Electromotive force measurements of LiCoO_2 electrode on a lithium ion conducting glass ceramics under mechanical stress

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Abstract

Two LiCoO_2 dense film electrodes were prepared on both surfaces of a lithium ion conducting glass ceramics, and electromotive force measurements were performed between the film electrodes under mechanical compressive and tensile stresses by four points bending tests. Electromotive force appeared immediately after applying the stress, and disappeared after releasing the stress. The larger stress was applied, the larger electromotive force was observed. These results clearly demonstrated that the lithium chemical potential in the

LiCoO₂ electrode varies under mechanical stress. The influence of the mechanical stress on the lithium chemical potential was discussed based on the relation between the CoO₂ interlayer distance and the lithium concentration in LiCoO₂.

Keywords: Lithium chemical potential; Mechanical stress; Electromotive force; All solid state lithium batteries

1. Introduction

Lithium ion secondary batteries have been widely used in mobile electronic devices because of its high energy density and excellent cyclability [1,2]. Recently, lithium ion secondary batteries are going to be applied as a power source of electric vehicles. However, it has been pointed out the energy density, power density, capacity, and safety are not sufficient enough for the use in electric vehicles. All-solid-state lithium ion secondary batteries are one type of promising next generation batteries to potentially satisfy the above requirements [3]. Since the all-solid-state batteries consist of only solid materials, downsizing and non-flammability can be achieved, resulting in improvements of energy density, power density and safety.

In lithium ion secondary batteries, understanding of the electrode/electrolyte interface, where electrochemical reactions progress, is important to improve the performance. Particularly in all-solid-state batteries, mechanical stress, which can be introduced at the interface due to the difference of crystal structure and chemical/thermal expansion

coefficients between the electrode and the electrolyte, is one issue to be considered. Mechanical stress may affect electrochemical properties of the electrode and the electrolyte. For instance, Ichitsubo *et al.* reported a constrained electrode showed the voltage change and the capacity degradation [4]. However, the influences of mechanical stress on electrochemical properties of electrode and electrolyte materials are not well-understood yet.

From the backgrounds mentioned above, in this study, we aim to obtain fundamental knowledge about effects of mechanical stress on thermodynamic properties of batteries' components. LiCoO_2 (LCO), which is the most conventional cathode material, was chosen as a model cathode material. LCO dense thin films were deposited on the both surfaces of a lithium ion conducting glass ceramics (LICGC). External mechanical load was applied to the LCO film electrodes by four points bending tests, and electromotive force between two LCO electrodes was measured. Based on the results, the relationship between lithium chemical potential in the LCO electrodes and mechanical stress was discussed.

2. Experimental

2.1. Sample preparation

A schematic illustration of the specimen used in this study is shown in Fig.1. Lithium ion-conducting glass ceramics (LICGC) was used as a solid electrolyte. A commercially-available LICGC plate ($\text{Li}_{1+x+y}\text{Al}_x(\text{Ti,Ge})_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$, OHARA Inc., Japan) was cut into the size of 16 x 16 x 1 mm. Both surfaces of the LICGC electrolyte were

mirror-polished. The dense thin film electrodes of LiCoO_2 (LCO) were fabricated on the both surfaces of the LICGC plate by the pulsed laser deposition (PLD) method at 873K under $P(\text{O}_2)$ of 20 Pa for 1 hour [5]. The fourth harmonic of Nd:YAG laser (10 Hz, 266 nm, 75mJ) was used. The thickness of the LCO films was approximately 200 nm. Aluminum dense thin films having 150 nm of the thickness were also deposited next to the LCO electrodes by the Ar ion sputtering at room temperature in Ar atmosphere of about 0.67 Pa for 5 minutes. The aluminum electrodes were used as counter electrodes for charging the LCO electrodes, *i.e.* controlling the lithium composition in the LCO electrodes. Finally, as a current collector, gold thin films were coated on the LCO electrodes by the Ar ion sputtering.

The lithium composition in the LCO electrodes was controlled electrochemically by the constant-current charging with the approximately 0.50 μA (0.05 C). 10, 20, 30 and 40% of lithium were extracted from the LCO electrodes. In other words, Li_xCoO_2 with $x = 0.9, 0.8, 0.7$ and 0.6 were prepared. Then, the specimen was cut into two pieces to remove the aluminum electrodes' side. The LCO electrodes on the both LICGC surfaces were short-circuited for about 24 hours to ensure the equivalent lithium contents in the both electrodes. After this procedure, the electromotive force between the two LCO electrodes became nearly zero, indicating the lithium chemical potential, *i.e.* the lithium concentration, in the two LCO electrodes was equivalent. In the following discussion, we use the lithium concentration, x in Li_xCoO_2 , which is calculated from the charging current and time by

assuming 100% of the current efficiency.

