Experimental Evaluation of Influence of Stress on Li Chemical Potential and Phase Equilibrium in Two-phase Battery Electrode Materials

Yuta KIMURA,a,*,§ Keita FUNAYAMA,a Mahunnop FAKKAO,b,t Takashi NAKAMURA,a,b,T Tatsuya KAWADA,c,Junichi KAWAMURA,d Naoaki KUWATA,b,N and Koji AMEZAWA,a,N

Article
Electrochemistry, (in press) 1–8

ABSTRACT
We experimentally evaluated the influence of stress on the Li chemical potential (\(\mu_\text{Li}\)) and phase equilibrium in the two-phase battery electrode materials through the emf measurements while applying a mechanical load. In our measurements, we prepared an electrochemical cell by depositing a thin film of a two-phase electrode material (LiFePO4 or LiCoO2 in the two-phase region) on each of the solid electrolyte surfaces. Then we applied a mechanical load to the electrochemical cell through four-point bending, and the resulting \(\mu_\text{Li}\) variation in the electrode material was measured as the emf between the two thin films. Our results indicated that \(\mu_\text{Li}\) in the two-phase electrode materials immediately changed just after loading and then gradually changed while maintaining a constant mechanical load. Besides, the loading and unloading led to the \(\mu_\text{Li}\) variation in the opposite direction. Such characteristic \(\mu_\text{Li}\) variations could be explained by considering the change in the phase equilibrium between the two phases, which led to the Li content variation in the two phases and the stress relaxation due to the volume fraction variation of the two phases. Our results can provide valuable insights regarding the influence of stress on the performances of energy storage devices with two-phase electrode materials.

Keywords : Stress, Li Chemical Potential, Phase Equilibria, Two-phase Battery Electrode Materials

1. Introduction
Solid state batteries (SSBs) are one of the emerging options for next-generation energy storage systems owing to their robustness against thermal issues such as overheating and fire, as well as their potential to achieve higher power and energy densities.1–4 However, SSBs have some limitations that need to be addressed before they are put into practical application. One of such limitations is immense stress generation within SSBs that is resulted from the volumetric change of the component materials during (dis)charge.5–13 In SSBs, all the components (e.g. electrolyte, cathode, and anode) are mechanically confined at solid-solid interfaces. Therefore, the stress generation in SSBs is more pronounced than in conventional liquid-based Li-ion batteries. The magnitude of the stress generation in SSBs is estimated to range from several hundred MPa to several GPa.5–8 Such a pronounced stress evidently leads to the mechanical degradation of SSBs such as cracks in particles and delamination of the components.3,5,7,10,13 Furthermore, in recent years, stress is being recognized to significantly affect the material properties of the battery electrode and electrolyte materials such as ionic transport,16–17 defect concentration,18 electrochemical reaction,19,20 phase separation,21,22 and electrode potential.21–28 Therefore, fundamental understandings of the influence of stress on material properties of the battery electrode and electrolyte materials are essential in enhancing the performance and stability of SSBs. To this end, we have developed an experimental technique that can quantify the influence of stress on the Li chemical potential (\(\mu_\text{Li}\)) in a battery electrode material.25–28 Using this technique, we have revealed that stress significantly affected the \(\mu_\text{Li}\) of battery electrode materials such as LiCoO2 (LCO) and LiMnO2.\(\lambda\) \(\mu_\text{Li}\) is an important thermodynamic quantity that determines the electrode potential. Furthermore, it also governs the equilibria between phases. Therefore, when the two-phase electrode materials such as LiFePO429,30 are subjected to stress, it can change \(\mu_\text{Li}\) of the two phases and hence change the equilibrium between the two phases in the two-phase electrode materials. Thus, the electrode potential and the (dis)charge characteristics of two-phase electrode materials can be intricately affected by stress. However, the role of stress in two-phase electrode materials is not clearly understood. Therefore, in this study, we experimentally evaluated the influence of stress on \(\mu_\text{Li}\) and phase equilibrium in two-phase electrode materials using the aforementioned technique.

2. Experimental
Figure 1 schematically illustrates the experimental setup used in this study. We deposited a thin film of the electrode material of interest on both surfaces of the rectangular solid electrolyte. A mechanical load was then applied to the electrochemical cell in the

---

1 Present address: Faculty of Engineering, Thai-Nichi Institute of Technology, 1771/1 Pattanakarn Rd. Suanluang Bangkok 10250, Thailand
2 ECSJ Active Member

