Mechanical-energy influences to electrochemical phenomena in lithium-ion batteries

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In the lithium-ion batteries, Li ions usually infiltrate into the anode active material, which usually leads to the formation of Li compounds with expanding volumes. It is well known that the volume strain associated with dilatation/contraction at the intercalation/deintercalation cycles gradually deteriorates the electrode. The intention of this work devoting a simple Li/Sn battery system is to clearly show that such a mechanical strain accompanied by the formation of the Li-Sn compounds causes the following more fundamental phenomena: (i) the electrode potential tends to be lower than the value predicted from the chemical thermodynamics consideration, (ii) the kinetics rate of lithiation or delithiation is significantly retarded (i.e., much slower than expected from the diffusion of Li), and (iii) the electromotive force can be controlled by utilizing the elastic strain actively. Through this paper, we demonstrate the mechanical effects of such mechanical strain or energy on the electrochemical reaction with various experimental supports.

Keywords: Li-ion battery, Sn electrode, elastic strain energy, electrode potential

1. INTRODUCTION

Rechargeable batteries are indispensable for modern society. Lithium-ion battery, LIB, is widely used for mobile electronic devices such as cell phone and laptop, and currently being expected as one of the candidates for powerful energy sources for plug-in hybrid electric vehicles and electric vehicles in future. The capacity of carbon currently used as an active anode material of LIBs is coming to the theoretical value of about 370 $\mathrm{Ahkg^{-1}}$.[1] Thus, alternative materials exhibiting a larger capacity have been required for the future applications. Sn and Sn-based alloys or their composites have attracted much interest as one of the high capacity anode materials.[2–5] Sn forms several kinds of compounds with Li, and $Li_{22}Sn_5$ is the highest composition among the Sn-Li compounds, whose theoretical capacity is estimated to be about 990 $\mathrm{Ahkg^{-1}}$, thus greatly exceeding that of carbon.[6] As seen in Table I, for example, the volume of $Li_{22}Sn_5$ per Sn atom is about three times as large as that of Sn.[6, 7] It is, however, well known that with increase in cycles, Sn anodes in LIBs are markedly deteriorated by the large volume changes accompanied by the lithiation and delithiation processes, and thus, it cannot be alternative for carbon at present.

Despite the extensive works on Sn anode in LIBs, the influence of such volume change to the cell voltage or the formation kinetics of the lithium compound has not well understood yet. Recently, we have earlier focused on the strain-energy effect on the electrode potential in LIBs so far,[8] because it is just conceivable that the Gibbs free energy of formation would be significantly affected by the elastic strain due to the Li-compound formations. For example, when Li_2Sn_5 is formed with Li inserted into a pure Sn, it is easy to imagine that the accompanying volume expansion should be a barrier of the compound formation, so that the electrode potential or electromotive force is considered to be changed by the strain energy. Similarly, Cheng and Verbrugge[9, 10] also have discussed the strain effect on the electrochemical reaction. Thus, the strain-stress effect comes to be a fundamental issue to be considered in the intercalation battery system. In this study, we systematically demonstrate several experimental facts with some theoretical prevision of how the volume change associated with the formation of Li-Sn compounds affects the electrode potential and kinetics of the Li-compound formation, and discuss such mechanical influences to electrochemical reactions of LIBs in terms of the Gibbs energy and elastic-strain energy.

2. EXPECTED STRAIN-ENERGY CONTRIBUTION TO ELECTRODE POTENTIAL

Let us first estimate the strain energy accompanied by the Li-compound formation and discuss the effects on the electrode potential in the lithiation process. The physical properties used in the present estimation are taken from literature[8, 11]. As shown in other previous papers[12, 13], the elastic-strain energy can be estimated with the aid of micromechanics theory[14] based on Eshelby's ellipsoidal inclusion theory[15].

In the present calculation, we assume that an isolated spherical inclusion of the Sn-Li compound is formed in a Sn (or Sn-Li) matrix. The elastic strain inside inclusion is given by $\epsilon = \gamma - \epsilon^*$, where γ and ϵ^* are the total strain and eigenstrain (stress-free transformation strain), respectively. Here, ϵ^* represents an average eigenstrain determined from the volume per one mole of Sn atom in the Li-Sn compound, whose components can be approximately given by

$$\epsilon^*_{ij} = (\sqrt[3]{\Omega_{\rm I}/\Omega_{\rm M}} - 1)\delta_{ij} \equiv \epsilon^* \delta_{ij}, \tag{1}$$

where δ_{ij} is the Kronecker delta, Ω denotes the volume of the each phase including one mole of Sn atoms (hereafter, termed as molar volume), and subscripts "M" and "I" denote the matrix and inclusion, respectively. The values of ϵ^* are listed in Table I. When the spherical inclusion has a constant eigenstrain, ϵ^*, the elastic-strain energy $U_{\rm s}$ of the system including an isolated inclusion with molar volume Ω is given by

$$U_{\rm s} = -\frac{1}{2} C_{ijkl}(S_{klmn}\epsilon^*_{mn} - \epsilon^*_{kl})\epsilon^*_{ij}\Omega, \tag{2}$$

where S_{klmn} is the Eshelby tensor (see Refs. [14, 15] for details), C_{ijkl} denotes the fourth-rank elastic constant tensors of matrix (for example, $C_{1111} = c_{11}$, $C_{1122} = c_{12}$, $C_{2323} = c_{44}$, etc), and the polycrystalline isotropic elastic constants of β-Sn ($c_{11} = 111$ GPa, $c_{44} = 42.6$ GPa) are used for all the present calculations. Actually, the homogeneous elastic constants with spherical eigenstrains such as those in Eq. (1) assure that the strain energy does not depend on the shape of the inclusion, and the elastic stress and strain energy is briefly expressed as

$$\sigma_{ij} = B(S_{\rm I} + 2S_{\rm II} - 1)\epsilon^*_{\rm v}\delta_{ij}, \tag{3}$$

$$U_{\rm s} = -\frac{1}{2} B(S_{\rm I} + 2S_{\rm II} - 1)\epsilon^{*2}_{\rm v}\Omega, \tag{4}$$

$$S_{\rm I} = \frac{7 - 5\nu}{15(1-\nu)}, S_{\rm II} = -\frac{1 - 5\nu}{15(1-\nu)}, \tag{5}$$

where $\epsilon^*_{\rm v} = 3\epsilon^*$, B is the bulk modulus, ν is Poisson's ratio of the matrix, and $S_{\rm I}$ and $S_{\rm II}$ are the Eshelby tensors.