2.2. *EMF measurements with/without applying mechanical stress*

Figure 2 shows the experimental setup for electromotive force (*EMF*) measurements under mechanical stress. The measurements were carried out in the digital control universal testing machine (5565 type, Instron *Inc.*), which could precisely control the external mechanical load or strain to the specimen. The uniaxial mechanical load was applied to the LCO electrodes with the four points binding configuration. In this configuration, compressive and tensile stresses were given to the in-plane direction of the upper and the lower LCO electrodes, respectively. Various magnitudes of mechanical load were applied and released step by step while measuring *EMF* between the two LCO electrodes by the digital multimeter (type 2182A, Keithley Instruments *Inc.*, Japan). During the *EMF* measurements, the upper-side LCO electrode was used as a reference.

In this work, the influence of the mechanical stress on *EMF* between the two LCO electrodes, more specifically the lithium chemical potential change in the electrodes, was discussed as a function of the applied stress. However, as mentioned above, in our measurements, compressive and tensile stresses were applied to the electrodes at same time. So, in this work, we defined the compressive mechanical stress was positive directional stress, and assumed the influence of the stress on *EMF* was comparable for tensile and compressive stresses while giving the opposite sign. According to this assumption, the “nominal”

mechanical stress, which means the relative mechanical stress on the lower electrode (tensile side) with reference to that on the upper electrode (compressive side), was introduced in the following discussion. The nominal mechanical stress on the LCO electrode under four points bending tests was calculated by the following equation [6].

$$\sigma_{\text{LCO}} = \{2aWE_{\text{LCO}}/(2E_{\text{LCO}}I_{\text{LCO}} + E_{\text{LIC}}I_{\text{LIC}})\}y \quad (1)$$

where σ , W , E and I are the nominal stress, the mechanical load given by the testing machine, the Young's modulus and the cross-sectional secondary moment, respectively. The subscripts of LCO and LIC express the LCO electrode and the LICGC electrolyte. E_{LCO} , E_{LIC} , I_{LCO} and I_{LIC} were 150 GPa, 60 GPa, approximately $4.0 \times 10^{-4} \text{ mm}^4$ and 0.5 mm^4 , respectively. The Young's moduli were taken from the refs. 7 and 8, and the cross-sectional secondary moment was calculated from the size of the specimens. The parameters of a and y are the rod spacing and the vertical displacement as defined in Fig. 2, and were typically 2 mm and 0.4 mm, respectively.

2.3. XRD measurements

X-ray diffraction (XRD) measurements (D8 DISCOVER, Bruker Corporation, $\text{CuK}\alpha$) were carried out to identify the phase state of the LCO dense film electrode and to investigate the crystal structure change depending on the state of charge. The LCO electrode was charged with the rate of 0.05 C, and the XRD measurements were performed at various states of charge from $x = 1.0$ to 0.6 in Li_xCoO_2 .

3. Results and Discussion

XRD measurements showed that the LCO dense film electrodes could be successfully prepared in a single phase (space group: $R\bar{3}m$). The diffraction peak assigned to the (003) plane was preferentially observed for all the films, indicating the LCO films were oriented in the direction of [001]. This means the CoO_2 layer was directed parallel to the surface of the LICGC electrolyte.

The electromotive force (EMF) observed between the two $\text{Li}_{0.7}\text{CoO}_2$ electrodes with or without external mechanical loads is presented in Fig.3. The positive EMF was observed immediately after applying the nominal tensile stress, although the observed EMF value was small. The generated EMF returned to nearly zero just after the release of the stress. The mechanical load of 29 N corresponding to 75 MPa was repeatedly applied while changing the keeping time. The EMF value was reproducible and kept approximately constant around 0.4 mV during the keeping time, although it was slightly fluctuated at random probably due to background noises. The similar EMF behaviors were seen with the LCO electrodes with the different lithium contents *i.e.*, $x = 0.9, 0.8$ and 0.6 .

The EMF observed between the two $\text{Li}_{0.7}\text{CoO}_2$ electrodes with different magnitudes of the mechanical stress is shown in Fig.4. In this series of measurements various magnitudes of load from 10 to 26 N, which corresponds to from 30 to 80 MPa, were applied. The observed EMF value increased with increasing the stress. The observed EMF values are presented in Fig.5 as

a function of the nominal stress. In this figure, all the *EMF* values measured with Li_xCoO_2 having different the lithium composition x are plotted together. From Fig.5, it can be said that the *EMF* is roughly proportional to the mechanical stress and is not significantly affected by the lithium composition in the LCO electrode. The specimen was broken when the load exceeding about 40N, which corresponded to 100 MPa in the nominal stress, was given.