Y. Kimura orcid.org/0000-0002-3525-1366
K. Funayama orcid.org/0000-0002-8868-3613
M. Fakkao orcid.org/0000-0002-3637-3701
T. Nakamura orcid.org/0000-0001-5461-9958
N. Kuwata orcid.org/0000-0002-0736-6967
T. Kawada orcid.org/0000-0002-9830-2669
J. Kawamura orcid.org/0000-0002-3610-4990
K. Amezawa orcid.org/0000-0002-3430-6927
the in two load bars. Due to this strain, the upper electrode thin in the longitudinal direction of the electrochemical cell, between the upper and lower parts of the solid electrolyte, respectively, along with a uniform tensile strain were simultaneously imposed on the electrochemical cell in this geometry, a uniform compressive strain and a uniform tensile strain were imposed on the mechanical load applied to the electrochemical cell, as schematically illustrated in Fig. 2b. When the mechanical load is applied to the two electrode thin films, the thickness of the solid electrolyte, the elastic modulus of the electrode, the elastic modulus of the solid electrolyte, and the mechanical load applied to the electrochemical cell, respectively. The \( I_{SE} \) in the above equation represents the cross-sectional secondary moment of the solid electrolyte, which can be calculated using the following equation;

\[
I_{SE} = \frac{bh^3}{12}
\]

where \( b \) is the width of the solid electrolyte. The magnitude of the compressive stress in the upper electrode thin film is expressed as \(-|\sigma|\), while the magnitude of the tensile stress in the lower electrode thin film is \(|\sigma|\). Furthermore, we measured the electromotive force (emf) between the upper and lower electrode thin films with and without applying a mechanical load to the electrochemical cell, taking the upper electrode thin film as a reference electrode. In such a case, the emf between the two electrode thin films can be expressed as follows;

\[
emf = -\frac{1}{F} \left( \mu_{Li}^{lower} - \mu_{Li}^{upper} \right)
\]

where \( \mu_{Li}^{lower} \) and \( \mu_{Li}^{upper} \) are \( \mu_{Li} \) in the lower and upper electrode thin films, respectively. Thus, the \( \mu_{Li} \) variation in the electrode material of interest under stress can be evaluated by measuring the emf with and without applying a mechanical load. Hereinafter, the emf measurement under a mechanical load is referred to as the stress-\( \mu_{Li} \) measurement.

We used L\(_{29.23}\)La\(_{0.77}\)TiO\(_3\) (LLTO, TOHO TITANIUM Co., Ltd., Japan) as the solid electrolyte. As model two-phase electrode materials, we chose LiFePO\(_4\) (LFP) and LCO in the two-phase region. The thin films of LFP or LCO with dimensions of 6 \( \times \) 8 mm were deposited on the center part of both surfaces of the rectangular LLTO solid electrolyte with the size of 20 \( \times \) 10 \( \times \) 2 mm via pulsed laser deposition at 873 K and under \( P(\text{O}_2) \) of 20 Pa for approximately 15 min using an ArF excimer laser (20 Hz, 193 nm, and 200 mJ). The thicknesses of the LFP and LCO thick films were 100–200 nm, which were measured using a stylus surface profilometer (Dektak 6M, Veeco Instruments Inc., USA). An Au thin film was then deposited on each electrode thin film as a current collector via Ar ion sputtering at room temperature in an Ar atmosphere of approximately 10 Pa for 5 min. Thereafter, Al dense thin films were deposited on both ends of one surface of the LLTO solid electrolyte through Ar ion sputtering at room temperature in an Ar atmosphere \((\sim 0.7 \text{ Pa})\) for 5 min. Using the Au thin films as counter electrodes, the LCO and LFP thin films were charged to the two-phase regions \((x = 0.5, 0.7, \text{ and } 0.8, \text{ for LFP and } x = 0.8, \text{ for LCO})\). The Li contents of the LCO and LFP thin films after charging were approximately estimated from the amount of charge and the thickness of the thin film. The charging current was approximately 0.2 \( \mu \text{A} \). After charging, the two electrode thin films were short-circuited for approximately 24 h. Thereafter, the emf between the two electrode thin films approached zero, indicating that the two electrode thin films had the same \( \mu_{Li} \). The LFP and LCO thin films were characterized via X-ray diffraction (XRD) measurements (CuK\(_{\alpha}\), D8 DISCOVER, Bruker AXS GmbH, Germany). The mechanical load was applied using a digital control universal testing machine (INSTRON 5565, Instron Inc., USA). The magnitude of the mechanical load applied to the electrochemical cell was measured using a 5 kN static load cell (Instron Inc., USA). The emf between the two electrode thin films was measured using a nanovoltmeter (type 2182A, Keithley Instruments Inc., USA), taking the upper electrode thin film as the reference electrode. More detailed information about the experimental procedures has been provided in our previous works.\(^{25-28}\)

3. Results

3.1 XRD characterization of the LFP and LCO thin films

Figure 2a presents the XRD pattern of the LFP thin films with a Li content of \( x = 1.0 \), on the LLTO solid electrolyte. The 020 and 200/121 peaks of LFP were predominantly observed. This suggests that the \( c \)-axis of the LFP thin films was principally oriented parallel to the solid electrolyte, as schematically illustrated in Fig. 2b. Therefore, for simplicity, we assumed that the LFP thin films were predominantly subjected to stress in the direction parallel to the \( c \)-axis. Figure 2c shows the XRD pattern of the LCO thin films \((x = 1.0)\) on the LLTO solid electrolyte. The 003 and 006 peaks of LCO were predominantly observed, suggesting that the \( c \)-axis of the LCO thin films was principally oriented perpendicular to the solid electrolyte. Therefore, for simplicity, we assumed that the LCO thin films were mainly subjected to stress in the \( c \)-axis direction, as schematically illustrated in Fig. 2d.