In case of considering the Li/Sn cell shown in Fig. 1(a), the anode, cathode and total reactions are expressed as

$$\text{Anode}: \text{Li} = \text{Li}^+ + \text{e}^- \tag{6}$$

$$\text{Cathode}: x\text{Li}^+ + \text{Li}_y\text{Sn} + x\text{e}^- = \text{Li}_{x+y}\text{Sn} \tag{7}$$

$$\text{Total}: x\text{Li} + \text{Li}_y\text{Sn} = \text{Li}_{x+y}\text{Sn} \tag{8}$$

As intuitively understood from the figure, the elastic constraint associated with the Li-compound formation having a larger molar volume becomes significant when it is formed inside the (Sn or Li_ySn) matrix. In this case, the driving force of the total cell reaction is inevitably reduced by the strain energy illustrated in Fig. 1(b). Under such an elastically constrained condition, the electrode

potential $E_{\rm total}$ can be written as

$$E_{\rm total} = -\frac{\Delta G_{\rm chem} + U_{\rm s}}{nF} = E_{\rm chem} - \Delta E, \tag{9}$$

where $\Delta G_{\rm chem}$ (< 0) is the Gibbs free energy of the formation per one mole of Sn in Eq. (8) and a series of data can be taken from Ref. [16], F is the Faraday constant, the value of n is 2/5 for the first lithiation reaction, and 3/5 for the second reaction, etc, and ΔE (> 0) is the potential drop. The strain energy $U_{\rm s}$ and the value of the potential drop ΔE are also shown in Table I for all the reactions. It is seen in Table I that the electrode potential (open circuit voltage: OCV) is significantly reduced by the strain energy. As will be understood later, it is also noted that the elastic strain induced by the formation of the Li-Sn compound is much larger than the tensile strength of Sn matrix. It is thus considered that, in the actual electrode, the matrix around the compound is always under the creep deformation and releases the strain.

3. EXPERIMENTAL

We prepared simple Li/Sn cells, consisting of Sn "positive electrode" and Li "negative electrode" for the electrodes and for an electrolyte, 1M $LiPF_6$ in a solution of 33% ethylene carbonate and 67% dimethyl carbonate. The cells were assembled in an argon-filled glove box and all charge-discharge experiments were performed at room temperature. In the present experiments, various shapes of Sn electrodes were used. The typical shape of bulk Sn used here is disc-like of about 30 μm in thickness and 16 mm in diameter. Before the tests, all the cells were partially discharged (i.e., the Sn electrode is firstly lithiated) to a small amount of Li by passing current, to remove Sn oxides near the surface. In the present experiments, the maximum discharge (lithiation) rate was about 25 $\rm Am^{-2}$ (2.5 $\rm mA/cm^2$), and most of lithiation/detlithiation process were done below 0.6 $\rm Am^{-2}$ (0.06 $\rm mA/cm^2$).

The main focus of the present experiments was on the OCV values and their elapsed-time dependence for various types of cells, because the electrode potential in the open circuit condition corresponds to the equilibrium value excluding the other effects, such as IR drop, which enables us to observe the Li-compound formation in the Sn matrix under elastically constraint condition and discuss the formation kinetics affected by the elastic strain during the lithiation and delithiation processes.

4. RESULTS

The rest-time (hereafter, abbreviated to "RT") dependencies of the OCV values at various amounts of discharge (with varying p) are presented in Fig. 2. Interestingly, it is seen that the OCV values recover with RT in spite of the open circuit condition, which indicates that the internal structure of the electrode material changes with RT. We can see two plateaus at about 0.53 and 0.66 V in the OCV-RT curves, in which the OCV values at the first and second plateaus are almost the same, irrespective of the amounts of discharge. The appearance of the second plateau is clearly retarded with increase in the amount of discharge. When $p > 0.4$, the second plateau could not be detected within the present experimental time of 30 hours. When p was less than 0.4 in Fig. 2, the (Sn) positive electrode was supposed to be in the two-phase region of Sn and Li_2Sn_5, and the OCV value at the second plateau must be 0.777 V (vs. Li^+/Li) obtained thermodynamically. However, the present OCV value (0.66 V) in the second plateau is considerably lower than the thermodynamic value. Even when $p = 0.23$ (< 0.4), x-ray diffraction profiles in Fig. 2(b) shows the presence of

LiSn ($p = 1$) with higher Li composition. Thus, LiSn ($p = 1$) is formed, even though the amount of lithiation is only 10-50 Ahkg^{-1} ($p < 0.4$) far below than 226 Ahkg^{-1} ($p = 1$) for the formation of LiSn. Namely, the Li rich phase such as LiSn, which may be likely to be formed near the surface, gradually vanishes due to the diffusion of Li into the inner side, and the electrode would eventually be occupied with Sn and Li_2Sn_5in the equilibrium state. By considering this, the first and second plateaus may correspond to the OCV values in the LiSn/Li_7Sn_3 equilibrium and in the Li_2Sn_5/LiSn equilibrium, respectively. Nevertheless, the experimental OCV value about 0.66 V in the second plateau is still less than the thermodynamic value (0.69 V), which is considered due to the strain energy effect.

In order to make sure the strain-energy effects on OCV more clearly, we have investigated OCV in the higher lithiation stages. Figure 3(a) shows the OCV-RT curves at relatively large p values. Obviously, the OCV values for $p > 2.3$ are lower than the minimum value for the formation of $Li_{22}Sn_5$. Since there is no Li compound that possesses the Li composition higher than $Li_{22}Sn_5$, we cannot attribute these lower values to the compound formation of the higher Li concentration. Thus, it is strongly suggested that this lowered OCV is caused by the strain energy effect. The recovery or increase of OCV with RT means creep deformation or destruction of the matrix of the active material. Figure 3(b) summarizes the OCV values obtained at various lithiation stages. Several points at the same p value mean that the first, second or third plateau appeared with RT in the open circuit condition, in which the thermodynamically expected lines are also indicated. It can be seen that the most of OCV values are located below the thermodynamic prediction. Especially for $p \sim 4$, we have no obvious reasons to reduce the OCV value other than the strain energy, because $Li_{22}Sn_5$ would be formed in the final lithiation stage.

