

Steady-state polarization measurements of lithium insertion electrodes for high-power lithium-ion batteries

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Abstract Steady-state polarization measurements of lithium titanium oxide (LTO; $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) were carried out using the 0-V lithium-ion cells consisting of two identical LTO-electrodes with a parallel-plate symmetrical electrode configuration. The sinusoidal voltage with the peak amplitude of 1.0 V was imposed at 0.1 Hz upon the 0-V cells and the current response was measured as a function of time. The steady-state polarization, obtained by plotting the current versus applied voltage, was linear in current up to approximately 60 mA cm^{-2} or 4 A g^{-1} based on the LTO weight and suggested the resistance polarization only for the lithium insertion electrode of the LTO. The method was also applied to lithium aluminum manganese oxide (LAMO; $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$) and the resistance polarization of the LAMO-electrode was determined for currents up to approximately 25 mA cm^{-2} or 2 A g^{-1} based on the LAMO weight. The validity of the results was examined for the polarization measurements of the 2.5-V lithium-ion battery consisting of LTO and LAMO, and the significance of the polarization measurements of lithium insertion electrodes for high-power applications was discussed.

Keywords Polarization · Lithium-ion battery · Lithium titanium oxide · Insertion electrode

Introduction

Lithium-ion batteries consisting of two different lithium insertion materials, such as LiCoO_2 and graphite, have been developed as high-energy density batteries and widely used as power sources for mobile phones, laptop computers, and other advanced electronic devices. The batteries for such applications are usually charged at a constant current followed by a constant voltage, the so-called CCCV, and discharged at a constant current or power for 1–6 h of service. In addition to such applications, the lithium-ion batteries have been expected as the power source of choice for pure electric vehicles (EV) and hybrid electric vehicles (HEV) [1–3] (www.lithiumtech.com; <http://www.valence.com/>), and 12-V “lead-free” accumulators have been proposed using the basic lithium-ion battery concept and examined as whether or not the combination of lithium insertion materials is capable of storing and delivering a burst of energy for a short period of time [4, 5]. The batteries for HEV or 12-V lead-free accumulators usually have a larger volume and higher input and output power than currently available high-energy-density lithium-ion batteries. Therefore, the power density of the battery rather than the energy density is the most important parametric factor for evaluating the battery together with the battery life due to power fade and safety in addition to cycle life.

Battery power (P) is the product of the current (J) and the terminal voltage ($E(J)$) at current J . The product of the polarization and current is called power dissipation due to the dissipative processes generating heat inside the battery. Therefore, reducing the polarization of the batteries is a key

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issue for high-power applications. In this paper, the term “polarization” is used to describe a change in the potential E at current I , $E(I)$, as compared to the zero-current potential, $E(0)$. The voltage $E(I)$ is called the polarization voltage and $E(0)$ is the open-circuit voltage. If the zero-current potential is equal to the equilibrium potential, the polarization is synonymous with the overvoltage [6]. The polarization voltage $E(I)$ consists of the reversible terminal voltage of the battery, polarization at the positive electrode, polarization at the negative electrode, and the ohmic voltage drop in the battery including terminals. Of these, the high reversible terminal voltage and low ohmic voltage drop for producing a high power are attained by selecting electrode materials, electrolyte, separator, and metal substrates of both the positive and negative electrodes. However, polarization at the positive and negative electrodes has not been dealt with so far partly because researchers have been investigating the new lithium insertion materials for high-energy-density batteries and partly because polarization studies of lithium insertion electrodes were thought to be useless until the high-power applications were recognized.

In our previous papers, we reported the impedance measurements of the 2-V lithium-ion battery consisting of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{LiCo}_{1/2}\text{Ni}_{1/2}\text{O}_2$ [7] and the polarization and impedance measurements of the 3-V lithium-ion battery of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{Li}[\text{Ni}_{1/2}\text{Mn}_{3/2}]\text{O}_4$ [8]. These lithium-ion batteries only showed a resistance polarization [6]. We have not observed any “chemical” polarization of the lithium insertion electrodes. The word “chemical” polarization is a classical term [9]. It is now widely accepted as “activation overvoltage” combined with the Butler–Volmer equation after the establishment of electrochemistry for the redox electrode of soluble species, the hydrogen electrode, and the metal ion electrodes. We use “chemical” polarization for “activation” to represent the polarization of lithium insertion electrodes until a full understanding of the electrochemistry of lithium insertion materials is performed.