3.2 Stress-\( \mu_{Li} \) measurements

We performed stress-\( \mu_{Li} \) measurements using the LFP and LCO thin films in the two-phase region. The two-phase region of LFP is known to be in the Li content range of \(~0.05 \leq x \leq ~0.89\).\(^{28}\) Accordingly, we performed the stress-\( \mu_{Li} \) measurements with the
LFP thin films that were charged to $x = 0.8$, 0.7, and 0.5. Figure 3a presents the \( \text{emf} \) between the upper and lower LFP thin films (pink line), its magnified view, and the mechanical load applied to the electrochemical cell (sky blue line) when the Li content of LFP was $x = 0.7$. Under no mechanical load, the \( \text{emf} \) between the two LFP thin films was zero. On the other hand, a negative \( \text{emf} \) was immediately observed when a mechanical load was applied to the electrochemical cell. While keeping the mechanical load constant, the \( \text{emf} \) gradually increased and seemingly converged to a certain negative value. When the mechanical load was removed, a positive \( \text{emf} \) was instantly generated, and then the \( \text{emf} \) gradually decreased and approached zero. When a larger mechanical load was applied to the electrochemical cell, the negative \( \text{emf} \) with a larger absolute value was generated and then the \( \text{emf} \) gradually decreased and approached zero. When a larger mechanical load was applied to the electrochemical cell, the negative \( \text{emf} \) with a larger absolute value was generated and then the \( \text{emf} \) gradually s31 and converged to a certain negative value. The absolute value of the convergence \( \text{emf} \) was also larger as a larger mechanical load was applied. When a larger mechanical load was removed from the electrochemical cell, a larger positive \( \text{emf} \) was generated. Such \( \text{emf} \) variations were also observed when the Li contents of LFP were $x = 0.8$ and 0.5, as shown in Figs. 3b and 3c, respectively. To confirm whether the aforementioned \( \text{emf} \) variations are observed in other two-phase electrode materials, we performed the stress-$\mu_L$ measurements with the LCO thin films in the two-phase region. The two-phase region of LCO is known to be in the Li content range of $\sim 0.75 \leq x \leq 0.93$.31 Thus, we charged the LCO thin films to $x = 0.8$ and performed the stress-$\mu_L$ measurements (Fig. 3d). When a mechanical load was applied to the electrochemical cell, a positive \( \text{emf} \) was immediately generated. While maintaining a constant mechanical load, the \( \text{emf} \) gradually decreased and seemingly converged to a certain positive value. Consequently, a larger \( \text{emf} \) was generated when a larger mechanical load was applied. Furthermore, when the mechanical load was reduced, the \( \text{emf} \) immediately decreased and then gradually increased when the mechanical load was held constant. During the period for which the electrochemical cell was completely unloaded, a negative \( \text{emf} \) was instantaneously generated and then gradually approached zero. For comparison, we show the results of the stress-$\mu_L$ measurement when the LCO was in the single-phase region ($x = 0.6$).28 Similar to the results in the two-phase region, a positive \( \text{emf} \) was immediately generated upon application of the mechanical load. However, contrary to the case of the two-phase region, the \( \text{emf} \) remained almost constant while maintaining a constant mechanical load. Furthermore, the \( \text{emf} \) immediately returned to zero when the mechanical load was removed.

As described above, although the signs of the generated \( \text{emf} \) under loading and unloading in LFP were opposite to those in LCO, (1) immediate \( \text{emf} \) generation just after loading, (2) gradual \( \text{emf} \) change while maintaining a constant mechanical load, (3) \( \text{emf} \) generation with opposite signs during loading and unloading, and (4) gradual \( \text{emf} \) restoration to zero after unloading were commonly observed in the LFP and LCO thin films in the two-phase region. Conversely, the aforementioned \( \text{emf} \) variations (2), (3), and (4) were not observed in the LCO thin film in the single-phase region. Therefore, such \( \text{emf} \) variations are presumed to be characteristic in two-phase electrode materials. The \( \text{emf} \) variations (2), (3), and (4) indicate that $\mu_L$ in LFP and LCO in the two-phase regions gradually changed under a constant mechanical load, and the loading and unloading led to opposite $\mu_L$ variation. In the next section, we first theoretically consider the $\mu_L$ variation in the LFP and LCO thin films under stress in the framework of thermodynamics. Subsequently, we discuss why the \( \text{emf} \) generation under loading was opposite, namely, why the $\mu_L$ variation under loading was opposite.
between LFP and LCO. Thereupon, we discuss why $\mu_{li}$ gradually varied while keeping constant mechanical load and why loading and unloading led to the opposite $\mu_{li}$ variation in the two-phase electrode materials.

