

FULL PAPER

Thickly and densely sintered $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ electrodes for the anode of Li-ion batteries

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Thickly and densely sintered electrodes (TDSE) consisting of active materials can achieve highly capacitive Li-ion batteries and are one of the ideal electrode structures applicable for co-sintered-type solid-state batteries based on oxide-based solid electrolytes. This study focused on $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) as the TDSE for the anode. LLTO exhibits high Li-ion conductivity and a high capacity of 225 mAh g^{-1} with an operation potential below 1 V (vs. Li^+/Li). However, the electronic conductivity of LLTO is low (less than $10^{-8} \text{ S cm}^{-1}$), and the improved electronic conductivity seems necessary. In this paper, we investigated the electrochemical properties of LLTO sintered electrodes and improved the electronic conductivity of LLTO by Mn substitution for the Ti site. LLTO shows a huge overpotential during initial Li insertion due to low electronic conductivity of $1.1 \times 10^{-9} \text{ S cm}^{-1}$, resulting in extremely low capacity. On the other hand, Mn substitution enhances the electronic conductivity, resulting in improved first-cycle charging properties.

Key-words : Li-ion batteries, Thickly and densely sintered electrodes (TDSE), $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$

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1. Introduction

Lithium-ion batteries (LIBs) are widely used as an electric power source with high capacity and high output density, making it possible for us to use mobile electronic devices such as laptops and mobile phones. Moreover, with growing environmental concerns and a push towards a carbon-neutral society, LIBs have increasingly been adopted for electric vehicles and stationary energy storage systems. Thus, LIBs require higher capacity and energy density. Since the capacity of electrodes depends on the loading amount of active material in electrodes, various strategies have been underway. One approach to increase the amount of active material is to increase the thickness of the electrode. In this approach, methods such as electrodes using conductive agent/binder composite,¹⁾ designing bi-layer electrodes using finite elements method and machine learning,²⁾ introduction of foam current collectors to shorten the electronic conduction path,^{3,4)} electrodes made by 3D printing⁵⁾, composite electrodes using active materials and solid electrolytes,⁶⁾ electrode preparation by dry electrode coating process⁷⁾ and phase-inversion method⁸⁾ have been investigated.

Another approach involves an increase in the volume ratio of active material in the electrode, which has also been underway. Park et al. reported an all-in-one multi-layered

cathodes-separator-anode monolith architecture for ultra-thin flexible batteries, which achieved a high capacity of 44.5 mAh using the pouch cell with the thickness less than 1 mm .⁹⁾ In general, electrodes consist not only of active material but also of binders and conductive additives, which limit the volume ratio of active material in the electrode. Thickly and densely sintered electrodes (TDSEs) made by sintering only active material were proposed to overcome this limitation.¹⁰⁾ Since TDSEs are composed solely of active material, TDSEs can achieve high capacity. Additionally, TDSEs are produced by a high-temperature sintering process. Accordingly, TDSEs are a suitable electrode structure for co-sintered type solid-state batteries^{11–14)} based on oxide solid electrolytes such as garnet family^{15–17)} and perovskite family.^{18–20)}

The essential design for realizing TDSEs is a control of the mixed Li-ionic and electronic conductivity of the active materials because TDSE contains no conductive additives. Recently, we have demonstrated that Li-ion conductivity through LiCoO_2 TDSE is crucial for improving the capacity.²¹⁾ For instance, in the case of LiCoO_2 TDSE with $180 \mu\text{m}$ in thickness and 96 % relative density, Li-ion conductivity of more than $10^{-5} \text{ S cm}^{-1}$ is needed to achieve the theoretical capacity.