The three-electrode configuration consisting of a working electrode, a counter electrode, and a reference electrode with the Huber–Luggin capillary is popular for the polarization studies of electrode materials in electrochemistry. However, for lithium insertion materials, it is difficult to measure the accurate polarization voltages in such a normal three-electrode configuration, as was discussed in a previous paper [10]. In this paper, the cell with the parallel-plate symmetrical electrode configuration with identical lithium insertion electrodes is used for polarization measurements, and we discuss whether or not the “chemical” polarization of the lithium insertion electrodes is observed in addition to the resistance polarization.

Experimental

The lithium insertion materials selected for the polarization studies are the so-called zero-strain insertion material of lithium titanium oxide (LTO; $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$) and lithium aluminum manganese oxide (LAMO; $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$). LTO and LAMO used in this study are the same as described in [10] for LTO and [5] for LAMO. For preparing the electrodes, a black viscous slurry consisting of 88 wt.% LTO or LAMO, 6 wt.% acetylene black, and 6 wt.% polyvinylidene fluoride dispersed in *N*-methyl-2-pyrrolidone was cast using a blade on aluminum foil ($15 \times 20 \text{ mm}^2$). The electrodes were dried under vacuum at 150°C overnight. The lithium electrodes were prepared by cutting a piece from a lithium rod, rolling it into a sheet, and pressing it on a stainless steel sheet ($15 \times 20 \text{ mm}^2$). The electrochemical cell used in this study was the same as previously described [11]. The electrolyte was 1 M LiPF_6 dissolved in an ethylene carbonate or dimethyl carbonate (3/7 by volume) solution obtained from Kishida Chemical Corp., Ltd., Japan. Two sheets of a porous membrane (Celgard 2500) were used as the separator for the lithium cells. For fabricating the cells, all materials except the electrolyte and lithium metal were dried under vacuum at about 60°C for at least 2 h before fabrication to avoid any possible contamination by water.

A sinusoidal voltage was applied to the cell using a potentiostat (Model 363, Princeton Applied Research Co., Ltd., USA) connected to a function generator (FS-2121, TOA Electronics, Ltd., Japan). The current together with the voltage signals as a function of time was simultaneously recorded on a 12-bit digital memory scope (DMS-6440, Iwatsu Electric Co., Ltd., Japan). All the other experimental conditions are described in the following section.

Results and discussion

Figure 1 shows the discharge and charge curves of the LTO examined in two nonaqueous lithium cells. One has 48.3 mg of the LTO-mix with a $124\text{-}\mu\text{m}$ thickness on the 3-cm^2 electrode and the other has 48.6 mg of the LTO-mix with a $129\text{-}\mu\text{m}$ thickness for the same electrode area. The rechargeable capacities are 7.3 and 7.4 mAh corresponding to 172 mAh g^{-1} based on the LTO weight. The difference in the milliampere-hour capacity between the two LTO-electrodes is about 1%. Because the charge and discharge curves observed from the two cells are superimposed except at the end of the discharges, the operating voltage of one cell is offset upward by 1.0 V. Both cells show the flat operating voltage of approximately 1.55 V with the rechargeable capacity of approximately 170 mAh g^{-1} . No other reaction can be seen in the voltage range of 1.0 to