4. Discussion

4.1 Theoretical consideration of the $\mu_{li}$ variation in the LFP and LCO thin films under stress

We here theoretically consider the $\mu_{li}$ variation in the LFP and LCO thin films under stress. In this study, we employ the small strain assumption and consider the Cauchy stress and strain tensors as thermodynamic variables of the Gibbs free energy of LFP and LCO. In our previous study, we found that the $\mu_{li}$ variation of anisotropic battery electrode materials that are stressed in the $ii'$ direction ($ii' = 11, 22, 33$) can be expressed by the following equation:

$$\mu_{li}(T, \sigma_{ii'}, x) = \mu_{li}(T, 0, x) - \frac{v_{mol}}{2} \frac{\partial S_{eff}}{\partial x} \sigma_{ii'} + \frac{v_{mol}}{2} \frac{\partial a_{ii'}}{\partial x} \sigma_{ii'}$$

(4)

where the 11 and 33 directions correspond to the directions parallel to the $a$ and $c$-axes of the crystal, respectively. The 22 direction corresponds to the direction perpendicular to both these axes. $\mu_{li}(T, \sigma_{ii'}, x)$ and $\mu_{li}(T, 0, x)$ represent $\mu_{li}$ in the material of interest under stress and zero stress, respectively. $x$ and $v_{mol}$ represent the Li content and the molar volume of the material of interest, respectively. $\partial S_{eff}/\partial x$, $\sigma_{ii'}$, and $\partial a_{ii'}/\partial x$ represent the elastic compliance, the stress component, and the lattice constant in the $ii'$ direction. As described in the previous section, we assume that the LFP and LCO thin films are predominantly subjected to stress along the $c$-axis ($ii' = 33$) and $a$-axis ($ii' = 11$) directions, respectively. In these cases, the $\mu_{li}$ variation in the LFP and LCO thin films under stress can be expressed as follows:

**LFP:**

$$\mu_{li}(T, \sigma_{33}, x) = \mu_{li}(T, 0, x) - \frac{v_{mol}}{2} \frac{\partial S_{3333}}{\partial x} \sigma_{33} - \frac{v_{mol}}{2} \frac{\partial a_{33}}{\partial x} \sigma_{33}$$

**LCO:**

$$\mu_{li}(T, \sigma_{11}, x) = \mu_{li}(T, 0, x) - \frac{v_{mol}}{2} \frac{\partial S_{1111}}{\partial x} \sigma_{11} - \frac{v_{mol}}{2} \frac{\partial a_{11}}{\partial x} \sigma_{11}$$

(5)

In the above equations, the influence of stress on $\mu_{li}$ is expressed as the second and third terms on the right-hand side of the equations. The influence of the second term is proportional to the square of the stress, and that of the third term is proportional to the stress. To estimate which term has the dominant influence on $\mu_{li}$ variation, we calculated the ratio of the second and third terms, $\beta$:

$$\beta = \left| \frac{\partial S_{eff}}{\partial x} \sigma_{ii'} \right| / \left| \frac{\partial a_{ii'}}{\partial x} \sigma_{ii'} \right|$$

(6)

$$\beta = \left| \frac{\partial S_{eff}}{\partial x} \sigma_{33} \right| / \left| \frac{\partial a_{33}}{\partial x} \sigma_{33} \right|$$

(6)

According to this equation, the influence of the second term becomes relatively larger in proportion to the magnitude of the applied stress. The maximum stress applied to the LFP and LCO thin films in our measurements, which was estimated by the Eq. (1) and the elastic constants of LFP and LCO reported in the literature, was less than 150 MPa. We thus estimated the $\beta$ of LFP and LCO in the stress range of 0 to 150 MPa (Fig. 4). In this estimation, $\partial S_{eff}/\partial x$ was approximately estimated from the slope of the elastic compliances of LFP and LCO at the end compositions ($x = 0$ and 1.0), which was calculated from the elastic constants of LFP and LCO at each Li content in the literature. $\partial a_{ii'}/\partial x$ was calculated from the lattice constants of LFP and LCO reported in the literature. As shown in Fig. 4, although the $\beta$ monotonically increased with increasing applied stress, the $\beta$ of both LFP and LCO was less than 0.03 in this stress range. Therefore, in this stress range, the influence of the second term is considerably smaller than that of the third term.

