**Raman imaging for LiCoO₂ composite positive
electrodes in all-solid-state lithium batteries using
Li₂S-P₂S₅ solid electrolytes**

Misae Otoyama¹, Yusuke Ito¹, Akitoshi Hayashi¹, Masahiro Tatsumisago¹

¹Department of Applied Chemistry, Graduate School of Engineering,

Osaka Prefecture University,

1-1, Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

***Corresponding author:**

Akitoshi Hayashi (Associate Professor)

Department of Applied Chemistry, Graduate School of Engineering,

Osaka Prefecture University,

1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, JAPAN

Tel.: +81-72-2549331; Fax.: +81-72-2549334

E-mail address: hayashi@chem.osakafu-u.ac.jp.

Abstract

A composite positive electrode in an all-solid-state battery is prepared by mixing LiCoO₂ particles and Li₂S-P₂S₅ solid electrolytes. Raman spectroscopy is conducted for the composite positive electrodes before and after the initial charging process. Raman spectral changes are observed, which corresponds to structural changes of LiCoO₂ particles during the charge test. However, some spectra indicate that several LiCoO₂ particles show no structural changes although the cell is fully charged. A local state-of-charge (SOC) distribution map of the composite electrode is obtained by Raman mapping. The mapping image after the charge test shows that distributions of reactions exist in the composite positive electrode.

Keywords

All-solid-state battery; Lithium battery; Raman spectroscopy; LiCoO₂; Solid electrolyte

1. Introduction

Lithium ion batteries (LIBs) have been used as power sources for portable electronics devices because of their high energy density, light weight and long cycle life [1]. Recently, large-scale LIBs have attracted much attention as power sources for electric vehicles and stationary energy storage systems. However, conventional LIBs have risks of leakage and explosion of organic liquid electrolytes. It is important to solve such safety issues with increasing battery size [2]. All-solid-state batteries with nonflammable inorganic solid electrolytes, an alternative to conventional inflammable organic liquid electrolytes, are next generation batteries with low risk of leakage and explosion. All-solid-state batteries are categorized into bulk-type batteries and film-type batteries. Bulk-type batteries, which use composite electrodes of active materials and solid electrolytes, are especially capable of having high energy density. We have investigated the electrochemical performance of bulk-type all-solid-state cells using a LiCoO_2 composite positive electrode and a $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte [3-5]. Rechargeable all-solid-state cells can be fabricated by pressing positive and negative electrode layers and a solid electrolyte layer at room temperature [6]. One of these cells, which showed good cell performance, was charged and discharged during 700 cycles at

25°C [3]. To improve the cell performance, electrochemical reactions at electrode-electrolyte interfaces should be studied.

There are several reports investigating physical and electrochemical properties of positive electrode active materials in the cells using liquid electrolytes during charge-discharge cycling by using various analytical methods such as X-ray diffraction [7], X-ray absorption spectroscopy [8,9], scanning transmission X-ray microscopy [10], nuclear magnetic resonance (NMR) [11] and atomic force microscope (AFM) [12]. Raman spectroscopy is also suitable for investigating electrochemical reaction of active materials because Raman spectral changes of a composite electrode are closely related to the structural changes of active materials during charge-discharge cycling. There are several reports regarding Raman spectral changes of LiCoO₂ composite electrodes in lithium cells using liquid electrolytes during the charging process [13,14]. Furthermore, Raman mapping was conducted because of its feature of high spatial resolution and surface sensitivity [15-17]. Mapping images enable us to evaluate state-of-charge (SOC) distributions of each active material in electrodes. However, there are no reports conducting Raman spectroscopy for LiCoO₂ composite electrode in all-solid-state lithium cells.

LiCoO₂ composite electrodes in all-solid-state batteries have many solid-solid

interfaces, and thus electrochemical reactions at the interfaces are complicated. Furthermore, investigations of SOC distributions in the electrodes have not been carried out. Clarification of these issues is important to improve electrochemical performances of all-solid-state cells. In this study, *Ex-situ* Raman spectroscopy was carried out for cross-section of LiCoO₂ composite positive electrodes in bulk-type all-solid-state lithium batteries to observe spectral changes during the charging process. Moreover, Raman mapping was conducted for LiCoO₂ composite positive electrodes to investigate local SOC distributions.

