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State of Charge Dependency of Graphitized-Carbon-Based Reactions in a Lithium-ion Secondary Cell Studied by Electrochemical Impedance Spectroscopy

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ABSTRACT

Li-ion insertion/deinsertion reactions of the anode of a Li-ion secondary cell incorporating a reference electrode were analyzed by electrochemical impedance spectroscopy (EIS) at different temperatures and state of charges (SOCs). The cell uses graphitized carbon as anode electroactive material. Impedance spectra fittings were carried out using an equivalent circuit, so that the reaction kinetics could be evaluated accurately. The dependencies of the Li-ion conduction (R_{sl1}), Li-ion solvation/desolvation (R_{sl2}) and charge transfer (R_{ct}) reactions on the SOC and anode potential were evaluated. The results were compared with a dQ/dE vs. E curve of graphite to analyze how the structural changes of graphite affect the Li-ion insertion process. The charge transfer process was found to be dependent on the SOC and anode potential. On the other hand, Li-ion conduction and Li-ion solvation/desolvation processes did not depend on the SOC and anode potential.

1. Introduction

Lithium ion secondary cells possess high energy density, which is reflected in a small size and light weight. These cells have become the main power source of various portable devices. More recently, Li-ion secondary cells are used in large-scale applications, such as electric vehicles (EVs) and hybrid electric vehicles (HEVs). However, the use of Li-ion cells in these large applications demands high charge/discharge cycling performance, high thermal stability and safety performance.

Electroactive materials play an important role in cell performance, but, when a Li-ion is inserted into an electroactive material many reactions take place [1]. The crystal structure of the electroactive materials tends to change with the state of charge (SOC) of the cell, and the resulting changes affect the Li-ion insertion/deinsertion reactions [2–4]. Since the analysis of the electroactive materials is essential to design Li-ion cells with high performance, the techniques for evaluating the reactions of the electroactive materials are extremely important. Many efforts have been made to analyze the process of Li-ion insertion into electroactive materials using techniques such as XRD, cyclic voltammetry and single particle voltammetry [5–8]. However, these studies have been carried out using half-cells, and did not necessarily measure the reactions that are occurring in situ. Therefore, the development of a method that allows the in-situ analysis of the electroactive material reactions of a Li-ion cell is necessary, and is crucial to the analysis of the dependence of the electroactive material reactions on the SOC. For that purpose, the use of a Li-ion cell with a reference electrode is very helpful to analyze the positive and negative electrode reactions, separately.

Electrochemical impedance spectroscopy (EIS) is an in-situ and non-destructive method that allows the analysis of the electrode reactions of a Li-ion cell [9,10]. Some kinetic studies of the characterization of the electrochemical properties of Li-ion secondary cell electrodes have been reported, where the Li-ion insertion/deinsertion reactions are analyzed at different SOCs [11–18]. But, these studies were carried out using half-cells and other special cells that do not essentially measure the reactions that are occurring in situ.

In this work, the term “Li-ion secondary cell incorporating a reference electrode” refers to a sealed Li-ion cell that contains a positive electrode, a negative electrode and a reference electrode. The use of these cells allows in situ analysis of the interfaces between the electroactive materials and electrolyte in a separate way. So

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far, a few EIS studies that use Li-ion secondary cells incorporating a reference electrode are reported. M. Dolle et al., carried out EIS using a Li-ion secondary cell incorporating a reference electrode, they compared the impedance measurements of the electroactive materials with the impedance measurements of the full cell, validating the use of a Li-ion cell incorporating a reference electrode to analyze the electroactive materials in a separate way [19]. J. Y. Song et al., carried out EIS measurements using half-cells and a Li-ion cell incorporating a reference electrode and compared the results among the cells [20]. However, these works did not analyze the kinetic of the electroactive material reactions and their dependency on the state of charge.

In this work, we analyze the reactions of the negative electrode of a Li-ion secondary cell incorporating a reference electrode by carrying out EIS measurements at different SOCs and temperatures. The cell uses graphitized carbon as the negative electrode. By recording EIS measurements at different temperatures and SOCs, it is possible to analyze the kinetic of the anode reactions and the dependency of these on the SOC. To analyze the electrochemical behavior of the process of the Li-ion insertion/deinsertion into a graphitized carbon electrode, and to evaluate how the structural changes of graphitized carbon affect the Li-ion insertion/deinsertion process, the kinetic behavior of the anode reactions are compared with the anode dQ/dE vs. E curves.

