Effect of Mechanical Stress on Lithium Chemical Potential in Positive Electrodes and Solid Electrolytes for Lithium Ion Batteries

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ABSTRACT

Effects of mechanical stress on lithium chemical potential in electrodes and electrolytes for all-solid-state lithium ion batteries were investigated. Dense film electrodes of LiCoO2 or LiMn2O4 were symmetrically deposited on both surfaces of a plate of various solid state lithium ion conductors, such as Li0.29La0.57TiO3, Li7La3Zr2O12 and Li1+x+yAlx(2-Ti,Ge)2−x−ySi3P3−yO12. Mechanical stress was applied to the specimen by four points bending tests while measuring electromotive force (EMF) between the two electrodes. EMF proportional to the applied stress was observed. EMF was significantly dependent on the electrode material, but was almost independent of the electrolyte material. These results indicated that lithium chemical potential varied under mechanical stress both in the electrode and electrolyte but the influence of mechanical stress appeared notably in the electrode than the electrolyte. The lithium chemical potential changes in the electrode and the electrolyte under mechanical stress were discussed based on the idea of local equilibrium.

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1. Introduction

All-solid-state lithium ion batteries (LIBs) are one of promising candidates of next generation energy storages and power sources. For their use in large-scale applications such as electric vehicles, it was expected to achieve high energy density.1 In all-solid-state batteries, electrode reaction takes place at the solid-solid heterointerface between an electrolyte and an electrode active material in contrast to conventional batteries using liquid electrolytes. Therefore the investigation on the solid-solid heterointerface is important to improve the performance of all-solid-state batteries.

At the solid-solid heterointerface, it is considered that mechanical stress is generated because of the difference in the crystal structure and the thermal/chemical expansion coefficient between the electrolyte and the electrode. The mechanical stress is concerned to cause not only mechanical damages but also changes in thermodynamic/electrochemical properties of the batteries’ components, which may result in performance degradation of the batteries. In fact, some researchers pointed out that a mechanical stress and strain influences thermodynamic and electrochemical properties of solid materials.2–5 Thus, for the development of all-solid-state LIBs, it is important to understand effects of mechanical stress and strain on material properties of solids.

From the backgrounds mentioned above, we have been investigating effects of mechanical stress and strain on thermodynamic properties of electrode materials for all-solid-state LIBs. In another study,6 LiCoO2 (LCO) dense film electrodes were prepared on both surfaces of the lithium ion conducting glass ceramics (LiCGCC), and electromotive force (EMF) measurements between two LCO electrodes were carried out while applying mechanical stress to the electrodes by four points bending tests. The generation of EMF was clearly observed with the application of mechanical stress. The obtained results could be qualitatively explained by assuming that the lithium chemical potential in LCO increases/decreases with applying the tensile/compressive strain in the direction perpendicular to the CoO2 layer, respectively. However, effects of mechanical stress and strain on thermodynamic properties of the electrolyte materials still remained unknown. In this work, EMF measurements of LCO or LiMn2O4 electrodes on various types of solid-state lithium ion conductors were carried out under four point bending tests. Then effects of mechanical stress and strain on the lithium chemical potential in electrolytes as well as in electrodes were discussed based on the obtained results.

2. Experimental

2.1 Sample preparation

Two different types of solid-state lithium ion conductor, Li1-xLa0.57TiO3 (LLTO, Toho Titanium Co. Ltd., Japan) and Li1-xLa0.5Zr2O12 (LLZO, Toshima Manufacturing Co. Ltd., Japan) were used in this work. Dense thin films of LiCoO2 (LCO) or LiMn2O4 (LMO) were deposited symmetrically on both surfaces of the solid-state lithium ion conductor by pulsed laser deposition (PLD) using the ArF excimer laser (20 Hz, 193 nm, 200 mJ). Film fabrication conditions were 873 K, P(O2) of 20 Pa, and 10 min. of deposition time for LCO and 15 min. for LMO. The electrode area was 8 × 8 mm2, and the thickness was approximately 200 nm for LCO and 150 nm for LMO. As a counter electrode for charging LCO, an aluminum dense film was deposited next to the LCO or LMO electrodes by Ar ion sputtering at room temperature under P(Ar) of 0.67 Pa for 7 min. Finally, a gold thin film as a current collector was deposited on the LCO or LMO electrodes by Ar ion sputtering at room temperature under P(Ar) of 10 Pa for 5 min. The schematic illustration of the prepared cell is given in Fig. 1.