The *EMF* of the LCO electrode on the LICGC electrolyte can be related to the lithium chemical potential, μ_{Li} , in the LCO electrode. Thus, the observed *EMF* in this work can be related to the μ_{Li} change accompanied by the application of the external mechanical stress. To discuss the μ_{Li} change in LCO, we here consider the relation between the volume change and the lithium composition in LCO. For this purpose, XRD measurements were carried out with the LCO film electrode while it was charged from $x = 1.0$ to 0.6. The results obtained for the (003) diffraction of LCO are presented in Fig.6. It was found the (003) peak shifted to lower angle with decreasing the lithium composition. It is known that lithium ions in LCO are located between the CoO_2 layers. The result in Fig. 6 suggests the interlayer in LCO is expanded with de-lithiation. Similar results were reported by previous studies [9, 10].

As described in the beginning of this chapter, the LCO film electrode in our specimen was oriented in the direction of [001], meaning the CoO_2 layer was directed parallel to the LICGC electrolyte. Thus, when the external compressive stress is applied in the in-plane direction of the film electrode, the tensile strain is induced in the direction perpendicular to the CoO_2 layer.

That is, the interlayer distance expands when the external compressive stress is applied to the film by the four point bending tests. In our experimental setup, the upper-side LCO film electrode is considered to be in such a situation. An expansion of the interlayer distance is also observed when the LCO electrode is charged, *i.e.* when lithium ions are extracted from LCO, as discussed in Fig. 6. However, one should here note that the lithium concentration was kept constant during the *EMF* measurements under mechanical stress. These indicate that the lithium chemical potential in LCO, μ_{Li} , might become higher under the compressive stress than the stress-free condition. On the other hand, in the lower-side LCO film electrode where the external tensile stress was applied, the interlayer distance is considered to shrink. Since the lithium concentration did not change in this case too, lower μ_{Li} might be achieved in LCO under the tensile stress compared with LCO without any mechanical stress.

EMF can be expressed by the difference in μ_{Li} between two electrodes. Since the upper-side electrode is the reference (negative) electrode in our experimental setup, *EMF* can be expressed by the following equation.

$$EMF = -(\mu_{\text{Li}}^{\text{lower}} - \mu_{\text{Li}}^{\text{upper}})/F \quad (2)$$

where $\mu_{\text{Li}}^{\text{lower}}$ and $\mu_{\text{Li}}^{\text{upper}}$ are the lithium chemical potentials in the lower-side and the upper-side LCO electrodes, respectively. From the discussion above, μ_{Li} was higher in the upper-side electrode than the lower-side electrode, when the external mechanical stress was applied in our experimental setup with the four points bending configuration. Then, Eq. (2)

tells us positive EMF should be observed. This consideration qualitatively explains the experimental results shown in Figs.3 and 4.

According to the theoretical treatment by Durham and Schmalzried [11], the quasi-static mechanical work can be expressed by $2\sigma \cdot v_{Li} \cdot dn_{Li}$, when dn_{Li} mol of Li is transferred from the upper-side electrode under compressive stress to the lower-side electrode under tensile stress. Here v_{Li} is the molar volume change of LCO when 1 mol of Li is intercalated, and 2σ corresponds to the nominal stress in this paper. This mechanical work should be equivalent with the electrostatic work represented by $EMF \cdot F \cdot dn_{Li}$, where F is the Faraday constant. Then the differential of the EMF with respect to the nominal stress, *i.e.* the slope of the line in Fig. 5, can be expressed by v_{Li}/F , and is expected to be $-5.8 \times 10^{-12} \text{ V} \cdot \text{Pa}^{-1}$, since v_{Li} was estimated as $-5.6 \times 10^{-7} \text{ m}^3 \cdot \text{mol}^{-1}$ from the results of the XRD measurements shown in Fig. 6. This expected value is in a good agreement with the experimental value in Fig. 5, *i.e.* $6.1 \times 10^{-12} \text{ V} \cdot \text{Pa}^{-1}$. This fact supports our hypothesis that the observed EMF is caused by the lattice volume change due to the mechanical stress.

