharging profiles of the three-electrode cell, the cathode and the anode under constant current of 2 mA.

In order to study the intercalation and de-intercalation of Li ions in the cathode and the anode, the incremental capacity (IC) curves, the dQ/dV as a function of the voltage, are used to deduce the electrochemical evolution during charging process. The peaks in IC curves reveal the phase transitions and the magnitude, position, and the shape reflects the electrochemical dynamics.[6]

Figure 4 displays the IC curves of the cathode (figure 4a) and the anode (Figure 4b).The voltage of the cathode (vs. Li^+/Li) increases from 3.85 V to 4.22 V as

shown in figure 4a, and Li ions de-intercalate from the cathode during charging process. A main Li deintercalation peak appears around the 3.9 V. This peak may be a result from the phase transition of Li ions arrangements in the CoO_2 framework, and Li_xCoO_2 undergoes structural changes from $\text{Li}_{0.75}\text{CoO}_2$ to $\text{Li}_{0.5}\text{CoO}_2$ [7]. For the anode, the potentials of intercalation of Li ions range from 0.02 V to 0.22 V, and four peaks of Li intercalation (0.04 V, 0.075 V, 0.1 V and 0.18 V) can be observed in Figure 4b. Different potential regions of Li intercalation on the anode manifests the different depth of Li ion intercalation in the anode[8]. It is reported that there are different voltage stages for graphite, corresponding to x from 0.08 to 1, where x appears in Li_xC [6]. In the potential region between 0.01 V and 0.22 V, four stages of Li-C intercalation compounds exist with phase transitions from a higher stage to a lower stage. The voltage regions of peaks in this study are slightly lower than those in previous studies due to the polarization of electrode during charging process.[9-11]

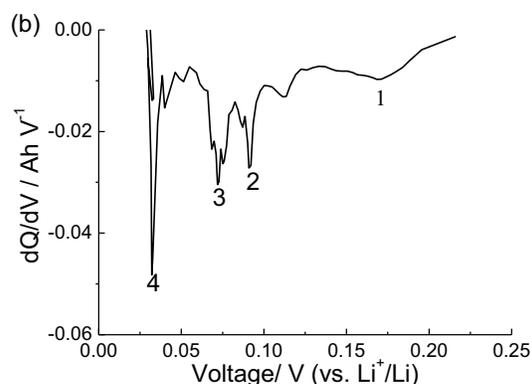
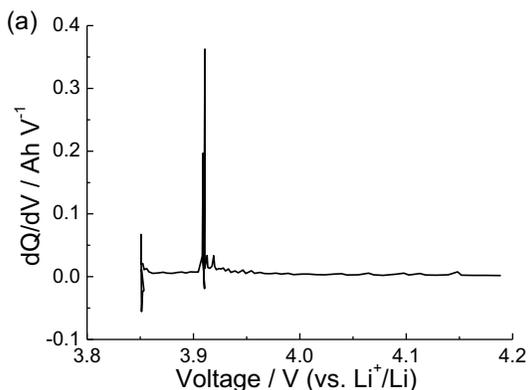


Figure 4. Incremental capacity (IC) curves of (a) the cathode and (b) the anode during the charge process

c) EIS measurement of the cathode, the anode and the full cell

EIS tests for the cathode, the anode and the three-electrode cell were performed respectively at discharge state, after one charge-discharge cycle under constant current of 2 mA. Figure 5a presents a semi-circle for full cell and the cathode in low-frequency range. It demonstrates that Li ion diffusion of the full cell at low frequency is mainly limited by the non-infinite diffusion on surface of the cathode. In figure 5b, two semi-circles can be observed for the anode at the medium-high-frequency range, and the semi-circle in high frequency and medium frequency range indicates the SEI impedance and charge-transfer resistance respectively. No obvious capacitive loop can be observed for cathode at the medium-high-frequency range, it means the electrochemical behavior of full cell depends on both cathode and the anode. The Li ion diffusion on the surface of the cathode dominates for the full cell at low-frequency range, and electrochemical impedance of the anode dominates at the medium-high-frequency.

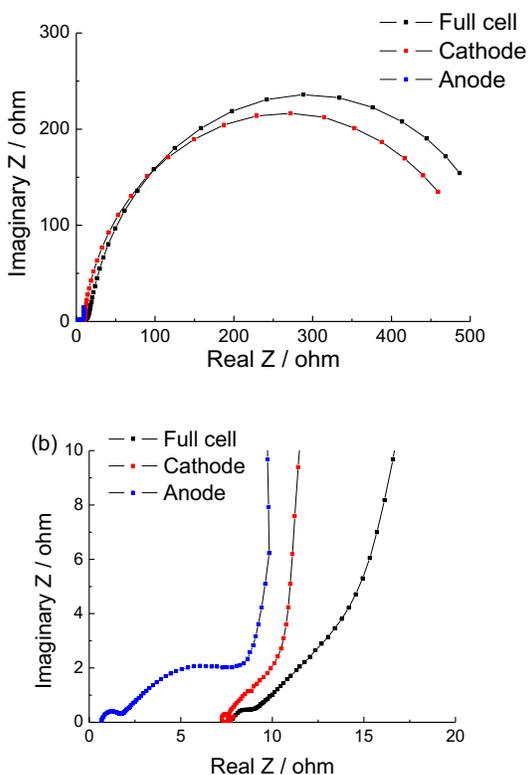


Figure 5. Impedance spectra of the full cell and the cathode after one cycle of charge and discharge at (a) frequencies ranged from 100 kHz to 0.1 Hz and (b) medium to high frequency ranges.

IV CONCLUSION

Three-electrode Li-ion batteries were reassembled using the materials from the commercial batteries, and the electrochemical performance of the cathode and the anode was measured simultaneously. The charging and discharging curves show that this three-electrode Li-ion batteries exhibit a good stability. The incremental capacity results indicate the intercalation and deintercalation of Li ions occur both in the cathode and the anode. The electrochemical impedance spectra of the full cell, the cathode and the anode were measured, the electrochemical behavior of full cell depends on both cathode and the anode. The Li ion diffusion on the surface of the cathode dominates for the full cell at low-frequency range, while electrochemical impedance of the anode dominates at the medium-high-frequency.

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