This paper focuses on $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO),¹⁸⁾ which exhibits a high bulk Li-ion conductivity of $10^{-3} \text{ S cm}^{-1}$, as TDSE for anode. LLTO has a perovskite structure and has been investigated as a candidate for oxide-based solid electrolytes due to its high Li-ion conductivity.^{22,23)} Re-

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cently, some studies have demonstrated that LLTO works as an active material.^{24,25)} Lu et al. reported that electrodes using LLTO powder achieved a high capacity of 225 mAh g⁻¹ and low operating potential under 1 V (vs. Li⁺/Li).²⁵⁾ Moreover, the authors also reported a high capability of nearly 100 mAh g⁻¹ at 10C and superior capacity retention of 79 % over 3000 cycles. Compared with Li₄Ti₅O₁₂ (LTO),²⁶⁾ LLTO exhibits higher capacity, lower operating voltage, and higher Li-ion conductivity, which is expected to be a promising anode material for TDSE. However, to our knowledge, LLTO TDSE has not been reported yet, and the explicit material design has not been established.

Regarding Li-ion conduction, LLTO is an excellent material, but its electronic conductivity is extremely low (less than 10⁻⁸ S cm⁻¹). Commonly, LLTO becomes an electronic conductor when it contacts Li metal due to the reduction of Ti⁴⁺ to Ti³⁺.¹⁸⁾ This means that Li insertion into LLTO causes electronic conduction. In other words, at the initial stage of the Li insertion reaction, the reaction site should be limited around the current collector due to the low electronic conduction of LLTO. Thus, in the case of LLTO TDSE, controlling electronic conduction through LLTO seems key for improving the initial Li insertion reaction.

In this paper, we first reveal the charge–discharge property for LLTO TDSE as the anode for LIBs. Then, we demonstrate the effect of Mn substitution for the Ti site, which has been reported as an efficient method to improve the electronic conductivity,²⁷⁾ for LLTO on the charge–discharge properties.

2. Experimental

2.1 Material preparation

Li_{0.33}La_{0.557}TiO₃ ($x = 0.11$ in Li_{3x}La_{2/3-x}TiO₃) and Li_{0.33}La_{0.557+1/3x}Ti_{1-x}Mn_xO₃ ($x = 0-0.075$) were synthesized by solid-state reaction. Lithium carbonate (Li₂CO₃, 99.99 %, Rara metallic Co., Japan), Titanium oxide (TiO₂, 99.8 %, Sigma-Aldrich Co., U.S.) and Lanthanum(III) hydroxide [La(OH)₃, 99.9 %, Sigma-Aldrich Co., U.S.], manganese oxide(IV) (MnO₂, 99.5 %, Wako Co., Japan) were used. Starting materials were weighted to obtain the desired composition and mixed using a planetary ball mill at 450 rpm for 15 h with isopropanol as the solvent. After ball milling, the solvent was evaporated to dryness, and the mixture was grounded with a mortar. The obtained precursor was calcinated at 800 °C for 4 h. The calcined powder was grounded, press-formed into a disk shape, and pressed again by cold isostatic pressing. The obtained disks were sintered at 1100 °C for 15 h. While sintering, the disks were covered with calcined powder to prevent contamination of other elements and evaporation of Li during sintering. Table S1 shows the relative density of LLTO and Mn-substituted LLTOs. All samples were densified well.

2.2 Material characterization

The crystal structure of sintered disks was evaluated by X-ray diffraction (XRD: MiniFlex600, RIGAKU, Japan)

with Cu K α as an X-ray source. Structural parameters were calculated by Rietveld refinement using PDXL2 (RIGAKU, Japan). Microstructure observation was conducted using a scanning transmission electron microscope (JCM-7000, JEOL Ltd., Japan).

2.3 Electrochemical property

The electronic and Li-ionic conductivities for the sintered samples were evaluated by the DC polarization method and AC impedance spectroscopy, respectively. First, to remove the as-sintered surface and adjust the thickness, the sintered disk was polished up to about 480 μ m in thickness with lapping film sheets (#320–#16000, 3M, U.S.). After polishing, the Ag electrode was deposited on both sides of the polished disk via sputtering. Then, samples were set in the hand-made cell shown in Fig. S1(a) in the Ar-filled groove box. DC polarization measurement was performed using squidstatTM Plus (Admiral Instruments, U.S.) with galvanostatic mode. AC impedance spectroscopy was conducted using VSP-300 (Biologic, France) with an amplitude of 10 mV and a frequency range of 7 MHz to 1 Hz.