Figure 3. The $emf$ between the upper and lower LiFePO$_4$ (LFP) thin films (pink line), its magnified view, and the mechanical load applied to the electrochemical cell (sky blue line) when the Li content of LFP was $x = (a) 0.7$, (b) 0.8, and (c) 0.5. The $emf$ between the upper and lower LiCoO$_2$ (LCO) thin films (pink line) and the mechanical load applied to the electrochemical cell (sky blue line) when the Li content of LCO was $x = (d) 0.8$ and (e) 0.6.28
In such cases, we can neglect the second term and the Eq. (5) can be written as:

\[
\begin{align*}
\text{LCO:} & \quad \mu_{Li}(T, \sigma_{11}, x) = \mu_{Li}(T, 0, x) - \frac{V_{\text{mod}}}{\sigma_{11}} \frac{\partial \mu_{Li}}{\partial x} \sigma_{11} \\
\text{LFP:} & \quad \mu_{Li}(T, \sigma_{33}, x) = \mu_{Li}(T, 0, x) - \frac{V_{\text{mod}}}{\sigma_{33}} \frac{\partial \mu_{Li}}{\partial x} \sigma_{33}
\end{align*}
\]

(7)

According to the Eq. (7), the extent of the \( \mu_{Li} \) variation in each phase under a certain stress is determined by \( V_{\text{mod}} \), \( \sigma_{ij} \), and \( \frac{\partial \mu_{Li}}{\partial x} \). Therefore, if these values are different between the two phases, the \( \mu_{Li} \) variation in each phase under stress can differ from each other. This implies that, in the stress-\( \mu_{Li} \) measurement, the two phases can be in a non-equilibrium state immediately after loading, and hence the emf just after loading corresponds to a certain type of mixed potential of the two phases.

4.2 The \( \mu_{Li} \) variation in the LFP and LCO thin films just after loading

As described in the Results section, the sign of the emf generation immediately after loading was opposite between the LFP and LCO thin films. This suggests that the \( \mu_{Li} \) variation just after loading was opposite between the LFP and LCO thin films. Here, we discuss the cause of the opposite \( \mu_{Li} \) variations between the LFP and LCO thin films. In the LFP thin films in the two-phase region, the Li-rich phase and Li-poor phase co-exist.\(^{29,30}\) When a mechanical load is applied, the \( \mu_{Li} \) in both phases is inferred to vary following the Eq. (7). According to this equation, the sign of the \( \mu_{Li} \) variation in each phase immediately after loading is determined by \( -\frac{\partial \mu_{Li}}{\partial x} \). In this term, \( V_{\text{mod}} \) and \( \sigma_{ij} \) are always positive irrespective of the material. Thus, the chemical expansion coefficient, \( \frac{\partial \mu_{Li}}{\partial x} \), determines the sign of the \( \mu_{Li} \) variation in each phase. The \( \epsilon \)-lattice constants of both Li-rich and Li-poor phases are reported to monotonically decrease with increasing Li content,\(^{30}\) namely, \( \frac{\partial \mu_{Li}}{\partial x} \) is negative. Therefore, the Eq. (7) predicts that compressive stress decreases \( \mu_{Li} \) while tensile stress increases \( \mu_{Li} \) in both Li-rich and Li-poor phases of LFP. Therefore, considering the Eq. (3), a negative emf should be generated when a mechanical load is applied to the electrochemical cell, which agrees with the experimental results. On the other hand, the LCO thin films, in which the Li-rich hexagonal phase and Li-poor hexagonal phase co-exist in the two-phase region,\(^{31,34}\) are assumed to be principally subjected to the stress in the \( a \)-axis direction in our stress - \( \mu_{Li} \) measurement. The \( a \)-lattice constants of both Li-rich and Li-poor hexagonal phases in LCO monotonically increase with increasing Li content,\(^{31,34}\) that is, \( \frac{\partial \mu_{Li}}{\partial x} \) is positive in both phases. Thus, according to the Eq. (7), the \( \mu_{Li} \) in the two phases in LCO is increased by compressive stress, while it is reduced by the tensile stress. Therefore, in our stress - \( \mu_{Li} \) measurements, the positive emf should be generated when a mechanical load is applied to the electrochemical cell with the LCO thin films, which coincides with the experimental results. Therefore, the different signs of the emf generation just after loading between the LFP and LCO thin films are presumed to be originate from the different sign of the chemical expansion coefficient of LFP and LCO in the principal direction of the applied stress.

4.3 Characteristic \( \mu_{Li} \) variations observed in two-phase battery electrode materials

The experimental results shown in Fig. 3 indicate that the \( \mu_{Li} \) of LFP and LCO in the two-phase regions gradually changed while maintaining a constant mechanical load, and the loading and unloading led to the opposite \( \mu_{Li} \) variation. These \( \mu_{Li} \) variations were inferred to be characteristic in the two-phase electrode materials. In this section, we discuss why the aforementioned \( \mu_{Li} \) variations occurred in the two-phase battery electrode materials. Hereon, we consider the \( \mu_{Li} \) variation in the lower LFP thin film, which is subjected to tensile stress under loading, as an example. Figure 5a schematically illustrates the relationship between \( x \) and \( \mu_{Li} \) of the Li-rich and Li-poor phases in the lower LFP thin film. The \( \mu_{Li} \) in each phase of LFP is presumed to increase with increasing Li content. In Fig. 5a, we approximate that the relationship between the Li content and \( \mu_{Li} \) was linear within the narrow Li content range near the Li content of interest. In Fig. 5a, we also present a schematic illustration of the distribution of Li-rich and Li-poor phases in the LFP thin film. In these illustrations, the red and turquoise regions represent the Li-rich and Li-poor phases of LFP. The shade of the color in each region represents the Li content in each phase. Figure 5b shows the schematic emf response with and without mechanical load application.