Moreover, we have further checked the depth dependence of the electromotive force at a very small current $I = 0.001$ mA. Figure 4 shows that the cell voltage gradually decreases with time, despite the fact that the activity of Li should be constant in the two-phase (Sn/Li_2Sn_5) region. As seen in the inset, this can be understood by considering that the strain energy should be enlarged as the infiltration depth of lithium increases, which is discussed more in detail later.

In the case where the active materials are nanoparticles, the strain energy is easily released in comparison with the bulk samples. In order to see the difference between nanoparticles and bulk samples, we have prepared the Sn nanoparticles on the Cu substrate by the high-vacuum sputtering method and measured the OCV values in the same way. Figure 5 shows the OCV-RT curves obtained for the thin film cathodes of 50 nm and 100 nm in thickness (Sn nanoparticles are naturally formed on the Cu substrate in the initial stage; see the SEM micrographs). The stationary OCV values are very consistent with the values estimated thermodynamically, whose values are indeed found to be higher than those observed in the bulk Sn. Furthermore, the characteristic features of nanoparticles of Sn are (i) the duration (100-400 minutes) needed for the equilibrium of Sn/Li_2Sn_5 is much shorter than the bulk Sn; compare with Fig. 2. Thus, as easily foreseen, the strain energy can be released in the case of nanostructured electrode materials.

Next, we try to show an enhanced strain effect by using Sn embedded in the lotus-type porous Cu[17, 18], that is, by using the Sn-fibered and Cu-matrix composite as a cathode. In Table I, we foresee, as a perspective value, the negative OCV value ($E_{\text{total}} = -0.039$ V) for the formation of Li_7Sn_3, which indicates that the Li atoms (ions) cannot be inserted without any deformation of the matrix with the quite high barrier of strain energy against the compound formation. The Sn matrix is fundamentally soft in mechanical viewpoint, so that deformation can easily take place. However, this is not the case for the Cu matrix; the Cu matrix itself is elastically and plastically much harder than Sn. Namely, it is considered that the creep deformation as observed for pure Sn hardly occurs in this case. Figure 6 shows the current versus time curve measured under the CC-CV (5 mA - 0V) condition, and the value of 0 V at the CV mode means the short-circuit condition. The current

rapidly decreases with time and vanishes at a certain amount of discharge. It is found that only about 1 % of the total capacity can be lithiated for the composite cathode, despite the fact that full discharge is possible without any interference for pure Sn cathode. As found from the photograph after discharge, we see that the lithiation occurs only in the front side and the back side is still fresh. Thus, when the elastically and plastically harder matrix exists, the lithiation becomes much harder in terms of the release of the elastic strain energy.

Finally, we show the opposite case where the Li anode is squeezed elastically. In the squeezed state, the elastic strain energy is stored in the Li anode, leading to the situation where the activity of Li exceeds 1. Therefore, the OCV value is expected to be higher than that of the usual one. Actually, as seen in Fig. 7, we have confirmed that the OCV value with the squeezed Li anode is slightly higher than the normal Li anode without any strain. The increase of the OCV value is very subtle, about 1 mV, but the reproducibility of this phenomenon was checked by several times of testing.

5. DISCUSSION

We have here made several demonstrations that strongly indicate the contribution of the elastic-strain energy to the electrode potential of a Sn electrode in a simple Sn-Li battery system. These intriguing experimental phenomena can be explained by considering the contribution of the elastic-strain energy to the Gibbs free energy of formation.

As shown in Table I, the lowering of the OCV values can be basically understood as the effect of the elastic strain energy. Especially, as shown in Fig. 3, the significant reduction of the OCV value for $p \approx 4$ cannot be explained without the strain effects. In Fig. 2, even for the second plateau corresponding to the equilibrium of Li_2Sn_5/LiSn, the OCV value is less by about 0.02 V than the thermodynamically estimated value. We simply assume that LiSn is formed in the matrix Li_2Sn_5. Then, by converting this drop to the strain energy with Eq. (9), it amounts to about 1160 kJmol^{-1} (58 MJm^{-3}) and the hydrostatic pressure of about 1800 MPa is applied to the compound with the large molar volume. Furthermore, the misfit strain (eigenstrain) can be estimated to be 0.022 with Eq. (4), which indicates that most of the strain (about 0.052) is considered to be released by creep in the light of the true eigenstrain of 0.074 (if any relaxation does not occur, the potential drop amounts to 0.235 V as seen in Table I). Thus, the compound newly formed by the lithiation is considerably subjected to high stress (pressure), and the lithiation is therefore impossible unless the large elastic strain is significantly released by the creep deformation of matrix, which straightforwardly means that the active materials are gradually degraded.

Figure 4 is indeed instructive for understanding of the strain-energy effect on the electrode potential, and Fig. 8 may be helpful to understand the result that the cell voltage decreases gradually with increase in the lithiation depth. As easily imagined, the strain energy associated with the Li-compound formation would be accumulated more and more as the front of the Li-compound region (termed here as "phase front") goes forward to the inner side. Therefore, this means that the lowering of the Li activation (i.e., the gain owing to the formation of the Li-compound) is gradually decreasing with increase in the lithiation (discharge) duration, not only in the inner side but even near the surface, from the standpoint of holding the local equilibrium all the time.

The intriguing phenomena caused by the formation of Li-rich compounds (as seen in Fig. 2) cannot be explained merely by the diffusion control of Li in Sn matrix, because the time needed for the diffusion distance of about 30 μm (thickness of the anode) of Li atoms is estimated to be about 900 s from the diffusion coefficient of the order 10^{-8} cm^{2}s^{-1}[2], which is found to be far shorter than the time, about 2800 s, required for reaching the composition ratio of Li/Sn = 2/5, estimated from the

lithiation rate of 25 Am^{-2} in the maximum of the present current condition (incidentally, 118400 s for 0.6 Am^{-2}). In case where the Li-Sn compounds are formed near the electrode surface, the elastic-strain energy accompanied by the compound formation can be released more easily than the formation inside the active material. Namely, the effect of the strain energy on the free energy of the compound formation becomes larger with the distance from the electrode surface. This situation can be experimentally seen in Fig. 4. Suppose that the compounds are successively formed along the depth direction in Fig. 9(a). Even when $p < 0.4$, at a certain point, the formation of the Li-Sn compound with a higher Li composition (such as LiSn, Li_7Sn_3) near the surface is thermodynamically more favorable than the formation of the Li-Sn compound with less Li inside the active material, because the strain energy of the inside obviously becomes larger than that on near the surface. Thus, the Li-rich compound can be formed, even though the amount of discharge, i.e., lithiation, is considerably less than that needed for the Li-rich compound.