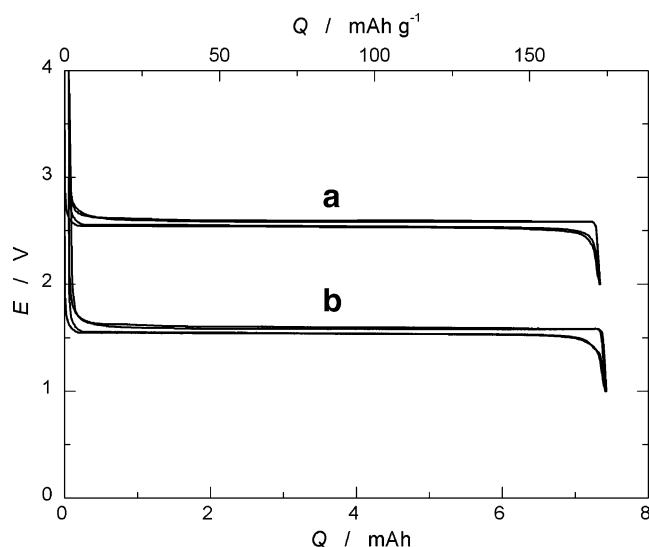


Fig. 1 Discharge and charge curves of lithium or LTO cells operated at 0.17 mA cm^{-2} in voltage range of 1.0 to 3.0 V. Cell (a) contains 48.3-mg LTO-mix with a 124- μm thickness and cell (b) contains 48.6-mg LTO-mix with a 129- μm thickness. After two cycles, cell (a) was discharged to 1.0 V at the rate of 0.17 mA cm^{-2} and then held at 1.0 V for 12 h, and cell (b) was charged to 3.0 V at 0.17 mA cm^{-2} and held at 3.0 V for 12 h. When drawing the curves for cell (a), a 1.0-V offset upward was done in order to distinguish the two curves

3.0 V. One LTO-electrode is identical to the other in the cells. After two cycles, one was discharged to 1.0 V at the rate of 0.17 mA cm^{-2} and then held at 1.0 V for 12 h, and the other was charged to 3.0 V at 0.17 mA cm^{-2} and held at 3.0 V for 12 h. In the cells, one has the reduced form of LTO and the other has the oxidized form. Actually, the oxidized form is LTO. In order to fabricate the 0-V lithium-ion battery consisting of two LTO-electrodes, the two cells were disassembled in a glove box and the LTO-electrodes separated by two sheets of a nonwoven cloth were placed in the cavity of a fresh cell. The electrolyte was introduced into the nonwoven clothes, and the parallel-plate symmetrical electrode configuration was attained.

Figure 2 shows the discharge and charge curves of the 0-V lithium-ion battery that consisted of the oxidized and reduced forms of the LTO. The fresh cell shows an open-circuit voltage of 0.974 V. The terms charge and discharge are arbitrary together with the positive and negative signs of the voltage because of the symmetrical electrode configuration of the LTO-electrodes. In this paper, the decreasing voltage in Fig. 2 is called the “discharge” and the increasing voltage is called the “charge.” Upon discharge, one LTO-electrode is reduced under cathodic polarization and the other is oxidized under anodic polarization. The charging process is the reverse direction for each electrode. Therefore, the operating voltage of the 0-V lithium-ion battery is polarization of the cell operated at the rate of 0.33 mA cm^{-2} , because the reversible voltage of the LTO-electrode is extremely flat at 1.564 V versus Li. It is clear in Fig. 2

that there is an inversion center at 0 V with 82 mAh g^{-1} . A rapid increase in the polarization from approximately 0 to 0.5 V at the end of the charge and rapid decrease in the voltage from approximately 0 to -0.5 V are also an indication that the 0-V lithium-ion battery is properly fabricated for the polarization measurements.

The steady-state polarization measurements are fundamental aspects in electrochemistry. However, it is very difficult to measure the steady-state polarization of lithium insertion electrodes because the state of charge (SOC), more specifically the composition, varies during the polarization measurements. Nevertheless, the steady-state polarization data are needed to provide some insights into the electrode kinetics of the lithium insertion electrodes. In order to measure the steady-state polarization, the cell was discharged to half of its capacity, marked by the arrow, which is the inversion center in Fig. 2, and the sinusoidal voltage with the peak amplitude of 1.0 V was imposed at 0.1 Hz on the 0-V lithium-ion battery. The selection of 0.1 Hz is derived from the condition that the burst of input or output power for a short period of time, typically 5 s, is required for automotive starter, HEV, or EV applications. Figure 3 shows the observed current and applied voltage as a function of time. The vertical axes of the current are given in milliamperes per square centimeter and ampere per gram based on the LTO weight. The polarization voltage is given in 10 cyclic seconds from -1.0 to $+1.0 \text{ V}$. It should be noted here that the polarization voltage is the sum of the cathodic and anodic polarizations of the LTO-electrodes in the cell, so that the real polarization of the LTO-electrode is half the observed value if the anodic and cathodic polarizations are the same. Integration of the current with respect to time