XRD measurements revealed all of the LCO or LMO films could prepared in a single phase LiCoO2 or LiMn2O4. In the case of the
LCO films, the diffraction peak assigned to the (003) plane was always observed preferentially. SEM observation showed the film consisted of columnar grains with approximately 100–200 nm in diameter. These indicated that the LCO films were polycrystalline but were oriented in the direction of [001]. In the case of the LMO films, no specific crystal orientation was detected.

The LCO or LMO film electrodes were charged individually to Li$_{0.5}$CoO$_2$ (x = 0.6) or Li$_{0.5}$Mn$_2$O$_4$ (x = 0.9) with the constant current rate of 0.05 C. After the charging, two LCO or LMO electrodes were short-circuited so that the state of charge became equivalent each other.

2.2 Electromotive force (EMF) measurements under mechanical stress

The prepared symmetric cell was set in the digital control universal testing machine (5565, Instron Inc.). As shown in Fig. 2, EMF of the lower side electrode with reference to the upper electrode was measured by the digital multimeters (2182A, Keithley Instruments Inc., Japan) under four points bending tests with the mechanical load of 0–130 N. In this experimental setup, compressive and tensile stresses were given to the in-plane direction of the upper and the lower side electrodes, respectively. In this work, as we did in another work,$^6$ it was assumed that the influence of the stress on EMF is comparable for tensile and compressive stresses while giving the opposite sign. Based on this assumption, we introduce the “nominal” mechanical stress in the following discussion, which is the mechanical stress on the lower electrode (tensile side) with reference to that on the upper electrodes (compressive side). The nominal mechanical stress was calculated by the following equation.$^7$

$$
\sigma = \frac{2aWE_{\text{c}}/(2E_{\text{c}}I_{\text{c}} + E_{\text{d}}d_s)}{y}
$$

where $\sigma$, $a$, $W$, $E$, $I$ and $y$ are the nominal mechanical stress, the distance between the inner and the outer supports, the mechanical load, Young’s modulus, the second moment of area, and the vertical distance from the neutral axis of the specimen, respectively. The subscripts e and s express electrode and electrolyte, respectively. The parameters of $a$ and $y$ are typically 4 mm and 1 mm, respectively. The Young’s moduli and the second moments of area used for the calculation of the nominal mechanical stress are listed in Table 1.$^8$ The value of the Young’s modulus of LLTO was given by Toho Titanium Co. Ltd., Japan, and that of LLZO was experimentally determined by the resonance method.

3. Results and Discussion

Typical results of electromotive force (EMF) measurements with/without mechanical load are presented in Fig. 3. The results were obtained with the symmetric cell of LCO/LLZO/LCO, in which the lithium content in the LCO electrodes, i.e. x in Li$_{0.6}$CoO$_2$, was 0.6. The EMF between the two LCO electrodes was nearly zero before applying the mechanical load, since the both LCO electrodes were in the same state of charge. The positive EMF was generated immediately after applying the load. The generated EMF was kept as almost constant while a constant stress was kept. The EMF became nearly zero after releasing the load. A similar EMF behavior was observed with the symmetric cell of LCO/LICGC/LCO in another work.$^6$