Moreover, we can explain with Fig. 9(b) the reason why once such a Li-rich compound is formed, it is retained metastably after a long duration (as experimentally seen in Fig. 2). As mentioned previously, upon the formation of the Li compound the creep deformation of the matrix inevitably occurs, so that the Li compounds are accommodated well in the matrix after the creep. Consequently, Li atoms are quite difficult to be desorbed from the Li-rich compounds, because the volume shrinking is accompanied by this reaction, and negative hydrostatic pressure is applied to the compound, leading to the appearance of the very stable plateaus for the non-equilibrium Li-rich compound. For example, let us consider the case that the metastable plateau for Li_2Sn_5/LiSn is retained and it does not change to the plateau for Sn/Li_2Sn_5 even for $p < 0.4$. For the shift to the equilibrium, the following

$$(3/5)\mathrm{Sn} + (2/5)\mathrm{LiSn} \rightarrow (1/5)\mathrm{Li_2Sn_5} \tag{10}$$

must occur as a total reaction. Then, the Li_2Sn_5 compound is to be formed both in the Sn and LiSn matrices as shown in Fig. 9(b). In both cases, the elastic-strain energies are inevitably accompanied by the formations. The chemical driving force of the above reaction can be estimated to be about -2 $kJmol^{-1}$, of course, being negative because Eq. (10) is of $p = 0.4$. The strain energies associated with the formations of Li_2Sn_5 in Sn and Li_2Sn_5 in LiSn are, respectively, evaluated to be 9.63 $kJmol^{-1}$ and 16.8 $kJmol^{-1}$ (this value can be obtained by using the LiSn matrix instead of the Li_2Sn_5 matrix, that is, $13.6 \times 24.6/19.9$; see Table I), so that the total strain energy associated with the above reaction is about 12.5 $kJmol^{-1}$. The total free energy of the above reaction therefore results in the positive value, which means that the above reaction is impossible without any creep deformation to release the strain energy. Thus, the metastable plateau comes to be kept for a duration as long as about 30 h, as seen in Fig. 2.

Table I strongly indicates that especially the third reaction of lithiation cannot occur without the creep deformation of the matrix from the negative OCV value. The present experiment using the Sn-porous Cu composite cathode strongly supports that the strain energy is possible to play an important role to the lithiation process (Fig. 6). In that case, since the Cu itself cannot be in the creep deformation, only very small amount of Li can infiltrate into the Sn embedded in the Cu matrix. On the contrary, the squeezed Li can yield a higher OCV than the normal Li without strain (Fig. 7). According to Eq. (9), the increase of 1 mV corresponds to the strain energy of 38.6 $Jmol^{-1}$, from which the elastic strain of Li is estimated to be about 0.8 %, where we used the bulk modulus of Li (11.6 GPa) and the molar volume of Li (12.8×10^{-6} m^3mol^{-1}). Based on this experimental fact, we can derive a new mechanism to enhance the cell voltage of the lithium ion batteries. By utilizing the compression to Li actively, the strain energy is accumulated in the anode, so that the driving force of the total cell reaction comes to be enlarged, which may provide higher electromotive forces in the lithium ion batteries.

6. CONCLUSIONS

By using a simple Li-Sn system, we have investigated the effects of the elastic-strain energy accompanied with the Li-compound formation through the lithiation and delithiation process. It has been revealed that the elastic strain associated with the formation of a new phase accompanying a volume change causes the formation of the Li-rich compound and affects the value of the electrode potential considerably. Through the present experiments, we have obtained the following results.

1. The OCV values change in spite of the open circuit condition, but in the case of bulk Sn the OCV value hardly reaches the equilibrium value (in Fig. 2, the OCV was supposed to reach about 0.78 V, but it was only about 0.64 V).
2. Even though the amount of discharge is lower than that for the compound with a higher composition of Li (e.g., LiSn when $p < 0.4$), such a Li-rich compound is likely to be formed. Therefore, the OCV-RT curves of the Sn electrodes partially lithiated have several plateaus.
3. Most of the experimental OCV values are lower than the ideal values expected purely thermodynamically.
4. The cell voltage is in principle supposed to be constant in the two-phase region, but the cell voltage decreases with time, i.e., with the infiltration depth of Li.
5. Sn nanoparticles exhibit the OCV values very close to the ideal thermodynamic values, and it is considered that the strain energy in nanoparticles can be released relatively easier than in bulk Sn cathode.
6. Li can hardly infiltrate into Sn embedded in the elastically and plastically hard Cu matrix.
7. The squeezed Li anode delivers a higher OCV value than the normal Li anode without strain.

These experimental results can be explained by considering the effects of the elastic-strain energy to the Gibbs free energy of formation. The volume dilatation in the lithiation process basically lower the reduction potential of Li, which will work for the enlargement of the electromotive force of the lithium-ion batteries, although the kinetics itself is retarded. Thus, the elastic strain caused by the formation of Li compounds accompanying volume changes considerably strongly affects the value of electrode potential and dominates their formation kinetics. Namely, we should pay attention to the fact that the cell voltage and kinetics come to be significantly discrepant from one simply estimated by a chemical thermodynamics only. This strain effects may be one of the policies to make the cell voltage higher even in the lithium ion batteries currently used.

