Ionic to mixed ionic/electronic conduction transition of chemically lithiated Li$_{0.33}$La$_{0.56}$TiO$_3$ at room temperature: Lithium-ion-motion dependent electron hopping

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The interfacial instability of metallic lithium and cation-vacant lithium lanthanum titanate results in the presence of Ti$^{3+}$ donors and an increased number of Li$^+$ ions at the Li$_{0.33}$La$_{0.56}$TiO$_3$ side. It is clarified that the intercalated Li$^+$ ion and the Ti-site electron are favorable to form a coupled Li$^+$/e$^-$ state to maintain the lowest electrostatic potential energy. Through the motion of these states, the interfacial instability is reflected in the electrical transition of Li$_{0.33}$La$_{0.56}$TiO$_3$, in which the change of bulk electronic conduction from an insulator to a $n$-type semiconductor is determined by the lithium-ion-motion dependent electron hopping. © 2006 American Institute of Physics. [DOI: 10.1063/1.2220480]

Solid compounds with high Li$^+$ conductivity are of considerable interest for applications in all-solid-state lithium batteries. Among Li$^+$ crystalline conductors, (Li$_3$La$_2$/Ti$^{4+}$)$_{1/3}$TiO$_3$ oxide (V: vacancy) with perovskite of the type ABO$_3$, regarded as a three-dimensional framework where the vertex-sharing BO$_6$ octahedra construct the structure and A ions are placed in 12-coordinate sites in the cubic lattice, have a higher grain ionic conductivity of ca. 10$^{-5}$ S/cm, found at 3x (Li$^+$ content)=ca. 0.3 at 27 °C. $^{2-4}$

The high conductivity is associated with the presence of A-site vacancies and a lot of equivalent sites for Li$^+$ ions to occupy and move freely in the A-site space. $^{4}$

When an ionic conductor is used as a solid electrolyte, the important parameter of electrolytic stability should be considered with regard to its electrochemical $^{5,6}$ and chemical aspects. Nevertheless, there have been few systematic investigations of the following: (i) interfacial instability between the solid electrolyte and the metallic lithium anode in all-solid-state lithium batteries and (ii) this instability’s effect on the electrical properties of an ionic conductor. Recently, we have studied the room temperature (RT) interfacial instability between 11% A-site vacant (Li$_{0.33}$La$_{0.56}$V$_{0.11}$TiO$_3$ and metallic lithium by using x-ray photoelectron spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS). The instability includes the lithium activated alternation of the Ti electronic structure from tetravalent state and the local electric field induced oxidized-Li$^+$ insertion into the A-site vacancies. The former alternation results in the discoloration of the sample from ivory to black and the existence of mixed Ti$^{3+}$/Ti$^{4+}$ states, similar to the result of the Ti$^{3+}$ donor doping into Li$_{0.33}$La$_{0.56}$Ti$_{1/3}$O$_2$. The latter insertion leads to an increased number of L$^+$ ions per unit volume of sample. The interfacial chemical lithiation is expected to affect the original electrical properties of Li$_{0.33}$La$_{0.56}$TiO$_3$.

The aim of the present study is to clarify the physical effects of the inserted Li$^+$ ions and the external Ti-site electrons (Ti$^{3+}$/e$^-$/Ti$^{4+}$) on the electrical transition of the RT chemically lithiated Li$_{0.33}$La$_{0.56}$TiO$_3$ from the ionic to the mixed ionic/electronic conduction, which will be further described by a simple phenomenological model.

The 11% La$^{3+}$/Li$^+$-site vacant (Li$_{0.33}$La$_{0.56}$V$_{0.11}$)TiO$_3$ powder was prepared using a solid-state reaction method. The stoichiometric mixture of La$_2$O$_3$, Li$_2$CO$_3$, and TiO$_2$ powders was calcined at 1100 °C for 12 h in air. The samples were sintered at 1250 °C for 8 h in air. The size of the sample was 9.73 mm in diameter and 4.45 mm in thickness. The molar ratio of the metals was analyzed by an inductively coupled plasma-mass spectrometer (ICP-MS). ICP-MS chemical analysis showed that the molar ratio of cations corresponded to the formula Li$_{3.24(10.0)}$La$_{0.57(0.01)}$Ti$_{0.34(3)0.01}$O$_{3.30(6)}$ which almost agrees with Li$_{0.33}$La$_{0.56}$TiO$_3$. Moreover, the crystallographic parameters of Li$_{0.33}$La$_{0.56}$TiO$_3$ were analyzed to be a=3.8751 Å and c=7.7530 Å.