As already discussed in detail,$^8$ it is considered that such an EMF behavior accompanied with the mechanical load can be interpreted as the change in the lithium chemical potential in the constrained LCO electrodes due to the mechanical stress. As described in the experimental section, the LCO films in this work were oriented in the direction of [001], meaning the CoO$_2$ layers deposited alongside the electrolyte substrate. Therefore, the tensile strain is introduced in the direction perpendicular to the CoO$_2$ layer, when the external compressive stress is applied in the in-plane direction of the film. In other words, the interlayer distance expands when the external compressive stress is applied to the upper-side LCO film electrode during the four point bending test. On the other hand, it is known that the CoO$_2$ interlayer distance in LCO increases/decreases with charging/discharging, i.e. the decrease/increase in the lithium

<table>
<thead>
<tr>
<th>Young’s modulus /MPa</th>
<th>Second moment of area /mm$^4$</th>
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<tbody>
<tr>
<td>LiCoO$_2$</td>
<td>150$^8$</td>
</tr>
<tr>
<td>LiMn$_2$O$_4$</td>
<td>203$^9$</td>
</tr>
<tr>
<td>Li$<em>{0.29}$La$</em>{0.57}$TiO$_3$</td>
<td>169</td>
</tr>
<tr>
<td>Li$_{1.5}$La$_2$Zr$_2$O$_12$</td>
<td>131</td>
</tr>
</tbody>
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Figure 1. Schematic illustration of the specimen of the symmetric cell for EMF measurements under mechanical stress. (i) LiCoO$_2$ or LiMn$_2$O$_4$ dense thin film electrode, (ii) aluminum dense thin film electrode, (iii) LiMn$_2$O$_4$ dense thin film electrode, (iv) gold current collector, and (v) Li$_{0.29}$La$_{0.57}$TiO$_3$ or Li$_{1.5}$La$_2$Zr$_2$O$_12$ electrolyte.

Figure 2. Schematic illustration of experimental setup for EMF measurements under four point bending test.

Figure 3. EMF between two Li$_{0.6}$CoO$_2$ electrodes on the Li$_{1.5}$La$_2$Zr$_2$O$_12$ electrolyte with or without mechanical loads.
contents $x$, when $x$ is between 0.5 and 0.8.\textsuperscript{10,11} During the EMF measurements under the mechanical load, the interlayer distance was supposed to increase/decrease in the upper/lower side electrodes because of the mechanical strain, although the lithium contents did not change. In these strained situations, higher/lower lithium chemical potential, $\mu_L$, can be expected for the upper/lower side LCO electrodes, respectively, resulting in the positive EMF between the electrodes.

The solid electrolytes used in this work may exhibit piezoelectricity since their electronic conductivity is very low. If so, EMF can be observed under mechanical stress, even when $\mu_L$ in the electrode and/or the electrolyte do not change. In order to check this possibility, piezoelectricity of LLTO was investigated by using the symmetric cell of Au/LLTO/Au under four point bending test. The strained LLTO did not exhibit detectable EMF even under mechanical stress. This result ensures that piezoelectric effect is negligible and that EMF generated under mechanical stress can be basically interpreted as the $\mu_L$ change in the electrodes and/or the electrolyte.

In the four point bending tests, the mechanical strain is introduced not only to the electrode but also to the electrolyte. Thus, the mechanical strain in the electrolyte may contribute to generate EMF under the mechanical load. In order to check this possibility, EMF measurements of a similar symmetric cell with the LLTO electrolyte, LCO/LLTO/LCO, were performed under four-point bending tests. The results for $x = 0.6$ in LCO were given in Fig. 4. The positive EMF was again observed with the application of the mechanical load.

For the quantitative comparison, the EMF values observed in LCO/LLZO/LCO (Fig. 3) and LCO/LLTO/LCO (Fig. 4) were plotted in Fig. 5 as a function of the nominal mechanical stress. In this figure, the EMF values observed in LCO/LICGC/LCO\textsuperscript{6} are also presented. A proportional relationship was observed between EMF and the stress, and moreover, all the EMF seemed to be on the same line having the slope of $-6.0 \times 10^{-12}$ V/Pa. It is emphasized here that the lithium contents in LCO, $x$, was equivalent as 0.6 for all the measurements in Fig. 5. Therefore it was hypothesized that the contribution from the electrolyte for generating EMF is independent of the kinds of electrolyte or negligibly small, and that EMF value was basically determined by $\mu_L$ in the electrode.