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[1] L.Y. Beaulieu, D. Larcher, R.A. Dunlap, and J.R. Dahn, J. Electrochem. Soc., 2000, **147**, 3206.
[2] R.A. Huggins, J. Power Sources, 1999, **81-82**, 13.
[3] J. Wang, I.D. Raistrick, and R.A. Huggins, J. Electrochem. Soc., 1986, **133**, 457.
[4] O. Mao, R.A. Dunlap, and J.R. Dahn, J. Electrochem. Soc., 1999, **146**, 405.
[5] I.A. Courtney and J.R. Dahn, J. Electrochem. Soc., 1997, **144**, 2045.
[6] M. Winter and J.O. Besenhard, Electrochimica Acta, 1999, **45**, 31.
[7] C. Yu, J. Liu, H. Lu, and J. Chen, Solid State Communications, 2006, **140**, 538.
[8] K. Hirai, T. Ichitsubo, T. Uda, A. Miyazaki, S. Yagi, E. Matsubara, Acta Mater., 2008, **56**, 1539.
[9] YT. Cheng, MW. Verbrugge, J. Appl. Phys., 2008, **104**, 083521.
[10] YT. Cheng, MW. Verbrugge, J. Power Sources, 2009, **190**, 453.
[11] G. Simmons, H. Wang, Single Crystal Elastic Constants and Calculated Aggregated Properties: A HANDBOOK Second Edition The MIT Press Cambridge, Massachusetts, and London, England, 1971, p.115.
[12] T. Ichitsubo, M. Nakamoto, K. Tanaka, and M. Koiwa, Mater. Trans. JIM, 1998, **39**, 24.
[13] N. Usami, T. Ichitsubo, T. Ujihara, T. Takahashi, K. Fujiwara, G. Sazaki, K. Nakajima, J. Appl. Phys., 2003, **94**, 916.
[14] T. Mura, Micromechanics of Defects in Solids, 2nd ed, revised (Martinus Nijhoff Pul, The Hegue, 1987).
[15] JD. Eshelby, Proc. Roy. Soc. A, 1957, **241**, 376.
[16] F. Yin, X. Su, Z. Li, and J. Wang, J.Alloys and Compounds, 2005, **393**, 105.
[17] H. Nakajima, Mater. Integrat. 1999, **12**, 37.
[18] T. Ichitsubo, M. Tane, H. Ogi, M. Hirao, T. Ikeda, H. Nakajima, Acta Mater., 2002, **50**, 4105.

TABLE I: The Li-Sn compounds, p value in Li_pSn, formation reaction of various LiSn compounds, corresponding electrode potential $E_{\rm chem}$, specific capacity $C_{\rm s}$ in unit of $\rm Ahkg^{-1}$, molar volume per one mole of Sn Ω in unit of $10^{-6}\rm m^3mol^{-1}$, relative volume $V_{\rm r}$, enignastrain (stress-free transformation strain) ϵ^*, the strain energy $U_{\rm s}$ in unit of $\rm kJmol^{-1}$, the potential drop ΔE in unit of V due to $U_{\rm s}$, and the total electrode potential $E_{\rm total}$. Ω denotes the value per one mole of Sn and is calculated by dividing the unit cell volume with the number of only Sn atoms without taking account of the number of Li. $V_{\rm r}$ is the value obtained by dividing each volume with the volume of βSn, i.e., defined as $\Omega/\Omega_{\beta\rm Sn}$ and the value in the parentheses is the ratio of Ω of the new phase to Ω of the matrix, and $C_{\rm s}$ is defined as electronic quantity per unit weight of Sn to transform into each Li-Sn compounds. The electrode potential, $E_{\rm chem}$, is calculated from the thermodynamic data reported in Ref. [16].

Compounds	Li_pSn	Lithiation reaction per one mole of Sn	$E_{\rm chem}$	$C_{\rm s}$	Ω	$V_{\rm r}$	ϵ^*	$U_{\rm s}$	ΔE	$E_{\rm total}$
Li_2Sn_5	$Li_{0.4}Sn$	(2/5)Li + Sn = (1/5)Li_2Sn_5	0.777	90.3	19.9	1.22	0.069	9.63	0.250	0.528
LiSn	Li_1Sn	(3/5)Li + (1/5)Li_2Sn_5 = LiSn	0.690	226	24.6	1.51 (1.24)	0.074	13.6	0.235	0.455
Li_7Sn_3	$Li_{2.3}Sn$	(4/3)Li + LiSn = (1/3)Li_7Sn_3	0.448	527	36.8	2.26 (1.50)	0.14	62.6	0.487	-0.039
Li_5Sn_2	$Li_{2.5}Sn$	(1/6)Li + (1/3)Li_7Sn_3 = (1/2)Li_5Sn_2	0.446	564	38.4	2.36 (1.04)	0.015	1.03	0.064	0.382
$Li_{13}Sn_5$	$Li_{2.6}Sn$	(1/10)Li + (1/2)Li_5Sn_2 = (1/5)$Li_{13}Sn_5$	0.439	587	39.5	2.43 (1.03)	0.0094	0.42	0.044	0.395
Li_7Sn_2	$Li_{3.5}Sn$	(9/10)Li + (1/5)$Li_{13}Sn_5$ = (1/2)Li_7Sn_2	0.437	790	48.3	2.96 (1.22)	0.069	23.6	0.272	0.165
$Li_{22}Sn_5$	$Li_{4.4}Sn$	(9/10)Li + (1/2)Li_7Sn_2 = (1/5)$Li_{22}Sn_5$	0.426	993	58.3	3.58 (1.21)	0.065	25.2	0.290	0.135

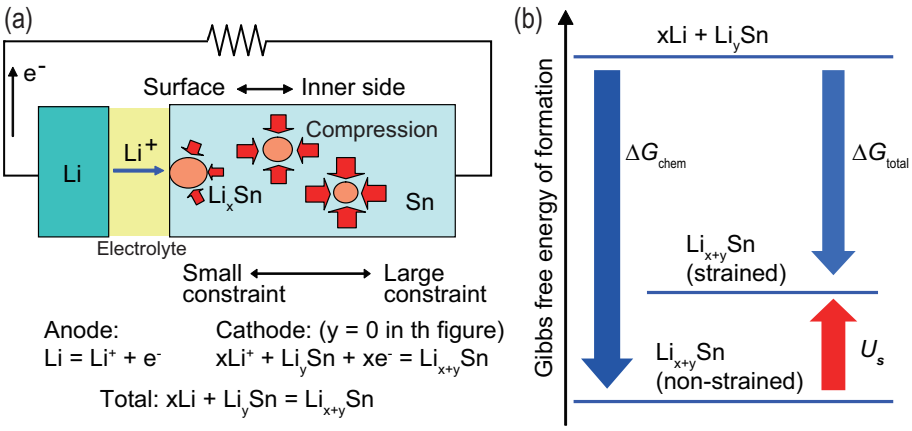

FIG. 1: (a) Schematic illustration showing the Li/Sn cell system, and in the anode the Li-compound with a larger molar volume per one mole of Sn is formed under the elastic constraint. (b) The Gibbs free energy of formation of the stress-free Li compound and total free energy taking account of the elastic strain energy.