The electrical conduction of the Li$_{0.33}$La$_{0.56}$TiO$_3$ was investigated by the alternating current (ac) impedance analysis (model: 1255B/1287, Solartron) and direct current (dc) digital multimeter (DMM; model: 34970A/34901A, Agilent). Using the DMM and metallic lithium electrodes, the effect of the mixed Ti$^{3+}$/Ti$^{4+}$ states on the electronic conductivity and the roles of the external electrons and the inserted Li$^+$ ions on the electrical transition were determined.

For a polycrystalline Li$^+$ ion conductor, the resistance of ionic conduction is contributed by the grains and grain boundaries of its microstructure. $^{4,7}$ Prior to reaction with lithium, the grain boundaries contribute to the bulk resistance of the Li$_{0.33}$La$_{0.56}$TiO$_3$ sample to a greater degree than does the grain and, thus, the total ionic conductivity (1.86×10$^{-5}$ S/cm) is lower than the known grain ionic conductivity (ca. 10$^{-3}$ S/cm). After the reaction with metallic lithium for 24 h, the ac impedance analysis shows that the total ionic conductivity increases from 1.86×10$^{-3}$ to 5.42×10$^{-3}$ S/cm due to the Li$^+$ insertion.

After the reaction with metallic lithium, the electrical conductivity of Li$_{0.33}$La$_{0.56}$TiO$_3$ is drastically changed from ca. 10$^{-5}$ to ca. 10$^{-1}$ S/cm, ascribed to the enhancement of electronic conduction. Inaguma et al. $^{7}$ have reported the electronic conductivity of Li$_{3}$La$_{2/3}$TiO$_3$ as $\sigma_e$<1×10$^{-5}$ S/cm at 27 °C. The electronic conductivity of...
Li_{0.33}La_{0.56}TiO_{3}, therefore, rises from ca. \(10^{-8}\) to ca. \(10^{-1}\) S/cm due to the presence of the Ti^{3+} donors. In the beginning, Ti^{3+} ions are observed at the Li/Li_{0.33}La_{0.56}TiO_{3} interface, but then the bulk conductivity is altered, which includes a spontaneous electronic transition without directly depending on the interfacial instability. It is suggested that the external Ti-site electrons from the interfacial instability are not localized at interfacial Ti sites, and the intervalence electron hopping occurs between the Ti^{3+} and Ti^{4+} states. Subsequently, the Li_{0.33}La_{0.56}TiO_{3} is changed from an electronic insulator to a n-type semiconductor. This kind of electronic conduction in oxides with mixed-valence transition metal ions is classified as hopping transport.

Prior to exploring the physical nature of the spontaneous electrical transition, we consider the static state of the inserted Li^{+} ions and the external Ti-site electrons (\(e'\)) as illustrated in Fig. 1(a). The bulk is thought to maintain the charge neutrality. The states of the inserted Li^{+} ion and the external Ti-site electron can be regarded as two charged particles, existing in the charge-neutral environment. Based on the concepts of classical physics, there is an electrostatic force of attraction between the positive charge and the negative charge; therefore, the distance between the charged particles is expected to close in order to maintain the lowest electric potential energy. In the perovskite-type Li_{0.33}La_{0.56}TiO_{3}, the ideal shortest distance is pointed out in the classical-physics-expected model as shown in Fig. 1(a), which also indicates that the inserted Li^{+} ion and the external electron favorably form a dipolelike state in the crystal.