In order to support this hypothesis, EMF measurements of the symmetric cell of LMO/LLTO/LMO were carried out under mechanical stress, and the results were compared with those obtained with the symmetric cell of LCO/LLTO/LCO. In this measurement, different kinds of electrode but the same kinds of electrolyte were used. The result was shown in Fig. 6. The linear relationships were observed from both symmetric cells. However, the slopes of the line between EMF and the applied stress were obviously different, $-6.1 \times 10^{-12}$ V/Pa for LCO while $-1.9 \times 10^{-12}$ V/Pa for LMO. The results presented in Figs. 5 and 6 confirmed that EMF under mechanical stress is affected by the kinds of electrode but not by the kinds of solid electrolyte. It is supposed that the mechanism of the EMF generation in LMO/LLTO/LMO is basically same as that in LCO/LLTO/LCO. That is, the change in the crystal lattice in LMO accompanied by the application of mechanical stress is considered to induce the change in $\mu_L$ in the LMO electrode.

In the following discussion, we will consider how EMF is affected by $\mu_L$ in the electrodes and the electrolyte based on the assumption of local equilibrium. Without any mechanical loads, $\mu_L$ balances between the electrode and the electrolyte [Fig. 7(a)]. When the mechanical stress is applied, $\mu_L$ of the electrode and the electrolyte are considered to change respectively. The magnitude of the $\mu_L$ change might be different in the electrode and the electrolyte [Fig. 7(b)], even though the same magnitude of the mechanical stress or strain is applied. In Fig. 7(b), positive changes of $\mu_L$ are illustrated as an example. However, the situation shown in Fig. 7(b) is not equilibrium state between the electrode and the electrolyte. Then a small amount of lithium ions and electrons was transported between the electrode and the electrolyte until an equilibrium state is established. In the case of Fig. 7(b), a certain amount of lithium ions moves from the electrolyte to the electrode and the same amount of electrons moves in the same direction while keeping the electroneutrality until $\mu_L$ in the electrode becomes comparable to that in the electrolyte. In general, a single-phase
electrode material like LiCoO₂ has a wide range of the lithium contents. In other words, LiCoO₂ can easily change the lithium content while keeping its phase state. This indicates the change in the LCO electrode may be minor when the change of the lithium contents is small. In contrast, the compositional range of lithium in the electrolyte is generally very narrow. This implies that in the electrolyte changes significantly even for a small change of the lithium contents. Thus, when the same amount of lithium is transported between the electrode and the electrolyte, the change in the electrolyte is much larger than the change in the electrode [Fig. 7(c)]. That is, the chemical potential in the electrode does not change significantly from the non-equilibrium state shown by Fig. 7(b) to the equilibrium state shown by Fig. 7(d), and the change of the lithium chemical potential in the electrodes. This hypothesis is discussed thermodynamically by assuming the local equilibrium between the electrode and the electrolyte.

4. Conclusions

Effects of mechanical stress on lithium chemical potential in electrodes and electrolytes for lithium ion batteries were investigated through electromotive force (EMF) measurements of symmetric cells consisting of LiCoO₂ or LiMn₂O₄ electrodes and solid-state lithium ion conductors under four points bending tests. In particular, for evaluating effects of mechanical stress on lithium chemical potential in the electrolyte, symmetrical cells with different kinds of electrolytes were examined. A similar EMF behavior was observed regardless of the kinds of electrolytes as long as the same kind of electrodes was used. This demonstrated that influences of mechanical stress on the electrolytes are not significant and the EMF generated under mechanical stress can be basically interpreted by the change of the lithium chemical potential in the electrodes. This hypothesis is discussed thermodynamically by assuming the local equilibrium between the electrode and the electrolyte.

Acknowledgments

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