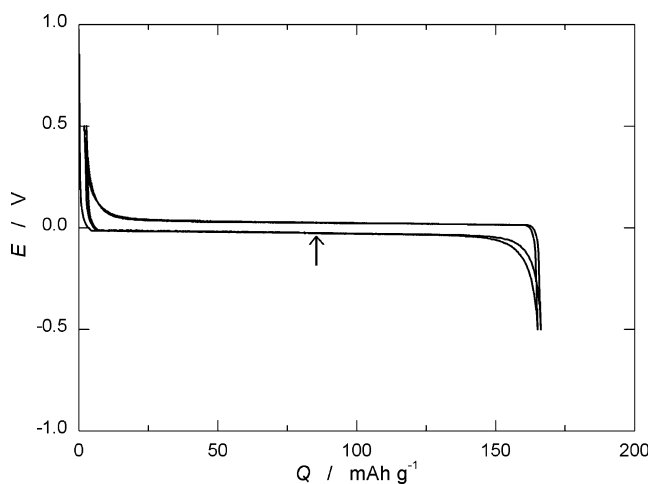


Fig. 2 Discharge and charge curves of the 0-V lithium-ion cell prepared by combining the oxidized and reduced forms of the LTO. The cell was operated at 0.33 mA cm^{-2} in the voltage range of -0.5 to 0.5 V . After two cycles, the cell was discharged to the point marked by the arrow at which the “big voltage wave” polarization measurements were carried out (see the text)

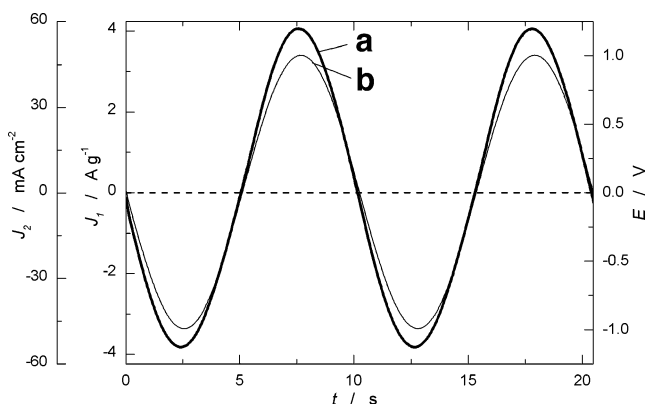


Fig. 3 Observed current (a) combined with the applied voltage (b) imposed on the 0-V lithium-ion cell consisting of the identical LTO-electrodes with the parallel-plate symmetrical electrode configuration. The fifth and sixth waves are shown in this figure

from 0 to 5 s and from 5 to 10 s gives almost the same value of 0.15 mAh (3.5 mAh g^{-1} based on LTO), indicating that the variation in the composition is small, i.e., $x=0.5 \pm 0.02$ in $\text{Li}_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$, during the steady-state polarization measurements. As can be seen in Fig. 3, the current shows a linear response to the polarization voltage ranging from -1.0 to $+1.0$ V. The steady-state polarization is obtained by plotting $I(t)$ versus $E(t)$, which is shown in Fig. 4. A linear relation of the current and the applied voltage is clearly seen in Fig. 4. The current (J) as a function of voltage (E) is empirically represented as $J_1 = 7.8 \times E$ (in ampere per gram based on the LTO weight) or $J_2 = 110 \times E$ (in milliamperere per square centimeter), which is

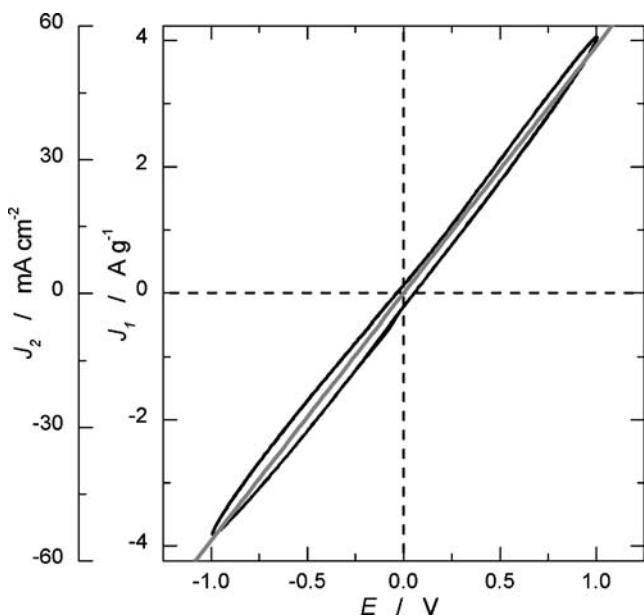


Fig. 4 Steady-state polarization curves obtained for the LTO-electrodes. The curve is approximately linear, so the current (J_1 in ampere per gram or J_2 in milliamperere per square centimeter) and applied voltage (E) relation is empirically represented as $J_1 = 7.8 \times E$ or $J_2 = 110 \times E$