The occurrence of the spontaneous electrical transition should originate from the motion of the dipolelike states. We can perhaps become aware of the driving force which results in this motion. As mentioned above, the inserted Li^{+} ions and the external Ti-site electrons come from the interfacial instability so that their concentrations are the highest at the Li/Li_{0.33}La_{0.56}TiO_{3} interface. Such a concentration gradient implies that a chemical potential drives these charged particles to diffuse. However, from their diffusion phenomena we cannot easily understand the dependence of the inserted Li^{+} ions and the Ti-site electrons. Here, by using the DMM to apply a small driving force, it is relatively easy to observe the nonstatic state to further clarify the dependence. According to the studies of Inaguma et al., the activation energy of Li^{+} motion (\(E_{a,i}=ca. 0.3\) eV) is larger than that of electron hopping (\(E_{a,e}=ca. 0.07\) eV). Consequently, it is expected that the external Ti-site electrons will be dragged by the inserted Li^{+} ions when a small electric field or current is applied, as shown in Fig. 1(b).

Experimentally, the apparatus, shown in Fig. 2(a), uses the metallic lithium electrodes and a DMM to observe the change of the specimen discoloration which is attributed to the presence of trivalent Ti^{3+} states. Although the interfacial instability takes place at both the Li/Li_{0.33}La_{0.56}TiO_{3} interfaces, the discolored zone only expands from one lithium electrode to the other, as indicated by the arrow of discoloration direction. Moreover, the Li^{+} ions move along the reverse direction of the DMM electron current. As a result, the expansion of the discolored zone not only reemphasizes that the external Ti-site electrons can hop between the Ti^{3+} and Ti^{4+} states, but also indicates that the discoloration direction, showing where the electrons hop, strongly depends on the Li^{+} motion in Li_{0.33}La_{0.56}TiO_{3}. This phenomenon demonstrates the condition of the nonstatic state, in which the intervalence hopping electrons are dragged by the inserted Li^{+} ions, as shown in Fig. 1(b). Furthermore, the local charge neutralization effect to reduce the electrostatic interaction in crystal is supported in this process. Such a phenomenological model indicates that the behavior of the electrons is a lithium-ion-motion dependent electron hopping process.

Since the dependence of the inserted Li^{+} ions and the external electrons has been proven, a simple, time-dependent diffusion phenomenon can perhaps become aware of the driving force which results in the spontaneous electrical transition.
independent, and generalized description about the electrical transition of the chemically lithiated \( \text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 \) can be established in accordance with the above phenomenological model, which rules out the kinetics of the interface reaction and the diffusion effect. It is known that the discolored and undiscolored zones have different electrical properties as a result of the presence of the \( \text{Ti}^{3+} \) donors and the increased number of the \( \text{Li}^+ \) ions in the discolored zone.

For electronic conduction [Fig. 2(b)], the variation of total electronic conductivity with the expanding distance \( x \) of the discolored zone is derived by using the following assumptions: (1) The sample dimensions are thickness \( t \) and cross-section area \( A \), (2) the electronic conductivities of the discolored and undiscolored zones are \( \sigma_{\text{ea}} \) and \( \sigma_{\text{eb}} \), respectively, and (3) the distribution of \( \text{Ti}^{3+} \) ions is uniform in the discolored zone. In a dc measuring system, the circuit is simplified to consider only resistance as the effective current-flow element. The discolored and undiscolored zones can be thought of as the serial combination of two electronic resistors [Fig. 2(b)]. Using the well-known equation of \( R=(1/\sigma)(L/A) \), where \( R \) is the resistance, \( \sigma \) is the conductivity, \( L \) is the sample thickness, and \( A \) is the cross-section area, the total electronic resistance \( (R_{\text{e},t}) \) is expressed as

\[
R_{\text{e},t} = \frac{\sigma_{\text{eb}}}{\sigma_{\text{eb}} + \sigma_{\text{ea}}} = \frac{1}{\sigma_{\text{eb}} A} \frac{L - x}{\sigma_{\text{eb}} A} + \frac{1}{\sigma_{\text{ea}} A},
\]

where \( \sigma_{\text{eb}} \) is the electronic resistance of the undiscolored zone, \( \sigma_{\text{ea}} \) is the electronic resistance of the discolored zone, and \( \sigma \) is the total electronic conductivity. The relation of total electronic conductivity \( (\sigma_e) \) and variable \( (x) \) is derived as

\[
\sigma_e = \frac{\sigma_{\text{eb}}}{[(\sigma_{\text{eb}} - \sigma_{\text{ea}})/\sigma_{\text{ea}}] x(1/L)} + 1,
\]

where \( 0 \leq x \leq L \). We assume \( p \) \( (\text{length factor})=(x/L) \), where \( 0 \leq p \leq 1 \).