Before the mechanical load is applied to the electrochemical cell, both phases are in equilibrium. Therefore, at the equilibrium Li content (\( x_i \) and \( x_0 \) for Li-rich and Li-poor phases in Fig. 5a-(i), respectively), both phases have the same \( \mu_{Li} \) (\( \mu_{Li}^{eq} \) in Fig. 5a-(i)) in the lower LFP thin film. Similarly, in the upper LFP thin film, both phases have the same \( \mu_{Li} \) (\( \mu_{Li}^{eq} \)). Therefore, the emf between the upper and lower LFP thin films is zero before loading, as schematically illustrated in Fig. 5b-(i).

When a mechanical load is applied to the electrochemical cell, the lower LFP thin film is subjected to tensile stress. Therefore, in both phases in the lower LFP thin film increases according to the Eq. (7). The extent of the \( \mu_{Li} \) increase in each phase is different from each other since they have different chemical expansion coefficients. Conversely, in the upper LFP thin film, \( \mu_{Li} \) in both LFP and LCO phases decreases just after compressive stress is applied. Thus, a negative emf is generated between the upper and lower LFP thin films (Fig. 5b-(ii)). The extent of the \( \mu_{Li} \) variation in each phase is expressed as \( \frac{d \mu_{Li}}{dx_{33}} \). The |\( d \mu_{Li}/dx_{33} \)| in the Li-rich phase is ~150 % larger than that in the Li-poor phase.\(^{30}\) Therefore, in the lower LFP thin film, \( \mu_{Li} \) in the Li-rich phase just after loading, \( \mu_{Li}^{eq, rich} \), should be larger than that in the Li-poor phase, \( \mu_{Li}^{eq, poor} \), as shown in Fig. 5a-(ii). In contrast, in the upper LFP thin film, the Li-poor phase is presumed to have a higher \( \mu_{Li} \) than the Li-rich phase. Such a \( \mu_{Li} \) difference between the Li-rich and Li-poor phases can be the driving force of the Li diffusion between the phases in each LFP thin film. In the case of the lower LFP thin film, Li ions are presumed to gradually diffuse from the Li-rich phase with a higher \( \mu_{Li} \) to the Li-poor phase with a lower \( \mu_{Li} \). Because of this Li-ion diffusion, the Li content in the Li-rich phase should decrease, while that in the Li-poor phase should increase in the lower LFP thin film. The Li content variation in both

Figure 4. Ratio of the second and the third terms of the Eq. (6), \( \beta \), of LiFePO_4 and LiCoO_2 as a function of stress.
phases can gradually change $\mu_{Li}$ in the two phases, namely, $\mu_{Li}$ in the Li-rich phase should decrease (from $\mu_{Li, rich}^{LFP}$ to $\mu_{Li, rich}^{LFP}$ in Fig. 5a-(iii)) whereas that in the Li-poor phase should increase (from $\mu_{Li,poor}^{LFP}$ to $\mu_{Li,poor}^{LFP}$). In the upper LFP thin film, on the other hand, Li ions should diffuse from the Li-poor phase to the Li-rich phase. Accordingly, $\mu_{Li}$ in the Li-rich phase should gradually increase, while that in the Li-poor phase should gradually decrease in the upper LFP thin film. The aforementioned gradual $\mu_{Li}$ variation in both phases in each thin film, which is caused by the Li content variation, is presumed to be one of the reasons for the gradual emf change that was observed under constant mechanical load (Fig. 5b-(iii)). Furthermore, when the Li content in the both phases changes, the volume fraction of the two phases must also change following the lever rule as the total amount of Li ions in each thin film is kept constant. The change in the volume fractions of the two phases is presumed to occur to relax the applied stress and hence to reduce the total energy of the LFP thin film. For example, in the lower LFP thin film, the applied tensile stress is inferred to be relaxed (from $\sigma$ to $\sigma'$ in Fig. 5a-(iii)), where $|\sigma'| > |\sigma|$) by increasing the volume fraction of the Li-rich phase with a larger $c$-lattice constant. When the tensile stress is reduced in the lower LFP thin film owing to the increase in the volume fraction of the Li-rich phase, the $x - \mu_{Li}$ curves of the two phases should approach to the one before loading, as shown in Fig. 5a-(iii). Therefore, when Li-ion diffusion occurs between the