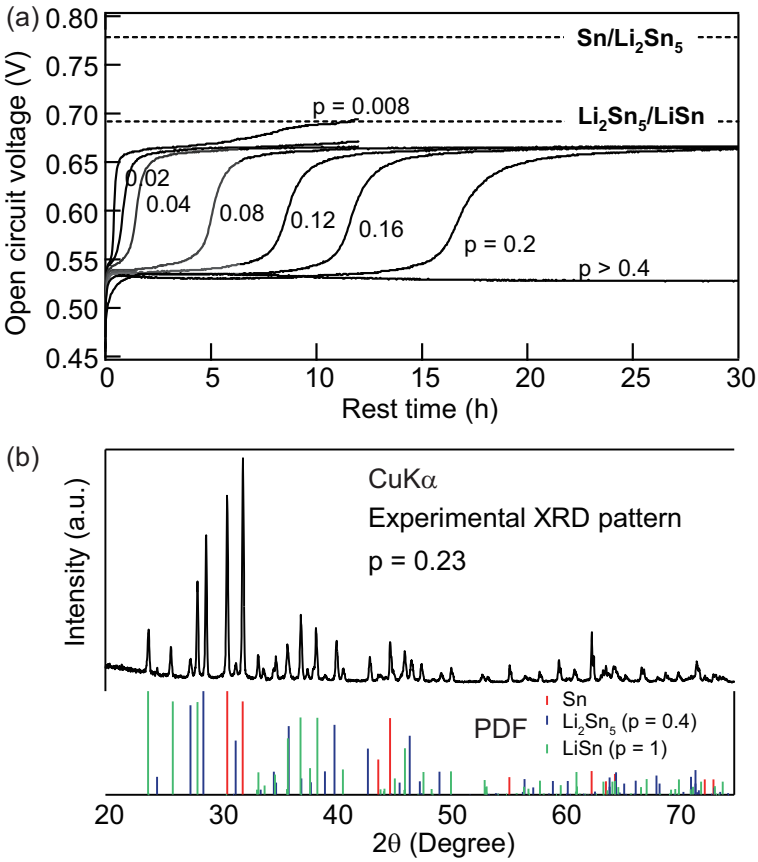

FIG. 2: (a) The OCV-RT curves at various p values. Most of these OCV tests were made below $p < 0.4$, where $p = 0.4$ means the formation of Li_2Sn_5, corresponding to 90.3 Ah kg^{-1}). (b) X-ray diffraction profile (CuKα) of the Sn electrode after lithiation of $p = 0.23$ against Sn. In this Li concentration, the two-phase regions of Sn/Li_2Sn_5 are supposed to be in thermodynamically equilibrium.

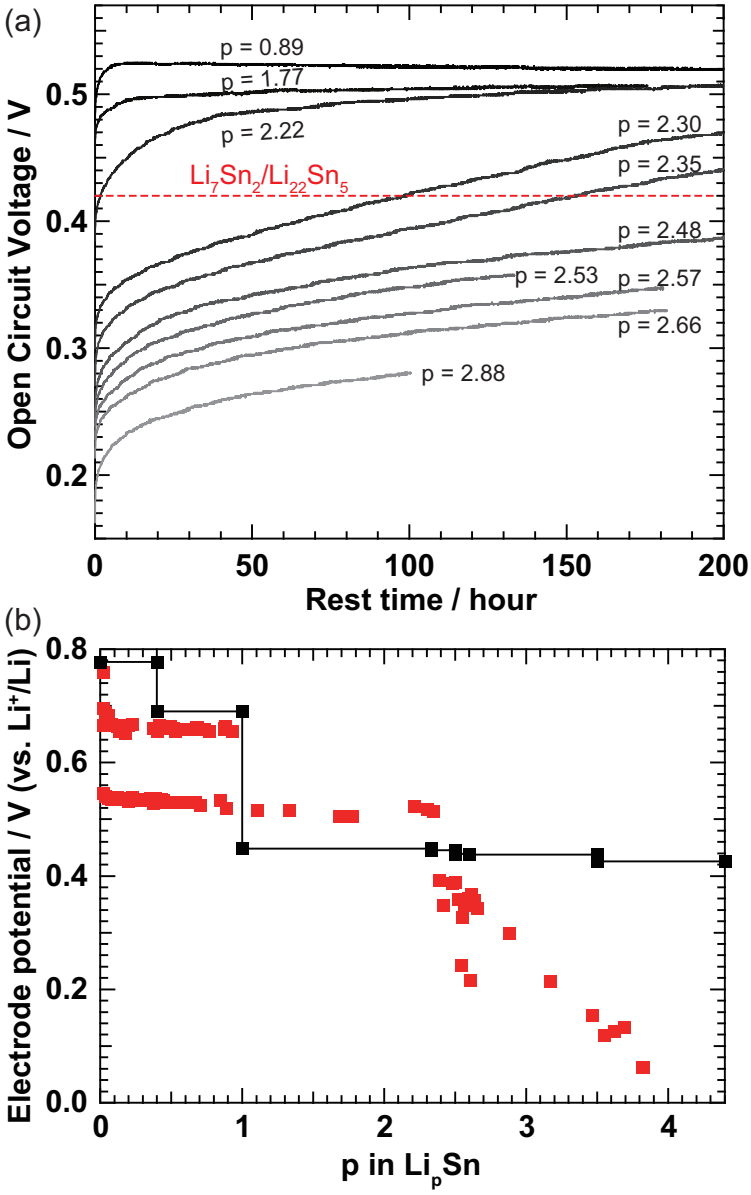

FIG. 3: (a) The OCV-RT curves at various p values. The dashed line is the OCV value obtained thermodynamically for the $Li_7Sn_2/Li_{22}Sn_5$ equilibrium. (b) The stationary OCV observed in the open circuit condition at various p values. The solid lines are the thermodynamic OCV values.