The electrode performance of Li_{0.33}La_{0.557}TiO₃ TDSE for an anode of LIBs was evaluated using a half-cell with the liquid electrolyte and Li metal as a reference electrode. First, LLTO TDSE was polished up to 180 μ m, and the Pt current collector was sputtered on one side of the disk. Then, samples were transferred to an Ar-filled groove box. Then, the half-cell shown in Fig. S1(b) was assembled. The charge–discharge performance of the half-cell was evaluated by galvanostatic charging–discharging with a constant current at 0.019C using HJ1001SD8 (Hokuto Denko Co., Ltd., Japan). The theoretical capacity was calculated based on previous research, which reported that Li is inserted into O4 square window sites located between Li-Li atoms,²¹⁾ resulting in 323 mAh g⁻¹. The upper and lower cut-off voltages were set at 3.0 and 0 V (vs. Li⁺/Li).

3. Results and discussion

3.1 LLTO TDSE

First, the crystal structure and microstructure were characterized to confirm the quality of the fabricated LLTO. **Figure 1(a)** shows the XRD pattern of Li_{0.33}La_{0.557}TiO₃ after sintering. All diffraction peaks can be assigned to tetragonal Li_{0.33}La_{0.557}TiO₃ with space group P4/mmm. However, the SEM-EDS mapping shown in Fig. 1(b) suggests a small amount of Ti aggregation. Jonderian et al. reported that obtaining the pure LLTO phase is too difficult, and impurity phases such as TiO₂ and Li₂Ti₃O₇ always coexist. Therefore, the obtained LLTO is suitable for TDSE in terms of crystal structure and microstructure.

Figure 2(a) shows the Nyquist plot of Li_{0.33}La_{0.557}TiO₃ at 25 °C. There are two typical semicircles in the frequency range from 7 MHz to 300 Hz. The equivalent circuit shown in Fig. 2(a) was used to estimate three resistance components: R_1 , R_2 , and R_3 . R_1 , R_2 , and R_3 are assigned to the bulk, grain boundary, and interfacial resistance. The estimated bulk Li-ion conductivity was 1.0×10^{-3} S cm⁻¹, two orders of magnitude greater than the grain boundary of

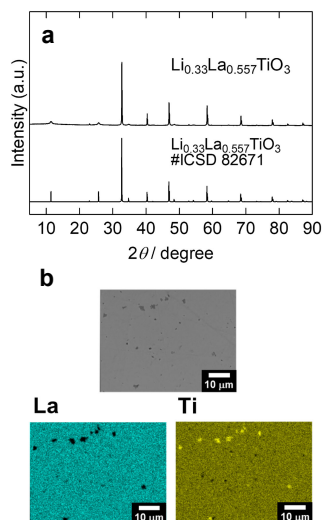


Fig. 1. (a) XRD pattern of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$. (b) SEM image of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ sintered disk and elemental mappings of La and Ti.

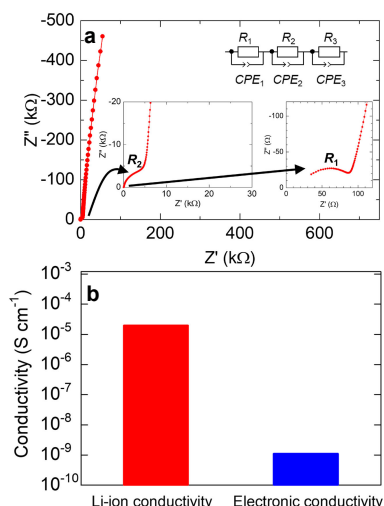


Fig. 2. (a) The complex impedance spectra of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ sintered disk and an equivalent circuit for fitting. (b) Electron conductivity and Li-ion conductivity of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ sintered disk.