2. Experimental

2.1. Preparation of solid electrolyte

The 75Li₂S·25P₂S₅ (mol%) glass used as a solid electrolyte was prepared using a mechanical milling technique. Li₂S (Idemitsu Kosan, 99.9%) and P₂S₅ (Aldrich, 99%) crystalline powders were used as starting materials for sample preparation. The batches (1 g) of these mixed materials with the composition of 75Li₂S·25P₂S₅ (mol%) were mechanically milled at 510 rpm for 45 h using a planetary ball mill (Pulverisette 7; Fritsch) with a zirconia pot (45 mL volume) and 500 zirconia balls (4 mm diameter).

2.2. Fabrication of all-solid-state cells

LiNbO₃-coated LiCoO₂ was used as a positive electrode active material because a LiNbO₃ buffer layer decreases the interfacial resistance between LiCoO₂ particles and solid electrolytes [18]. LiNbO₃-coated LiCoO₂ particles (Toda Kogyo Co., 10 μm) and the 75Li₂S·25P₂S₅ (mol%) glass particles (2-5 μm [6]) with a weight ratio of 80 : 20 were mixed using an agate mortar to prepare composite positive electrodes. The optimized weight ratio to operate the cells was 70 : 30 [5], and the ratio studied here includes layer amounts of LiCoO₂, that may lead to a partial formation of insufficient Li⁺ ion conduction paths to LiCoO₂. Moreover, the amount of LiCoO₂ particles in the composite electrode with the ratio of 80 : 20 is larger and more LiCoO₂ particles are able to be examined by Raman microscopy. The ratio of 80 : 20 was thus selected in this study. Indium foil (99.999%; Furuuchi Chemical Corp.) was used as a negative electrode. A bilayer pellet consisting of the composite positive electrode (10 mg) and the 75Li₂S·25P₂S₅ (mol%) glass (80 mg) was obtained by pressing under 360 MPa. Indium foil was then attached to the bilayer pellet and pressed with stainless steel powder (SUS304L, Kojundo Chemical) (150 mg) used as a current collector under 240 MPa. A cuboid pellet (8 mm x 4 mm x 2 mm³) pressed using two stainless-steel plates which were used as current collectors for both positive and negative electrodes. Figs.

1(A) and (B) show a schematic diagram of the four-layered pellet and a photograph of the all-solid-state cell used in this study. The white box in Fig. 1(B) denotes the pellet. All the processes for preparation of solid electrolyte and fabrication of all-solid-state cells were carried out at room temperature in a dry Ar-filled glove box.

2.3. Electrochemical measurements

The cells were charged to 4.2 V (Li^+/Li) or different capacities of 20, 40, 60 and 80 mAh per gram of LiCoO_2 using a charge-discharge measuring device (BTS-2004; Nagano Co Ltd., Japan). The measurements were conducted at 25°C under a current density of 0.064 mA cm^{-2} .

2.4. Raman spectroscopy

After the 1st charging process, the layered pellet of $\text{In} / 75\text{Li}_2\text{S} \cdot 25\text{P}_2\text{S}_5$ (mol%) / LiCoO_2 was dismantled from the all-solid-state cells. The cells were sealed in a container with an optical flat glass window under dry Ar atmosphere. *Ex-situ* Raman spectroscopy was carried out for cross-section of the positive electrodes by Raman microscopy (LabRAM HR-800; Horiba-Jobin Yvon) with a green laser (532 nm) and a 50x objective (NA = 0.35, Olympus). The laser power at the sample was *ca.* 1 mW with

a laser spot size of *ca.* 2 μm . Acquisition time for each spectrum was 360 s. At least 10 spectra were collected at the different locations on the positive electrode.

Raman imaging was done for a surface part of the positive electrodes before and after the 1st charging process using a Raman microscope (RAMANtouch; nanophoton). An Ar ion-milling technique was done for removing irregularities on the surface using an ion-milling system (IM4000; HITACHI). The laser beam was focused onto the sample using a 50x objective (NA = 0.70, Nikon) with excitation at 532 nm. The intensity of the laser beam was *ca.* $5.3 \times 10^4 \text{ W cm}^{-2}$. Before conducting Raman spectroscopy, the morphologies of the electrodes prepared by Ar ion-milling technique were investigated by using scanning electron microscopy (SEM) (SU8220; HITACHI).