Similarly, for \( \text{Li}^+ \) conduction [Fig. 2(c)], the relation of total ionic conductivity \( (\sigma_i) \) and length factor \( (p) \) is derived as

\[
\sigma_i = \frac{\sigma_{\text{ib}}}{[(\sigma_{\text{ib}} - \sigma_{\text{ia}})/\sigma_{\text{ia}}] p + 1},
\]

where the ionic conductivities of discolored and undiscolored zones are \( \sigma_{\text{ia}} \) and \( \sigma_{\text{ib}} \), respectively.

The total electrical conductivity \( (\sigma_t) \) is expressed as follows:

\[
\sigma_t = \sigma_e + \sigma_i = \frac{\sigma_{\text{eb}}}{[(\sigma_{\text{eb}} - \sigma_{\text{ea}})/\sigma_{\text{ea}}] p + 1} + \frac{\sigma_{\text{ib}}}{[(\sigma_{\text{ib}} - \sigma_{\text{ia}})/\sigma_{\text{ia}}] p + 1}.
\]

A visualized result of Eq. (4), calculated using the approximate figures of \( \sigma_{\text{ea}}=10^{-8} \), \( \sigma_{\text{eb}}=10^{-1} \), \( \sigma_{\text{ib}}=10^{-5} \), and \( \sigma_{\text{ia}}=10^{-4} \) S/cm, is shown in Fig. 3, indicating the electrical transition that the electrical conductivity slightly rises from \( 10^{-5} \) \( (\sigma_{\text{ib}}) \) to \( 10^{-4} \) S/cm \( (\sigma_{\text{ib}}) \) with the expansion of the discolored zone, and a drastic change from the ionic conductivity of \( 10^{-4} \) S/cm \( (\sigma_{\text{ia}}) \) to the electronic conductivity of \( 10^{-1} \) S/cm \( (\sigma_{\text{ea}}) \) occurs at \( p=1 \) \( (x=L) \). Hence, the transition can be divided into \( \text{Li}^+ \) conduction and electronic conduction, which is determined by the interface position \( p \) between the discolored/undiscolored zones as well as by the electron hopping distance. Through the motion of the coupled \( \text{Li}^+/e^- \) states, \( \text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 \) is altered from an electronic insulator to a \( n \)-type semiconductor at \( p=1 \), due to the presence of \( \text{Ti}^{3+} \) donors, and the \( \text{Li}^+ \) insertion is reflected in the change of ionic conductivity in \( 0<p<1 \).

In summary, the inserted \( \text{Li}^+ \) ions and the external \( \text{Ti} \)-site electrons, originating from the chemical instability between \( \text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 \) and metallic lithium, are favorable to form a dipolelike state of the coupled \( \text{Li}^+/e^- \) due to the electrostatic force. When a driving force appears, these states are gradually dispersed so that a spontaneous electrical transition occurs. As a result of different activation energies of the \( \text{Li}^+ \) motion and the electron hopping, the external \( \text{Ti} \)-site electrons are dragged by the inserted \( \text{Li}^+ \) ions during the alternation process. Through the motion of the dipolelike states, the interfacial instability is reflected in this electrical transition. The simple phenomenological model describes that initially the total electrical conductivity of the polycrystalline \( \text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_3 \) rises from \( 1.86 \times 10^{-5} \) to \( 5.42 \times 10^{-5} \) S/cm due to the \( \text{Li}^+ \) insertion, and then a drastic change from ionic conductivity to electronic conductivity of ca. \( 10^{-1} \) S/cm takes place due to the intervalence-hopping electrons completely occupying the bulk sample. Hence the lithium-ion-motion dependent electron hopping determines the alternation from an electronic insulator to a \( n \)-type semiconductor.

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