Development of In Situ Cross-Sectional Raman Imaging of LiCoO₂ Cathode for Li-ion Battery

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ABSTRACT

A novel in situ Raman imaging technique has been developed to visualize the Li-ion battery reaction during the charge/discharge operation. A specially designed cell enables to measure Raman spectra at high speed so that the in situ measurements are carried out during the reaction. The distribution of the state of charge in cross-section of LiCoO₂ cathode has been visualized as a demonstration. Inhomogeneous state of charge distribution is observed and there are some active materials where Li⁺ does not completely return after discharging. This technique enables to evaluate not only the electrode performance but also battery degradation, and thus may promote the realization of the next generation batteries.

Keywords : In Situ Raman, Lithium Battery, Reaction Distribution, LiCoO₂

1. Introduction

Li-ion batteries (LIBs) are widely used in many portable electronic devices and are anticipated to be future energy storage devices for mass-produced electric vehicles. For these applications, it is essential to improve its capacity, power, durability, and safety. In order to satisfy these demands, it is crucial to optimize the structure of the electrode as well as exploring new materials because the kinetics of the electrode reaction depends on the structure of the composite electrode.

The main process in the electrode reaction of LIBs is an intercalation/deintercalation of Li⁺ into/from host materials. In case of LiCoO₂ cathode and carbon anode, for instance, the electrode reaction is represented as follows:

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\text{LiCoO}_2 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{Li}_x\text{CoO}_2 + \text{C}
\]

The reaction takes place by the transport of electrons and Li⁺ at the electrode surface. Thus, the behavior of the reaction is governed by the conductivity of electron and Li⁺ in the composite electrode and interfacial layer which is called solid electrolyte interphase (SEI). In order to improve the battery performance, it is important to control the structure of the composite. The electronic conductivity is governed by the contact configuration between active materials, conductive additives and binder and the Li⁺ transport is affected by the structure of vacancy in the composite.

To analyze the structure of the electrode in connection with the reaction, various methods, such as nuclear magnetic resonance (NMR), X-ray diffraction (XRD), X-ray absorption fine structure (XAFS), scanning Auger microscopy (SAM), and Raman spectroscopy, have been used. Also, the three-dimensional structure of the vacancy in electrodes has been well-studied by both simulation and instrumental analysis.

In situ Raman spectroscopy techniques are suitable tool to observe the distribution of the state of charge (SOC) in the composite electrodes because Raman spectra are sensitive to the structure of electrode materials. Hence, many efforts have been made to develop in situ techniques. However, most of them only measure the spectra. Therefore, it has not been possible to obtain the spatial distribution of the degree of reaction process in a single charge/discharge cycle. Recently, Nishi et al. reported the SOC mapping in an in-plane direction of a LiCoO₂ electrode by in situ Raman imaging. However, the information in an out-of-plane direction, i.e. cross-section of the electrode, is also important because Li⁺ transport takes place between the cathode and the anode, which means the vertical direction to electrodes.

Here, we developed a novel in situ and real time Raman imaging technique to investigate the distribution of SOC during the charge/discharge. The time resolution of 20 min was achieved by forming a flat cross section using Ar ion milling. The results showed an inhomogeneous Li⁺ intercalation in the LiCoO₂ cathode and the presence of electrochemically inactive LiCoO₂ particles. To the best of our knowledge, this is the first operando Raman imaging which measured the cross section of LIB electrodes. This method enables to analyze the reaction distribution and the degradation mechanism of LIBs.

2. Experimental

Electrodes were purchased from Piotrek Co., Ltd. The single-side coated graphite and LiCoO₂ electrodes were used as anode and cathode, respectively. Specific capacity of anode and cathode was 2.3 and 2.2 mAh/cm², respectively. 1 M LiPF₆ in a 1:1 volume fraction of ethylene carbonate (EC)/diethyl carbonate (DEC) (lithium battery grade) were purchased from KISHIDA CHEMICAL Co., Ltd. A polypropylene separator (Celgard 2400) was purchased from Polypropore International, Inc. All chemicals, electrodes and separators were used as received.