3. Results and discussion

All-solid-state cells (In / $\text{Li}_2\text{S-P}_2\text{S}_5$ glass / LiCoO_2) were charged to 4.2 V (vs. Li^+/Li) or different capacities of 20, 40, 60 and 80 mAh g^{-1} . After the charge test, Raman spectroscopy was conducted for cross-section of the LiCoO_2 composite positive electrode layers. Fig. 2 shows the schematic diagram of the cross-section of the all-solid-state cell and the optical micrograph of the cross-section of the positive electrode selected by a red box in the diagram. The laser beam was focused on LiCoO_2

particles (bright ones) with a laser spot size of *ca.* 2 μm . At least 10 particles were measured for each positive electrode of the cells charged to the different capacities.

Fig. 3(A) shows the initial charge curve of the all-solid-state cell. Fig. 3(B) shows the Raman spectra of LiCoO_2 electrode layers at the different charge capacities. The labels in Figs. 3(A) and (B) are as follows : (a) 0, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 103 mAh g^{-1} . A typical spectrum at each capacity is shown in Fig. 3(B). There are two strong Raman bands at 486 and 596 cm^{-1} , originating from the two Raman-active modes: E_g and A_{1g} modes corresponding to O-Co-O bending and Co-O stretching, respectively [13,19,20]. Those peaks shifted to the lower wavenumber side and their intensity decreased after the initial charging process. These spectral changes are mainly attributed to expansion in c-axis direction of LiCoO_2 lattice as Li^+ ion is deintercalated from LiCoO_2 [20,21]. When the cell charged to 4.2 V (vs. Li^+/Li), those peaks of E_g and A_{1g} modes shifted to 470 cm^{-1} and 582 cm^{-1} , respectively. Fig. 3(C) shows the capacity dependence of the peak positions for E_g and A_{1g} modes indicated in Fig. 3(B). These spectral changes are very similar to those of LiCoO_2 electrodes in lithium cells using liquid electrolytes [13,15].

After the cell was charged to 4.2 V (vs. Li^+/Li), different spectra were collected at the different locations on the electrode. These different spectra of (f-1) and (f-2) are

shown in Fig. 3(D). The spectrum (f-1) was similar to the spectrum (a) (before charging process), suggesting that the LiCoO₂ particle showed no structural changes. In this study, it is called “low SOC LiCoO₂”. The peaks of E_g and A_{1g} modes shifted to the lower wavenumber side and their intensity markedly decreased in the spectrum (f-2), suggesting that the LiCoO₂ particle underwent lithium deintercalation, and it is called “high SOC LiCoO₂”. Moreover, a peak at 675 cm⁻¹ attributable to Co₃O₄ was observed in the spectrum (f-2) [13,22]. It is reported for the LiCoO₂ cells using a liquid electrolyte that Co₃O₄ was formed with emission of oxygen gas by overcharging to 4.8 V (vs. Li⁺/Li) or elevating operation temperature [23-25]. This mechanism is proposed as follows [23]:

The formation of Co₃O₄ in this study indicates that some LiCoO₂ underwent overcharging even under the cut-off of 4.2 V (vs. Li⁺/Li) at 25°C, and electrochemical reactions at a LiCoO₂ positive electrode layer probably did not proceed uniformly.

To investigate the reaction distribution at the composite positive electrode in detail, Raman mapping was conducted for the surface of the LiCoO₂ composite positive electrodes before and after the 1st charging process as shown in Fig. 4(A). To prepare

flat surface for Raman mapping, Ar ion-milling was carried out for the electrode surface. The SEM image of the surface of the positive electrode is showed in Fig. 4(A). A clear image of LiCoO₂ particles and solid electrolytes was obtained. Fig. 4(B) shows Raman spectra for the LiCoO₂ electrodes after the initial charge at different positions. Each color on Raman bands corresponds to that for a mapping image. The red and blue colored areas denote pristine LiCoO₂ (including charged LiCoO₂ with low SOC) and charged LiCoO₂ (with high SOC), respectively. Green and yellow colored areas denote PS₄³⁻ unit of solid electrolyte and Co₃O₄ (by-product), respectively. Fig. 5 shows an optical micrograph (A) and a mapping image (B) of a LiCoO₂ electrode layer before the 1st charging process. The red box denotes the region selected for Raman mapping. The bottom part of the SEM image shows an interface of the LiCoO₂ composite positive electrode layer and the solid electrolyte layer. Only red and green colored areas were observed in the mapping image, suggesting that LiCoO₂ particles and solid electrolytes distributed in the composite electrode. Fig. 6 shows an optical micrograph (A) and a mapping image (B) of a LiCoO₂ electrode layer after the 1st charging process. Individual mapping images (C) in Fig. 6 are shown with each color. The cell charged to 4.2 V (vs. Li⁺/Li) showed the initial charge capacity of 117 mAh g⁻¹. Blue colored areas distributed widely in the mapping image. They indicated that Li deintercalation proceeded entirely