2. Experimental

2.1. Cell specifications

We tested a laminated lithium ion secondary cell containing a reference electrode. A schematic illustration of the cell is shown in Fig. 1. The cell consists of a negative electrode, a separator, a reference electrode, and a positive electrode. The size and position of the reference electrode were optimized so that it does not affect the charge and discharge performance of the cell. This cell used lithium cobalt oxide and graphitized carbon as the cathode and anode materials, respectively. The positive electrode consists of a mixture of an active material, an electroconductive material, and a binder resin, at a weight ratio of 90:3:7. The negative electrode consists of a mixture of an active material and a binder resin, at a weight ratio of 90:10. The capacities of the anode and cathode active materials were 1520 and 1200 mAh cm^{-3}, respectively. Lithium foil was used as the reference electrode, which was inserted between the positive and negative electrodes. The electrolyte contained 1 mol dm^{-3} LiPF$_6$, the solvent was ethylene carbonate: diethyl carbonate = 7:3 (volume), and the size of the cell electrodes was 46 mm × 46 mm (including the laminate package). The capacity of this lithium ion secondary cell with the reference electrode was 20 mAh.

2.2. dQ/dE vs E curve

To obtain the capacity of the lithium ion secondary cell incorporating the reference electrode, the cell was cycled using a battery tester (KIKUSUI, PFX2011). The cell was charged and discharged following a constant current/constant voltage and constant current discharge method, respectively. During the constant current/constant voltage stage, the current was 4.2 mA, the maximum cell voltage was 4.2 V and the constant voltage was applied for 1 hour and 30 minutes. At the constant current discharge stage, the current value was 4.2 mA and the discharging voltage of the cell was set to 2.7 V.

After obtaining the value of the capacity C of the cell using the above method, a constant current charging and discharging test was carried out. The charging/discharging conditions were set at 0.2 C for the current and 2.7 V for the discharging voltage. The dQ/dE vs. E curves were obtain by plotting the electrode potential (E) and the capacity (Q).

2.3. Electrochemical Impedance Spectroscopy measurements

The EIS measurements were carried out using a frequency response analyzer (Solartron 1260) in combination with a potentiostat (Solartron 1286), the frequency range and AC amplitude were 100 kHz-10 mHz and 5 mV$_{\mathrm{rms}}$, respectively. Before recording the EIS measurements, the cell was charged at the desired SOC using the battery tester. The cell was tested inside a constant temperature chamber (ETAC, FL414P). The tests were carried out at 20, 30, 45 and 60 °C, so that the reaction kinetics could be evaluated accurately by using the proposed equivalent circuit. All measurements were carried out after the Li-ion cell was activated (aging by potential cycling).

3. Results and discussion

3.1. dQ/dE vs E curve

Fig. 2 shows the anode dQ/dE vs. E curve of the lithium ion secondary cell. The characteristic peaks a-e during the charging can be attributed to the structural changes in the graphite incorporated in the anode. Comparing the results with a reported ex-situ voltammogram [2,7,21], in the electrode potential range of 0.3~0.22 V vs. Li/Li$^+$, the Li ion density in graphite is very low, the Li ions are randomly inserted between all layers, and the graphite structure goes from the dilute stage-1 to stage-4 [2,7,21–25]. In the range of 0.18 ~ 0.22 V vs. Li/Li$^+$, a clear phase transition from stage-4 to stage-3 did not occur at peaks b and c. The phase transition from stage-3 to stage-2 occurs at peak d, and the phase transition from stage-2 to stage-1 occurs at peak e. By using a lithium ion secondary cell

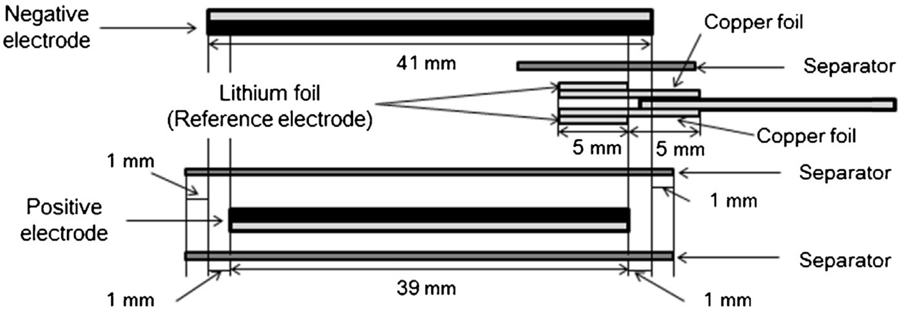

Fig. 1. Schematic illustration of the Li-ion secondary cell incoporating a reference electrode.