Throughout this work, it was empirically demonstrated that mechanical stress can affect thermodynamic properties of battery components. In the case of Li_xCoO_2 , the compressive/tensile strain in the direction perpendicular to the CoO_2 layer decreases/increases the lithium chemical potential. This means that the charging voltage increases/decreases or the discharge voltage decreases/increases when Li_xCoO_2 is subjected to compressive/tensile strain.

in the direction perpendicular to the interlayer. Such a voltage change during the charge or discharge due to the mechanical strain might be taken into account in the design of all-solid-state lithium batteries, in which significant mechanical strain is possibly introduced at solid-solid interfaces during the batteries' fabrication and the charge/discharge cycles.

Mechanical stress may influence thermodynamic properties of not only the electrode but also the electrolyte. However, at this moment, we think that the contribution to EMF from the electrolyte is much smaller compared with that from the electrode. In fact, the dependence of EMF on the mechanical stress was closely similar with the different solid electrolyte and the same electrode materials, while it was obviously different with the same solid electrolyte and the different electrode materials. Detailed discussion together with experimental results will appear in a separated paper [12].

4. Conclusions

Through EMF measurements between the two Li_xCoO_2 (LCO, $x = 0.9, 0.8, 0.7$, and 0.6) dense film electrodes on the lithium ion conducting glass ceramics, the effect of the mechanical stress on thermodynamic properties of the electrode was experimentally demonstrated. EMF was generated immediately after applying the mechanical stress and returned to zero just after the release of the stress. The EMF value became larger with increasing the stress. The cause of the EMF change due to the mechanical stress was discussed based on the relation between the lattice volume and the lithium concentration of

the electrode. In the case of LCO, it was considered that the compressive/tensile strain in the direction perpendicular to the CoO₂ interlayer decreases/increases the lithium chemical potential. This thermodynamic consideration could explain the experimental results well.

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References

- [1]Y. Nishi, *J. Power Sources*, **100** (2001) 101-106.
- [2]K. Ozawa, *Solid State Ionics*, **69** (1994) 212-221.
- [3]K. Takada, *ActaMater.*,**61** (2013) 759-770.
- [4]T. Ichitsubo, S. Yukitani, K. Hirai, S. Yagi, T. Uda, E. Matsubara,*J. Mater. Chem.*, **21** (2011) 2701-2708.
- [5] N. Kuwata, N. Iwagami, Y. Tanji, Y. Matsuda, J. Kawamura, *J. Electrochem. Soc.*, 157 (4) (2010) A521-A527.
- [6] F. P. Beer, E. R. Johnston, Jr., J. T. Dewolf, D. F. Mazurek, *Mechanics of materials*; Fifth Edition in SI Units, The McGraw-Hill Corporation, Inc., 2009, p.208-p.306.
- [7] H. Zhang, P. S. Grant, *Sensor.Actuator. B*, **176** (2013) 52-57.

- [8] G. M. Krishna, N. Veeraiah, N. Venkatramaiah, R. Venkatesan, *J. Alloy. Compd.*, **450** (2008) 477-485.
- [9] G. G. Amatucci, J. M. Tarascon, L.C. Klein, *J. Electrochem. Soc.*, **143**, 1114-1123 (1996).
- [10] T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, **141**, 2972 (1994).
- [11] W. B. Durham, H. Schmalzried, *Ber. Bunsenges. Phys. Chem.*, **91**, 556-561 (1987).
- [12] K. Funayama, T. Nakamura, N. Kuwata, J. Kawamura, T. Kawada, K. Amezawa, *Electrochemistry*, **in print**.

Figure Captions

Fig. 1: Schematic illustrations of (a) the top view and (b) the cross sectional view of the cell for *EMF* measurements; (i) LiCoO_2 dense thin film electrode, (ii) aluminum dense thin film electrode, (iii) gold current collector, and (iv) lithium ion conducting glass ceramics (LICGC).

Fig. 2: Experimental setup for *EMF* measurements under mechanical stress. The arrows described in this figure express the distribution of mechanical stress in-plane direction in the specimen during four points bending tests.

Fig. 3: *EMF* between the two $\text{Li}_{0.7}\text{CoO}_2$ electrodes with or without a constant mechanical loading of 29N.

Fig. 4: *EMF* between the two $\text{Li}_{0.7}\text{CoO}_2$ electrodes with or without mechanical loading from 10 to 26 N.

Fig. 5: *EMF* between the two Li_xCoO_2 ($x = 0.9, 0.8, 0.7$, and 0.6) electrodes as a function of the nominal mechanical stress.

Fig. 6: XRD diffraction peaks of the (003) plane of Li_xCoO_2 when the Li composition x was varied from 1.0 to 0.6.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6