A schematic illustration of the specially designed cell is indicated in Fig. 1. The geometric electrode area was ca. 5 mm × 10 mm. The electrodes were cut by an Ar ion milling system (693 Illion Iload, Gatan Inc.) to form a flat cross section. The cell was assembled in an Ar-filled glove box as follows. The electrodes and the separator were firstly stacked by metal plates. Ni and stainless steel plates were used for anodic and cathodic side, respectively. After setting the electrodes into the cell, 500 µl of the electrolyte solution was injected. Finally, the cell was covered by a quarts glass window. The electrical contact with external device was made by screws and a spring connected to the plates.
The cross section of the electrodes was put against the window to minimize the distance between the electrodes and the window, which was less than a few microns. There are two reasons of this arrangement. One is to suppress the ion diffusion between the window and the electrodes, i.e. to imitate the situation in the real battery. The other one is to reduce the fluorescence from electrolyte. The presence of electrolyte in the optical path causes the large background of the Raman spectrum.

The electrochemical measurements were operated using the charge/discharge system (SD8, HOKUTO DENKO Co.). Constant-current/constant-voltage (CC/CV) charging and constant-current (CC) discharging were performed with cutoff voltages of 4.2 V and 3.0 V, respectively. The current was set at 0.2 mA and 0.5 mA for 0.2 C and 0.5 C operation, respectively. The cut off current of CV charging was set at one-tenth of the operating current.

Raman measurements were carried out using a confocal Raman microscope (Raman-11, Nanophoton Co.) with a 50× microscope objective lens. An excitation source is a 532 nm line shaped radiation from a solid-state laser. Raman scattering from the line-shaped area on the sample is simultaneously detected by parallel detection system. The beam size at the focal point on the sample plane is 464 nm × 160 µm. The pixel size, i.e. the spatial resolution in a horizontal direction, is 506 nm. The nominal spatial resolution in a perpendicular direction to the sample plane is 700 nm. It should be noted that this value depends on materials. The laser power at the sample plane was ca. 0.3 mW. Raman imaging of 30 × 160 µm region was obtained every 20 min during the charge/discharge. The obtained raw spectra were used for the further analysis without any correction, i.e. background subtraction and normalization.

3. Results and Discussion

The capability of the developed cell was firstly confirmed. Figure 2 shows charge/discharge curves obtained at the first cycle at 0.2 C and further two cycles at 0.5 C of the in situ Raman cell. Although the Coulombic efficiency of the first cycle, 0.76, was relatively low, the following cycles showed the stable operation. Hence, the cell indeed worked as a battery.

Figure 3 shows a series of in situ Raman spectra obtained during the first charge/discharge cycle. From the top, before charging, 3.69 V, 3.74 V, 3.76 V, 3.80 V, 3.86 V, 3.88 V, 3.97 V, 4.12 V, 4.20 V, 4.08 V, 3.96 V, 3.84 V, 3.79 V, 3.72 V, 3.65 V, and 3.41 V. The A\textsubscript{1g} peak position reaches to 567 cm\textsuperscript{-1} at 4.20 V and returns to the original position after discharging. These results are consistent with that in the previous literature.\textsuperscript{18,19} The change in the intensity and frequency are attributed to the change in the symmetry of LiCoO\textsubscript{2} lattice and expansion of the lattice in c-axis direction due to the Li\textsuperscript{+} intercalation/deintercalation.

In order to obtain the SOC distribution, the spectra were analyzed using the frequency of A\textsubscript{1g} peak. Figure 4 shows a series of mapping images. The measured area is indicated by a yellow square in the corresponding confocal micrograph. The amount of peak shift from 596 cm\textsuperscript{-1} at 4.20 V and returns to the original position after discharging. These results are consistent with that in the previous literature.\textsuperscript{18,19} The change in the intensity and frequency are attributed to the change in the symmetry of LiCoO\textsubscript{2} lattice and expansion of the lattice in c-axis direction due to the Li\textsuperscript{+} intercalation/deintercalation.

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active materials, particularly in the left part of images, disappear during discharging. This is because of defocusing of the laser beam. There are two possible explanations for the defocusing: the drift of the sample due to the long-term experiment, and the change in the shape of the electrode due to expansion and shrinkage of the electrode caused by charge and discharge, respectively. The focus is very important and sensitive in this experiment because the Raman system has a confocal optics.