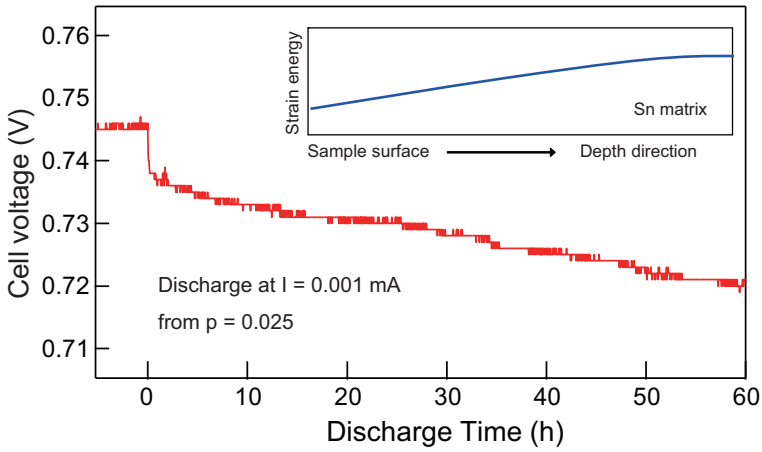

FIG. 4: Time dependence of the cell voltage at a current $I = 0.001$ mA (5.0×10^{-4} mAcm^{-2}) after a small amount ($p = 0.025$) of lithiation at $I = 0.3$ mA (0.15 m A/cm^{-2}). The schematic inset qualitatively shows that the strain energy increases as the formation site (i.e., the phase front) goes into the inner side.

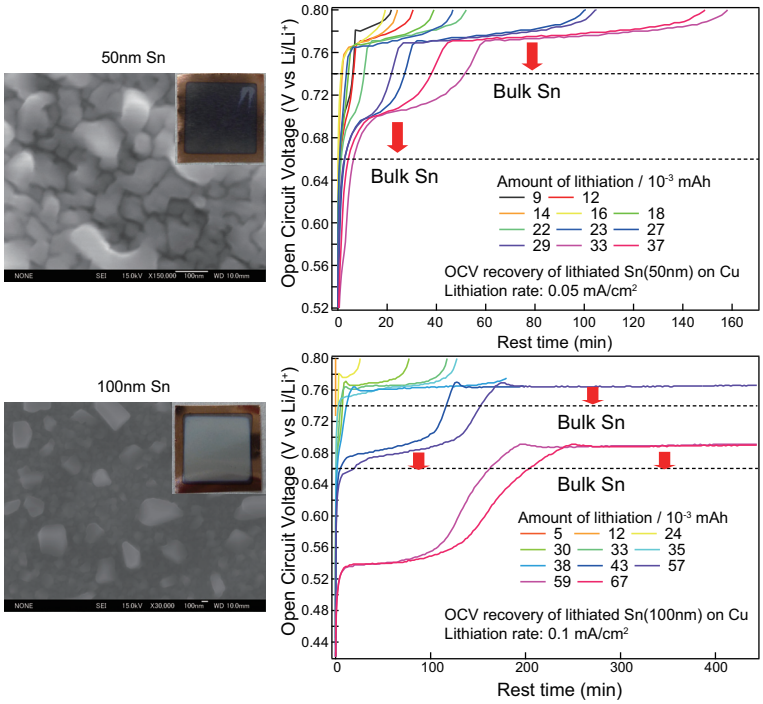

FIG. 5: The OCV-RT curves measured for the Sn thin films with 50 nm and 100 nm thicknesses (the depossited area is 9 mm × 9 mm in the both cases) on Cu substrates prepared by the sputtering method. The FE-SEM micrographs are also shown, from which almost nanoparticles are formed on the substrate in both cases. The OCV behavior that is going to increase over 0.8 V may be caused by the reaction with the Cu substrate or Sn-Cu compound which seems to be formed near the substrate surface.

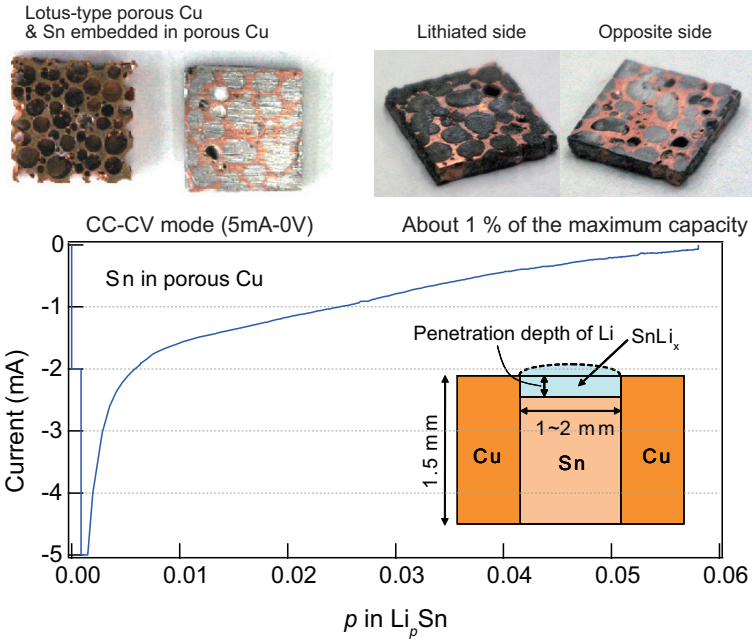

FIG. 6: Porous Cu and Sn embedded in lotus-type porous Cu before and after discharge test, and current-RT curves with the Sn-porous Cu cathode measured under the CC-CV mode (CC: 5 mA, CV: 0 V, i.e., short-circuit condition). The negative current value means the discharge current (the positive current for charge, vice versa). After discharge (lithiation), the surface of the front side appears to be convex, but the back side is still fresh. The total amount of discharge was only 1 % of the ideal capacity of Sn.