Figure 5. (a) Schematic $x - \mu_{Li}$ curves of the Li-rich and Li-poor phases in the lower LiFePO$_4$ (LFP) thin film and the schematic illustration of the distribution of the Li-rich and Li-poor phases in the LFP thin film during (un)loading. In these illustrations, the red and turquoise regions represent the Li-rich and Li-poor phases of LFP. The shade of the color in each region represents the Li content in each phase. (b) Schematic emf response with and without applying mechanical load.
phases, $\mu_{Li}$ in each phase varies because of both Li content variation and stress relaxation. $\mu_{Li}$ hence changes to the point indicated by the black arrow ($\mu_{Li-rich}$ and $\mu_{Li-poor}$, respectively) in Fig. 5a-(iii). When such $\mu_{Li}$ changes occur, $\mu_{Li}$ in the Li-poor phase is increased by the increase in the Li content and simultaneously decreased by the stress relaxation. On the other hand, $\mu_{Li}$ in the Li-rich phase is reduced by both the decrease in the Li content and stress relaxation. Therefore, the net $\mu_{Li}$ decrease in the Li-rich phase is more significant than that in the Li-poor phase. Thus, while maintaining a constant load, $\mu_{Li}$ in both phases gradually decreases, and they finally become equal ($\mu_{Li}$ in Fig. 5a-(iv)) under a certain stress ($\sigma_{e}$) and at certain Li contents ($X_{Li}$ and $X_{R}$ for Li-rich and Li-poor phases, respectively). Contrary to the lower LFP thin film, in the upper LFP thin film, the compressive stress is relaxed by the increase in the volume fraction of the Li-poor phase with a smaller c-axis lattice constant, and the $x$-$\mu_{Li}$, curves of both phases gradually approach to the ones before loading. Owing to this stress relaxation and the Li content variation, $\mu_{Li}$ in both phases gradually increases and finally becomes equal in the upper LFP thin film. The $\mu_{Li}$ variation in the two LFP thin films due to the aforementioned mechanisms can lead to a gradual emf change, as illustrated in Fig. 5b-(iii), and eventually, the emf can become constant (Fig. 5b-(iv)).

When the lower LFP thin film is at equilibrium under a certain tensile stress, the volume fraction of the Li-rich phase is presumed to be larger than that before unloading. The average c-lattice constant of the lower LFP thin film can hence be larger than that before loading and be comparable to the lattice constant of the tensilely-strained solid electrolyte. When the electrochemical cell is unloaded and the strain is released from the solid electrolyte, therefore, the LFP thin film can be compressively strained by the solid electrolyte. Thus, the lower LFP thin film is subjected to compressive stress just after the mechanical load is removed. In such a case, the $\mu_{Li}$ in both phases in the lower LFP thin film is reduced as shown in Fig. 5a-(v). In contrast, the upper LFP thin film is subjected to tensile stress, and thus the $\mu_{Li}$ in the upper LFP thin film should be increased just after unloading. Therefore, a positive emf should be generated immediately after unloading, as illustrated in Fig. 5b-(v). After the mechanical load is removed, the Li-ion diffusion is driven by the $\mu_{Li}$ difference in both phases, leading to the Li content variation and the change in the volume fraction in the two phases in each LFP thin film. These changes cause the $\mu_{Li}$ variation in both phases and they gradually approach the ones before unloading (Fig. 5a-(vi)) and thus the emf should gradually approach zero (Fig. 5b-(vi)). After sufficiently long time passes, the $\mu_{Li}$ in the Li-rich and Li-poor phases in each thin film should return to the values before loading, as described in Fig. 5a-(vii), and the emf becomes zero (Fig. 5b-(vii)). As described above, the characteristic emf variations observed in the two-phase electrode materials can be explained by the change in the phase equilibrium (changes in the Li content and volume fraction variations) in the two phases, which led to the $\mu_{Li}$ variations in the two phases.

Taken together, the above discussions suggest that the stress can vary $\mu_{Li}$ and therefore the electrode potential of the two-phase electrode materials. Thus, the stress can change the (dis)charge voltage of the batteries. Although the influence of stress on the electrode potential of LiFePO$_4$ is presumed to be less significant (~several tens of mV/GPa when the stress is induced in the c-axis direction), the influence of stress can be non-negligible in two-phase electrode materials with larger chemical expansion coefficients of each phase, $\delta_{Li-rich}$ and $\delta_{Li-poor}$, in the Eq. (7). Furthermore, our results and discussion suggest that the stress applied to the two-phase electrode materials can change the phase equilibrium in the two phases, leading to the Li content and volume fraction variations of the two phases. The volume fraction variation can relax the stress induced in the two-phase electrode materials during (dis)charging.

Therefore, the influence of stress on the material properties of the two-phase electrode materials can be mitigated because of the volume fraction variation of the two phases. As the volume fraction variation results from the Li-ion diffusion between the two phases, the stress of the stress relaxation due to the volume fraction variation is presumed to be more significant under low rate (dis)charging. On the other hand, under high-rate charging, stress may be insufficiently relaxed by the volume fraction variation and hence the impact of the stress on the material properties is inferred to be larger. As described above, stress can significantly and intricately affect the (dis)charge characteristics of two-phase electrode materials. Thus, it is important to consider the influence of stress on $\mu_{Li}$ and phase equilibrium in the development of energy storage devices with two-phase electrode materials.