From the results of in situ Raman imaging, one can distinguish electrochemically active and inactive active material particles. As shown in Fig. 4, the color of some active material particles remained blue from the beginning until the end of charge/discharge process. Figure 5 shows the spectra obtained at an active material, referred to as Particle A indicated by the arrow in the image. Although the $A_{1g}$ peak intensity slightly changes due to the drift of the electrodes, the peak position does not shift at the particle. As seen in Fig. 3, the peak shift is observed at the most of particles. This result indicates that there are some active materials which do not react as an electrode material, probably due to the isolation of the particle from the electronic conductivity network or the poor conductivity of Li$^+$ in the vacancy around the particle. The presence of inactive particles in the electrode causes the loss of energy density because such particles do not contribute to the electrode reaction. Therefore, it is important to find how many particles can act as electrode. The in situ Raman imaging technique helps to find such particles.

The reaction distribution can also be analyzed by the technique. $A_{1g}$ peak positions of three particles, referred to as Particle B, C, and D, during charge/discharge were plotted in Fig. 6, together with the voltage curve. The positions of each particle are indicated by arrows in the image. This plot shows the kinetic change of each particle during charge/discharge. The Particle B and C (red and green squares, respectively) showed approximately the same behavior, but the particle D (blue square) showed slower change in the range 0–4 h, the early phase of charging process, than B and C, showing that the electrode reaction at the particle D is slower than that at B and C.

A kinetic analysis can only be achieved by real-time measurements. In situ Raman imaging at steady-state performed in the previous study can measure the distribution of SOC correlated with contact resistance between active materials but cannot study the kinetics of electrodes correlated with both electronic and ionic conductivity. We have achieved 20 min acquisition time for taking each Raman image of 30 $\times$ 160 µm region by preparing a flat cross section and suitable optical cell which decrease the distance between the electrode and the optical window to minimize the fluorescence from the electrolyte solution. In case of low C-rate charge/discharge such as 0.2 C, 20 min is short enough to analyze the reaction kinetics.

Figure 4. In situ Raman mapping images. The measured area is indicated by a yellow square in the corresponding confocal micrograph.

Figure 5. In situ Raman spectra obtained at Particle A, indicated by the arrow in the image.

Figure 6. A plot of $A_{1g}$ peak frequency as a function of charge/discharge time at Particle B, C, and D, indicated by the arrows in the image, together with voltage behavior.
Figure 7. In situ Raman spectra obtained at Particle E, indicated by the arrow in the image. From the top, before charging, 3.74 V, 3.86 V, 4.20 V, 3.96 V, 3.72 V, and after discharging.

Furthermore, there is a possibility that the degradation mechanism of batteries can be clarified by this method. Figure 7 shows a series of spectra obtained at an active material, referred to as Particle E, indicated by the arrow. The peak position of the Particle E does not return to 596 cm⁻¹, which is corresponding to LiCoO₂, after discharging, indicating that the active material does not completely return to LiCoO₂ but still remains Li₁₋ₓCoO₂ state after discharging. Similar trend is observed at some other particles. The presence of such particles may lead the capacity fade of the battery because the discharging capacity of these particles must be smaller than the charging capacity.

4. Conclusions

An in situ and real-time Raman imaging technique has been developed and availability of the method as an analysis tool for LIB electrodes is shown by the demonstration using LiCoO₂ cathode. A specially designed cell allows high speed Raman imaging measurements during charge/discharge. A cross sectional Raman image of 30 × 160 μm region of LiCoO₂ electrode is obtained within 20 min and the SOC distribution is visualized.

The result of the analysis provides a criterion for evaluation of inactive electrode materials which should be excluded in manufacturing process. The analysis technique can also be utilized for kinetic analysis of electrode reaction at low C-rate by analysis of sequential images of SOC distribution. Moreover, change in chemical state of active materials caused by charge/discharge cycle can be detected, indicating the possibility of the method to analyze the degradation mechanism of active materials.

It is expected that the developed analysis technique can contribute to the improvement of battery manufacturing and the clarification of battery degradation mechanism. Further study about applicability of the method to other electrode materials is still in progress.

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References