illustrated as the straight line in Fig. 4. According to the polarization equations, the LTO-electrode is capable of high-rate operation, i.e., 0.8 A g^{-1} or 11 mA cm^{-2} at the polarization of 0.10 V, 2.0 A g^{-1} or 28 mA cm^{-2} at the polarization of 0.25 V, etc. The difference in the zero-current voltage in Fig. 4 is 90 mV resulting from the concentration polarization during the charge and discharge of the cell with the parallel-plate symmetrical electrode configuration. By using the Nernst equation, the ratio of the lithium-ion activity in the vicinity of the anode to cathode is calculated to be 5.8 . The hysteresis loop in the J versus E plots suggests a capacitive component. If a parallel resistor-capacitor circuit model was used for the explanation of the hysteresis loop in Fig. 5, the resistance and capacitance are calculated to be $18 \text{ } \Omega \text{ cm}^2$ and 3.83 mF cm^{-2} . Of course, the calculated $18 \text{ } \Omega \text{ cm}^2$ resistance well agrees with the value calculated from the polarization equation. However, a detailed consideration of the concentration polarization in relation to the impedance is not the object of this paper.

In order to determine the resistance polarization of the lithium insertion electrodes, the 0-V lithium-ion battery consisting of identical LAMO-electrodes was fabricated using the same method described above and its polarization was then examined. Figure 5 shows the discharge and charge curves of the 0-V lithium-ion battery. One has a 48.8 -mg LAMO-mix with a 107 - μm thickness and the other has a 48.2 -mg LAMO-mix with a 104 - μm thickness both with 3 - cm^2 electrodes. One LAMO-electrode was prepared by charging the lithium cell to 4.5 V at 0.17 mA cm^{-2} then held

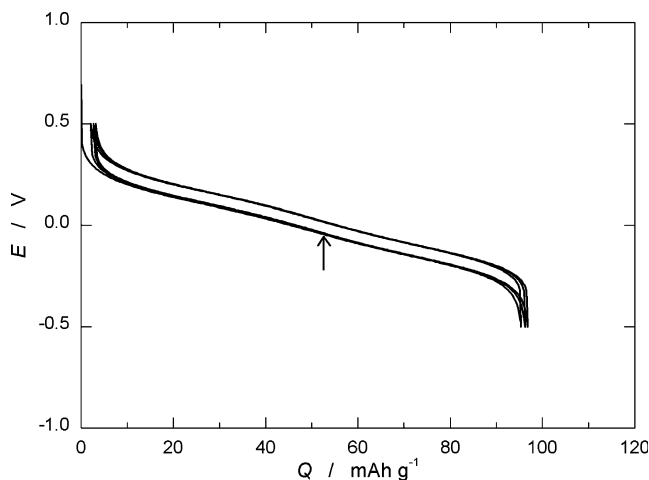


Fig. 5 Discharge and charge curves of the lithium-ion cell prepared by combining the oxidized and reduced forms of the LAMO-electrodes. One contains a 48.8 -mg LAMO-mix with a 107 - μm thickness and the other contains a 48.2 -mg LAMO-mix with a 104 - μm thickness, both 3 - cm^2 electrodes. The cell was cycled at 0.33 mA cm^{-2} in the voltage range of -0.5 to 0.5 V. After three cycles, the cell was discharged to 0 V marked by the arrow at which the polarization measurements were carried out

at 4.5 V for 12 h, and the other was prepared by discharging the cell to 3.0 V then kept at that voltage for 12 h. One is then used as the positive electrode and the other is used as the negative electrode in a fresh cell. The open-circuit voltage of the cell was 0.692 V. After one cycle, the discharge and charge curves reached steady state with respect to their shapes. The difference in the discharge and charge curves in Figs. 2 and 5 is due to the reversible voltage profiles as a function of the SOC. The LAMO-electrode shows the SOC-dependent voltage curve while the reversible voltage of the LTO-electrode is independent of the SOC [5, 12]. Because of this, the understanding of the charge and discharge curve in Fig. 5 is complicated when it is compared to that in Fig. 2. At 0 V in Fig. 5, the sinusoidal voltage with the peak amplitude of 1.0 V was imposed on the 0-V lithium-ion battery. This result is shown in Fig. 6. The general observations are the same as those for the LTO-electrodes. The difference is the degree of the current response to the applied voltage. This is better illustrated in Fig. 7. The current (J) and the applied voltage (E) for the LAMO-electrodes is linear, i.e., $J_1=3.8\times E$ (in ampere per gram) or $J_2=54\times E$ (milliampere per square centimeter), which is illustrated as the straight line in Fig. 7. In other words, the LAMO-electrode also only shows a resistance polarization.