$2.0 \times 10^{-5} \text{ S cm}^{-1}$. Figure 2(b) shows the total Li-ion and electronic conductivity of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$. The obtained electronic conductivity of $1.1 \times 10^{-9} \text{ S cm}^{-1}$ was much lower than the total Li-ion conductivity of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ of $1.9 \times 10^{-5} \text{ S cm}^{-1}$. The obtained values are comparable with those previously reported.¹⁹⁾

Figure 3(a) shows charge–discharge curves of the half-cell using $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ TDSE at 0.53 mA cm^{-2} . The diameter of the LLTO sintered disk used in the charging/discharging test in Fig. 3(a) was 7.78 mm. At the first charging, a huge overpotential was observed, and the capacity gradually increased with an increase in the cycle number. After charge–discharge test, the formation of cracks was observed, indicating that the penetration of the liquid electrolyte through cracks may enhance the capacity

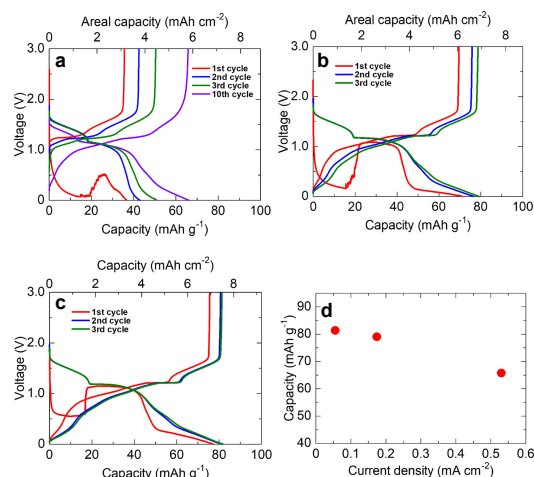


Fig. 3. The charge–discharge curves for sintered disks of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ sintered disk at (a) 0.53 mA cm^{-2} , (b) 0.17 mA cm^{-2} , (c) 0.06 mA cm^{-2} . (d) Correlation between current density and areal capacity.

as the cycle number increased. However, the capacity at the 10th cycle was less than 70 mAh g^{-1} , much lower than the previously reported value for $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ powder, 225 mAh g^{-1} .²⁵⁾ This means that the electrode reaction of LLTO TDSE is different from that of the general powder-based electrode. The current density dependence of the capacity was investigated to understand the electrode property for LLTO TDSE in detail. Figures 3(b) and 3(c) show charge–discharge curves at 0.17 and 0.06 mA cm^{-2} , respectively. The diameter of the LLTO sintered disk used in the charging/discharging test in Figs. 3(b) and 3(c) was 7.77 and 7.72 mm, respectively. As the current density decreased, the overpotential at first charging lowered, and the capacity gradually increased. Figure 3(d) summarizes the dependence between current density and discharge capacity. Even at a current density of 0.06 mA cm^{-2} , the discharge capacity was 81 mAh g^{-1} , which seems saturated. In addition, the capacity above 1 V (vs. Li^+/Li) was $\sim 50 \text{ mAh g}^{-1}$ and shows a good agreement with the previous report, indicating that the electrode reaction below 1 V (vs. Li^+/Li) of TDSE differs from the normal electrode. Here, we are considering two possible reasons for the lower capacity. One is the suppression of phase transformation. During the Li insertion process into LLTO, the phase transformation from tetragonal to pseudo-cubic occurs.²⁵⁾ This phase transformation causes the volume change of LLTO. In the case of TDSE, grains are tightly connected and there is no free space to allow the volume expansion, although the normal electrode has enough free space for volume change in LLTO particle. This suppression of phase transformation caused by dense structure for TDSE may prevent the Li insertion reaction. The other is that the discharge capacity for LLTO TDSE may reach the theoretical capacity. This means that the structural difference between the normal electrode using $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ powder and TDSE causes a big difference in the capacity. According to a previous report,²⁵⁾ the authors fabricated