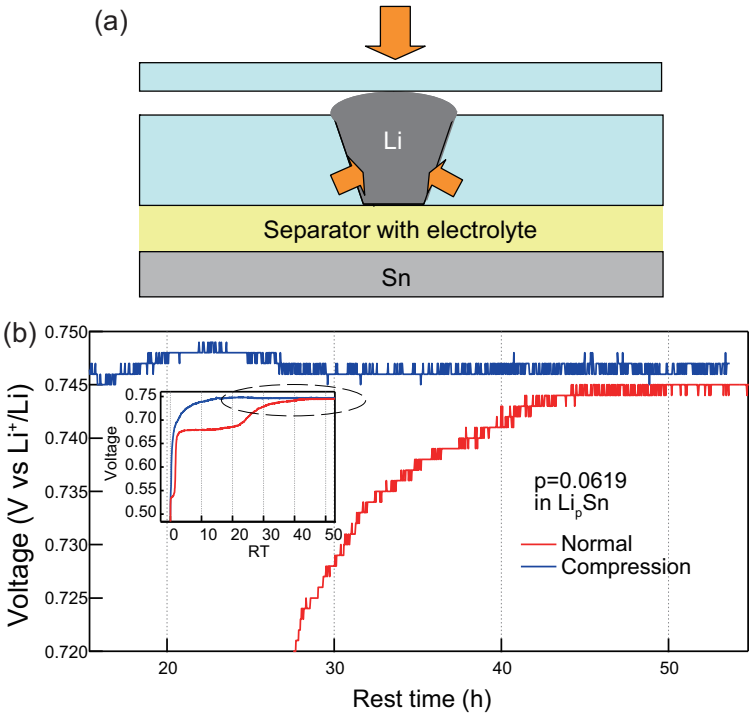

FIG. 7: (a) The way to squeeze the Li anode and (b) the OCV-RT curves obtained for the squeezed Li anode and non-squeezed one (the inset is the whole OCV data and the part of dashed circle is magnified). By forcing bulk Li to be inserted into the stainless jig like dice and applying it the compression by the top flange, the elastic-strain state can be realized. In the practical experiment, first we measured with non-strained normal Li after reaching the equilibration of the second plateau, and subsequently, by removing the normal anode and altering to the squeezed Li anode, we re-measured the OCV-RT curves. The amount of pre-discharge of Li was as small as $p = 0.0619$.

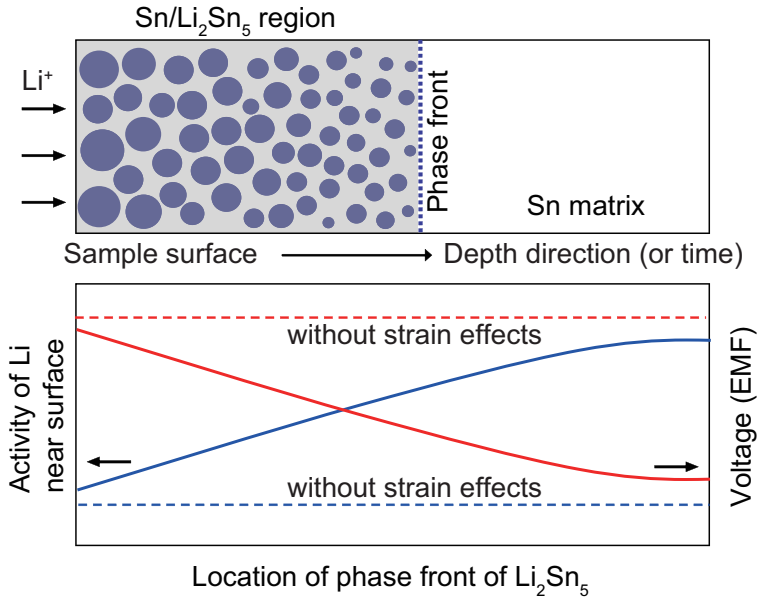

FIG. 8: Schematic illustrations showing that (upper) the formation of the Li compound (Li_2Sn_5 in this figure) goes toward the inner side with increase in the discharge amount and (lower) the activity of Li increases and the corresponding voltage decreases as the phase front proceeds. The dashed lines indicate the Li activity and cell voltage without taking account of the strain-energy effects.

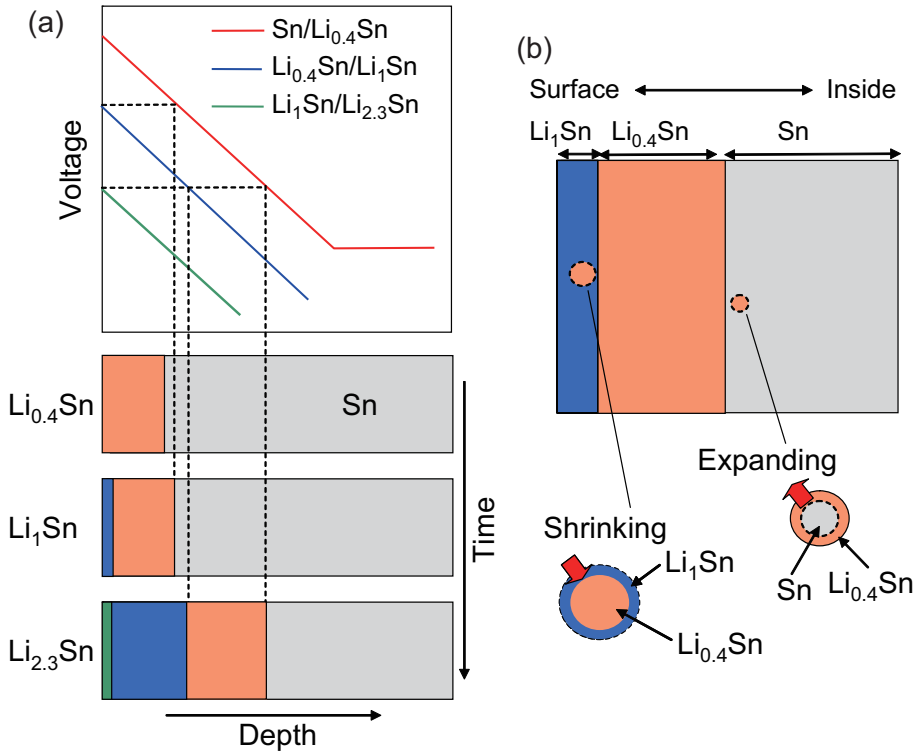

FIG. 9: Schematic illustrations explaining (a) that the Li-rich compounds are likely to be formed near the surface due to the strain-energy effects, and (b) that the non-equilibrium plateaus are retained metastably for a long while.