As clearly seen in Figs. 4 and 7, the lithium insertion electrodes of the LTO and LAMO only show a resistance polarization. “Chemical” polarization, such as a nonlinear current response to the applied voltage, is not observed for both the LTO- and LAMO-electrodes. Because of this, polarization of the lithium-ion battery consisting of the LTO and LAMO is easily estimated from the empirically obtained polarization equations. By assuming the same weight of the positive and negative electrodes, the polarization equation for the lithium-ion battery is calculated to be $2.56\times(E-E_{\text{rev}})$ in ampere per gram by using the

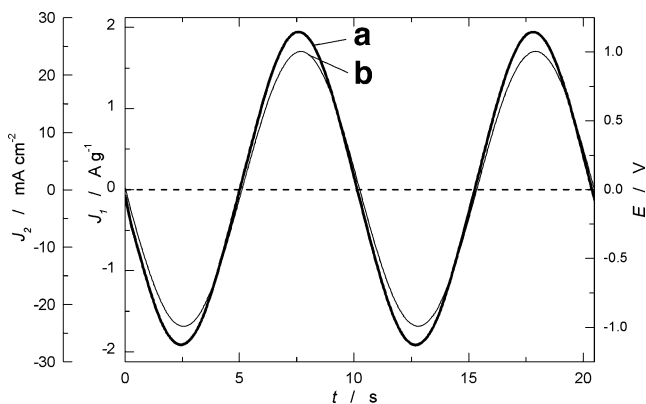


Fig. 6 Observed current (a) and the voltage (b) applied to the 0-V lithium-ion cell consisting of the identical LAMO-electrodes with the parallel-plate symmetrical electrode configuration. The fifth and sixth waves are shown in this figure

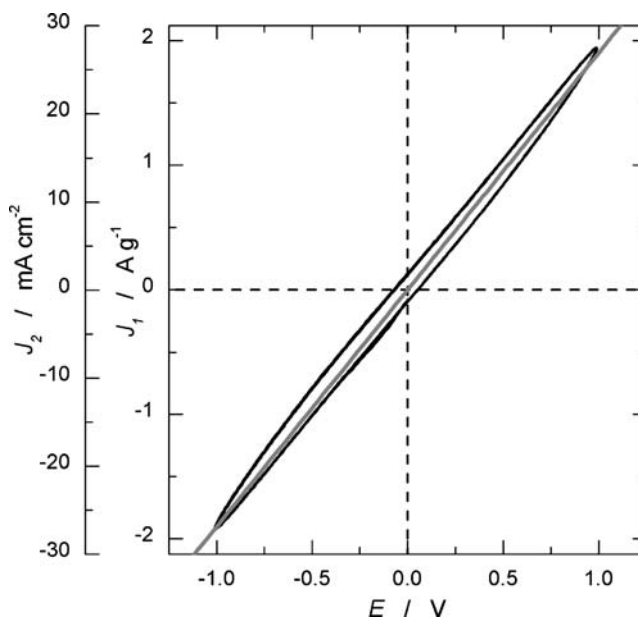


Fig. 7 Steady-state polarization curves obtained for the LAMO-electrodes. The curve is approximately linear, so that the current (J_1 in ampere per gram or J_2 in milliampere per square centimeter) is represented as a function of the applied voltage (E), i.e., $J_1=3.8\times E$ or $J_2=54\times E$ (see the text)

polarization equations of $J_1=3.8\times E_{\text{LAMO}}$ and $J_1=7.8\times E_{\text{LTO}}$ in ampere per gram for the LAMO- and LTO-electrodes, respectively. E_{rev} is the reversible voltage of the lithium-ion battery. The value of $2.56\ \Omega^{-1}\ \text{g}^{-1}$ is obtained by calculating $3.8\times 7.8/(3.8+7.8)$ or $7.8\times 3.8/(3.8+7.8)$. The current J_2 in milliampere per square centimeter as a function of the terminal voltage (E) is also calculated to be $J_2=36.2\times(E-E_{\text{rev}})$, in which the value of $36.2\ \text{k}\Omega^{-1}\ \text{cm}^{-2}$ is obtained by calculating $54\times 110/(54+110)$ or $110\times 54/(54+110)$.