in the electrode. However, red colored areas (showed by black circle) were observed in the image, suggesting that low SOC LiCoO_2 still remained. Aggregated LiCoO_2 particles without contact to solid electrolyte particles especially became low SOC state because of less Li^+ ion conduction paths. Moreover, Co_3O_4 colored yellow was mainly distributed at a bottom part of the mapping image, indicating that LiCoO_2 particles near the solid electrolyte layer tended to be overcharged. It is noteworthy that electrochemical reactions at the LiCoO_2 composite positive electrode did not proceed uniformly, and distributions of reactions existed because of insufficient contacts between LiCoO_2 and solid electrolyte. The electrodes studied here had relatively many insufficient contacts because they were prepared by only mixing of LiCoO_2 and solid electrolyte particles. Coating of sulfide solid electrolyte thin films on LiCoO_2 particles [26] will give sufficient interfaces and large contact areas, and therefore uniform electrochemical reactions will be achieved. Raman spectroscopy for a positive electrode layer with electrolyte-coated LiCoO_2 particles will be examined in the future.

4. Conclusions

Bulk-type all-solid-state lithium cells were fabricated with composite positive electrodes prepared by mixing LiCoO_2 particles and solid electrolyte particles. Raman

spectroscopy was conducted for LiCoO₂ particles at the cross-section of composite positive electrodes at different capacities. The peaks of E_g and A_{1g} modes shifted to the lower wavenumber side and their intensities decreased after the initial charging process. These Raman spectral changes were very similar to those of LiCoO₂ electrodes in lithium cells using liquid electrolytes. Raman mapping was carried out for the surface of the composite electrodes prepared by an Ar ion-milling technique. The mapping image after the initial charging process indicated distributions of reactions in the composite positive electrode.

Acknowledgements

This research was supported by the Japan Science and Technology Agency (JST), Advanced Low Carbon Technology Research and Development Program Specially (ALCA) Promoted Research for Innovative Next Generation Batteries (SPRING) project, and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. We also thank Mr. Y. Shiozaki (nanophoton corp.) for conducting Raman mapping measurements and fruitful discussions.

References

- [1] J. M. Tarascon, M. Armand, *Nature* 414 (2001) 369-367.
- [2] W. Li, J. R. Dahn, D. S. Wainwright, *Science* 264 (1994) 1115-1118.
- [3] T. Minami, A. Hayashi, M. Tatsumisago, *Solid State Ionics* 177 (2006) 2715-2720.
- [4] M. Tatsumisago, A. Hayashi, *Funct. Mater. Lett.* 1 (2008) 31-36.
- [5] A. Sakuda, A. Hayashi, M. Tatsumisago, *Chem. Mater.* 22 (2010) 949-956.
- [6] A. Sakuda, A. Hayashi, M. Tatsumisago, *Sci. Rep.* 3 (2013) 2261.
- [7] J. N. Reimers, J. R. Dahn, *J. Electrochem. Soc.* 139 (1992) 2091-2097
- [8] D. Takamatsu, Y. Koyama, Y. Orikasa, S. Mori, T. Nakatsutsumi, T. Hirano, H. Tanida, H. Arai, Y. Uchimoto, Z. Ogumi, *Angew. Chem.* 51 (2012) 11597-11601.
- [9] K. Yamamoto, T. Minato, S. Mori, D. Takamatsu, Y. Orikasa, H. Tanida, K. Nakanishi, H. Murayama, T. Masese, T. Mori, H. Arai, Y. Koyama, Z. Ogumi, Y. Uchimoto, *J. phys. Chem. C* 118 (2014) 9538-9543.
- [10] W. C. Chueh, F. E. Gabaly, J. D. Sugar, N. C. Bartelt, A. H. McDaniel, K. R. Fenton, K. R. Zavadil, T. Tyliczszak, W. Lai, K. F. McCarty, *Nano Lett.* 13 (2013) 866-872.
- [11] K. Shimoda, M. Murakami, D. Takamatsu, H. Arai, Y. Uchimoto, Z. Ogumi, *Electrochimica Acta* 108 (2013) 343-349.