5. Conclusions

We experimentally evaluated the influence of stress on $\mu_{Li}$ and the phase equilibrium in the two-phase electrode materials through the stress - $\mu_{Li}$ measurements. As model two-phase electrode materials, we chose LFP and LCO in the two-phase region in this study. In our stress - $\mu_{Li}$ measurements, (1) the immediate emf generation just after loading, (2) the gradual emf change while maintaining a constant mechanical load, (3) the emf generation with opposite signs during loading and unloading, and (4) the gradual emf restoration to zero after unloading were commonly observed in the LFP and LCO thin films in the two-phase region. On the other hand, the emf variations (2), (3), and (4) were not observed in the LCO thin film in the single-phase region. Therefore, such emf variations are presumed to be characteristic in the two-phase electrode materials. The aforementioned emf variations (2), (3), and (4) indicate that $\mu_{Li}$ in the two-phase electrode materials gradually changed while maintaining a constant mechanical load, and the loading and unloading led to the opposite $\mu_{Li}$ variation in the two-phase battery electrode materials. Such characteristic $\mu_{Li}$ variations were able to be explained by considering the change in the phase equilibrium between the two phases, which results in the Li content variation in the two phases as well as the stress relaxation due to the volume fraction variation of the two phases. The aforementioned changes in $\mu_{Li}$ and phase equilibrium between the two phases can intricately affect the (dis)charge characteristics of two-phase electrode materials. Thus, it is important to take these changes into consideration in the design of the batteries using two-phase electrode materials.

Acknowledgments

This work was supported by JSPS KAKENHI Grant numbers 19H05814 and 20H05282.

References

1. J. Janek and W. G. Zeier, *Nat. Energy*, 1, 16141 (2016).
2. Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, and R. Kanno, *J. Power Sources*, 331, 135355 (2019).
3. T. Famprakis, P. Canepa, J. A. Dawson, M. S. Islam, and C. Masquelier, *Nat. Mater.*, 18, 1278 (2019).
4. K. Takada, *Acta Mater.*, 61, 759 (2013).
5. G. Bucci, T. Swamy, Y.-M. Chiung, and W. Craig Carter, *J. Mater. Chem. A*, 5, 19422 (2017).
6. T. H. Wan and F. Ciucci, *Electrochim. Acta.*, 331, 115355 (2020).
7. J. Tippens, J. C. Miers, A. Afdar, J. A. Lewis, F. J. Q. Cortes, H. Qiao, T. S. Marchese, C. V. Di Leo, C. Saldana, and M. T. McDowell, *ACS Energy Lett.*, 4, 1475 (2019).
8. H. Mendoza, S. A. Roberts, V. E. Brunini, and A. M. Griller, *Electrochim. Acta.*, 190, 1 (2016).
9. R. Koerver, W. Zhang, L. de Biais, S. Schweidler, A. O. Kondrakov, S. Kolling, T. Brezesinski, P. Hartmann, W. G. Zeier, and J. Janek, *Energy Environ. Sci.*, 11,
Electrochemistry, (in press) 1–8

10. Y. Zhao, P. Stein, Y. Bai, M. Al-Siraj, Y. Yang, and B.-X. Xu, J. Power Sources, 413, 259 (2019).
11. X. Zhang, W. Shy, and A. M. Sastry, J. Electrochem. Soc., 154, A910 (2007).
12. Y. Mao, X. Wang, S. Xia, K. Zhang, C. Wei, S. Bak, Z. Shadike, X. Liu, Y. Yang, R. Xu, P. Pianetta, S. Ermon, E. Stavitski, K. Zhao, Z. Xu, F. Lin, X. Yang, E. Hu, and Y. Liu, Adv. Funct. Mater., 29, 1900247 (2019).
13. N. Kotak, P. Barai, A. Verma, A. Mistry, and P. P. Mukherjee, J. Electrochem. Soc., 165, A1064 (2018).
14. A. Mukhopadhyay and B. W. Sheldon, Prog. Mater. Sci., 63, 58 (2014).
15. H. Liang, X. Zhang, L. Yang, Y. Wu, H. Chen, W. Song, and D. Fang, Sci. China Technol. Sci., 62, 1277 (2019).
16. C. Tealdi, J. Heath, and M. Saiful Islam, J. Mater. Chem. A, 4, 6998 (2016).
17. N. Muralidharan, C. N. Brock, A. P. Cohn, D. Schauben, R. E. Carter, L. Oakes, D. G. Walker, and C. L. Pint, ACS Nano, 11, 6243 (2017).
18. W. Yao, F. Long, and R. Shabanzaz-Yassar, ACS Appl. Mater. Interfaces, 8, 29391 (2016).
19. H. Ogawa, K. Takayama, S. Yagi, T. Kawada, J. Kawamura, T. Kawada, and K. Amezawa, J. Electrochem. Soc., 161, F3010 (2014).
20. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, J. Electrochem. Soc., 143, 1114 (1996).
21. K. Momma and F. Izumi, J. Appl. Crystallogr., 44, 1272 (2011).