In order to confirm the effective use of the polarization data in Figs. 4 and 7, the 2.5-V lithium-ion battery consisting of the LTO and LAMO is fabricated and its polarization is examined. Figure 8 shows the charge and discharge curves of the LTO/LAMO cell operated at the rate of $0.33\ \text{mA}\ \text{cm}^{-2}$ in voltages of 1 to 3 V. The positive and negative electrodes had the same weight in order to utilize the same current scale in ampere per gram, so that the material balance between the positive and negative electrodes is deviated from the optimum value. The positive electrode has a 47.3-mg LAMO-mix with a 97- μm thickness and the negative electrode has a 47.6-mg LTO-mix with a 132- μm thickness. Both are 3- cm^2 electrodes. The battery capacity is limited by the positive-electrode capacity. After three cycles, the battery was charged to half the capacity (marked by arrow in Fig. 8), and then the sinusoidal voltage with the peak amplitude of 1.0 V was imposed on the 2.5-V lithium-ion battery. These results are shown in Figs. 9 and 10. The steady-state polarization has a slight concave shape, but it is approximately linear as is

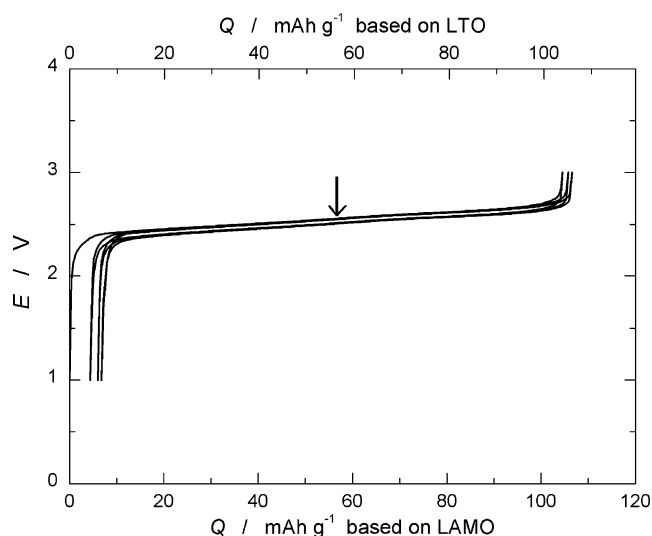


Fig. 8 Charge and discharge curves of the 2.5-V lithium-ion battery consisting of the LTO and LAMO. The cell was operated at 0.33 mA cm^{-2} in the voltage range of 1.0 to 3.0 V. The positive electrode contains a 47.3-mg LAMO-mix with a $97\text{-}\mu\text{m}$ thickness and the negative electrode contains a 47.6-mg LTO-mix with a $132\text{-}\mu\text{m}$ thickness. After three cycles, the cell was charged to the point marked by arrow and then the polarization measurements were carried out at this point

illustrated by two lines in Fig. 10. This may be due to the shift in the reversible voltage of the LAMO-electrode during the polarization measurements. The current in ampere per gram or milliamperere per square centimeter is approximately represented by the equations $J_1 = 2.8 \times (E - 2.571)$ in ampere per gram based on the active material weight and $J_2 = 38 \times (E - 2.571)$ in milliamperere per square centimeter, in which 2.571 V was determined from the midpoint voltage between the zero-current voltages in Fig. 10. The positive and negative signs of the current in

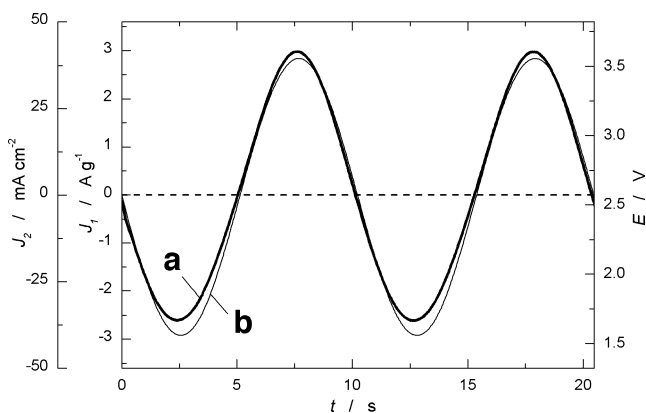


Fig. 9 Observed current (a) and the voltage (b) applied to the 2.5-V lithium-ion batteries consisting of the LTO and LAMO. A sinusoidal voltage of 1.0 V at 0.1 Hz was superimposed on the open-circuit voltage of 2.571 V using a potentiostat. The fifth and sixth waves are shown in this figure