- [12]D. E. Demirocak, B. Bhushan, J. Colloid Interface Sci. 423 (2014) 151-157.
- [13]M. Inaba, Y. Iriyama, Z. Ogumi, Y. Todzuka, A. Tasaka, J. Raman Spectrosc. 28 (1997) 613-617.
- [14]C. Julien, M. Massot, Phys. Chem. Chem. Phys. 4 (2002) 4226-4235.
- [15]T. Nishi, H. Nakai, A. Kita, J. Electrochem. Soc. 160 (2013) A1785-A1788.
- [16]T. Gross, C. Hess, J. Power Sources 256 (2014) 220-225.
- [17]J. Nanda, J. Remillard, A. O'Neill, D. Bernardi, T. Ro, K. E. Nietering, J. Go, T. J. Miller, Adv. Funct. Mater. 21 (2011) 3282-3290.
- [18]N. Ohta, K. Takada, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada, T. Sakai, Electrochem. Comm. 9 (2007) 1486-1490.
- [19]C. Julien, Solid State Ionics 887 (2000) 136-137.
- [20]M. Inaba, Y. Todzuka, H. Yoshida, Y. Grincourt, A. Tasaka, Y. Tomida, Z. Ogumi, Chem. Lett. 24 (1995) 889.
- [21]M. Inaba, H. Yoshida, Z. Ogumi, T. Abe, Y. Mizutani, M. Asano, J. Electrochem. Soc. 142 (1995) 20-26.
- [22]Y. Park, S. H. Shin, S. M. Lee, S. P. Kim, H. C. Choi, Y. Mee Jung, J. Molecular Structure 1069 (2014) 183-187.
- [23]H. Wang, E. Rus, T. Sakuraba, J. Kikuchi, Y. Kiya, H. D. Aburuna, Anal. Chem. 86

(2014) 6197-6201.

[24]J. Geder, H. E. Hoster, A. Jossen, J. Garche, D. Y. W. Yu, J. Power Sources 257

(2014) 286-292.

[25]D. Mohanty, H. Gabrisch, Solid State Ionics 194 (2011) 41-45.

[26]A. Sakuda, A. Hayashi, T. Ohtomo, S. Hama, M. Tatsumisago, J. Power Sources

196 (2011) 6735-6741.

Figure captions

Fig. 1 (A) Schematic diagram of the four-layered pellet and (B) photograph of the all-solid-state cell used in this study.

Fig. 2 Optical micrograph of the cross-section at electrode layer. (Yellow dots indicate the locations where Raman spectroscopy was carried out.)

Fig. 3 (A) Initial charge curve of the all-solid-state cell (In / Li₂S-P₂S₅ glass / LiCoO₂) at 25°C. The cell was charged to 4.2 V (vs. Li⁺/Li) at the current density of 0.064 mA cm⁻¹. (B) Raman spectra of LiCoO₂ electrode layer at the different charge capacities of (a) 0, (b) 20, (c) 40, (d) 60, (e) 80 and (f) 103 mAh g⁻¹. (C) Capacity dependence of the peak positions for *E_g* and *A_{1g}* modes indicated in Fig. 3(B). (D) Different Raman spectra of the LiCoO₂ electrode layer after the full charge test at position (f). Spectra (f-1) and (f-2) were obtained at the different locations of the electrode.

Fig. 4 (A) SEM image of the cross-section of LiCoO₂ electrode prepared by an Ar ion-milling technique and (B) definition of colors for mapping image. Red and blue colored area indicate the peak positions of pristine and charged LiCoO₂, respectively. Green and yellow colored areas show the peak position of PS₄³⁻ unit in solid electrolyte and Co₃O₄, respectively.

Fig. 5 (A) Optical micrograph and (B) mapping image of the LiCoO₂ electrode layer

before the 1st charging process.

Fig. 6 (A) Optical micrograph, (B) mapping image of the LiCoO_2 electrode layer after the 1st charging process and (C) individual mapping images of LiCoO_2 , electrolyte and Co_3O_4 .

(A)

(B)

Fig. 1

Fig. 2

Fig. 3

(A)

(B)

Fig. 4

(A)

(B)

■ LiCoO_2 ; ■ Electrolyte

I
SE layer

Fig. 5

Fig. 6

Graphical abstract