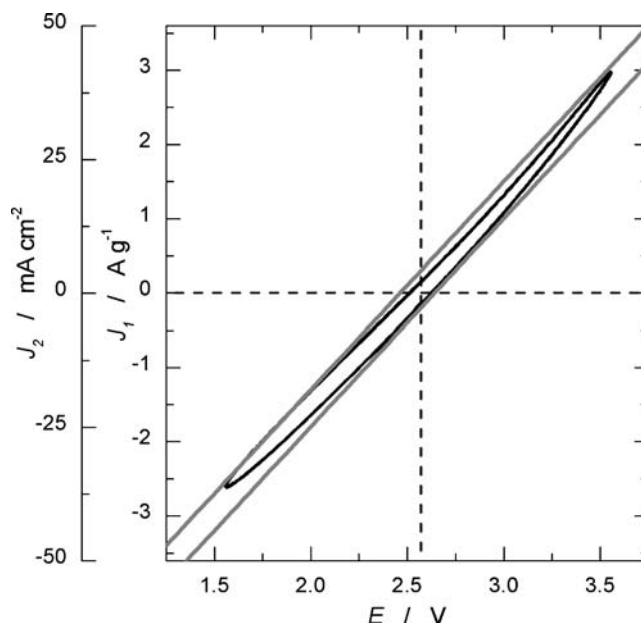


Fig. 10 Steady-state polarization curves obtained for the 2.5 V lithium-ion battery consisting of the LTO and LAMO. The curve is approximately linear, so that the current (J_1 in ampere per gram or J_2 in milliamperere per square centimeter) is represented as a function of applied voltage (E), i.e., $J_1 = 2.8 \times (E - 2.571)$ or $J_2 = 38 \times (E - 2.571)$

Figs. 9 and 10 indicate the charge and discharge, respectively, for the 2.5-V lithium-ion battery. The observed values of $2.8 \Omega^{-1} \text{ g}^{-1}$ and $38 \text{ k}\Omega^{-1} \text{ cm}^{-2}$ agree well with those of the calculated values, i.e., $2.56 \Omega^{-1} \text{ g}^{-1}$ and $36.2 \text{ k}\Omega^{-1} \text{ cm}^{-2}$, respectively. This clearly indicates that the polarization data obtained using the 0-V lithium-ion battery with the parallel-plate symmetrical electrode configuration are accurate and correct although the resistance polarization includes the ohmic voltage drop.

Concluding remarks

In this paper, we have reported the steady-state polarization measurements of lithium insertion electrodes. The lithium insertion electrodes, specifically the LTO and LAMO, only show a resistance polarization. “Chemical” polarization due to “activation” processes is not observed for the LTO- and LAMO-electrodes. We believe that the “chemical” polarization characteristic of the lithium insertion electrodes participated in the electrode processes for storing and delivering electricity in the batteries. However, the ohmic voltage drop is superimposed in the “chemical” polarization, and the elimination of the ohmic voltage drop is difficult mainly due to the porous nature of the electrodes separated by a thin electrolyte film with a separator. Charge carriers are electrons and lithium ions in the lithium insertion electrodes. Electron transfer is faster than the lithium-ion transfer, so that the lithium-ion transfer at the

phase boundary between the liquid and solid should be an “activation” process which may follow the logarithmic law of the type $J \propto \exp(\Delta U/\delta)$ in which ΔU = potential drop across the layer with the thickness δ . To detect such an activation process, improvements in the electrode, its configuration, and cell assembly are necessary for minimizing the ohmic voltage drop within the electrolyte.

Because lithium insertion electrodes only presently show a resistance polarization, the internal resistance of a lithium-ion battery is still effective when considering the battery power and power-dissipation-generated heat, as were already discussed for the lead-acid batteries by Vinal in 1954 [13]. In order to reduce the internal resistance and then safely increase the battery power, polarization studies of the lithium insertion electrodes are extremely important in both basic electrochemical science and applied technology. Such polarization studies including cell design of the three-electrode configuration are now in progress in our laboratory.

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