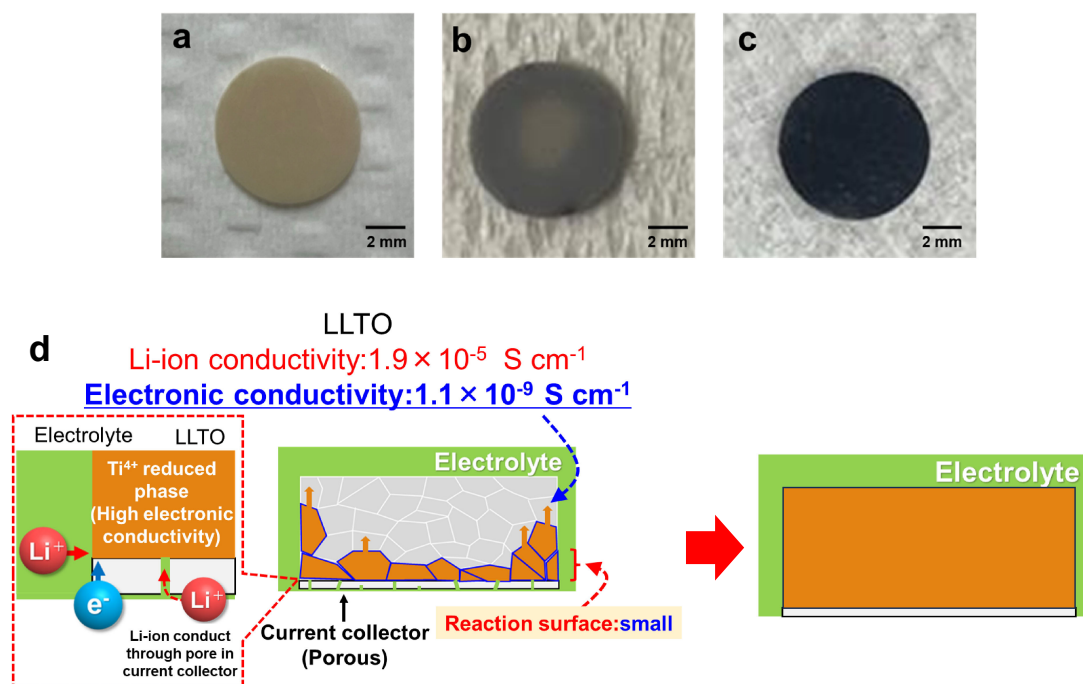


Fig. 4. Photo images of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ (a) before and after charging to (b) 0.03 mAh g^{-1} and (c) 5 mAh g^{-1} . (d) The schematic diagram of Li insertion reaction for $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ TDSE at the initial stage.

the electrode by mixing LLTO powder with carbon material as a conductive additive. It was reported that carbon black can intercalate/deintercalate Li^+ under 1.5 V (vs. Li^+/Li) and exhibit capacity.²⁸⁾ Thus, we believe that the capacity of the normal powder-based electrode contains the capacity of not only $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ but also carbon black, and the actual capacity of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ is estimated to be approximately 80 mAh g^{-1} corresponding to the reduction of 52 % Ti^{4+} to Ti^{3+} . However, further investigation is needed to clear the reason.

To reveal the origin of overpotential seen at the first charge, we investigated the reaction site of LLTO TDSE. **Figures 4(a)–4(c)** shows the photographs of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ before and after charging to 0.03 mAh g^{-1} (corresponding to 1 min) and 5 mAh g^{-1} . After charging to 5 mAh g^{-1} , the color of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ TDSE turned black [Fig. 4(c)]. According to the previous report,^{29,30)} this color change is attributed to the reduction of Ti^{4+} with an increase in electronic conductivity to $1.5 \times 10^{-4} \text{ S cm}^{-1}$. It is noted that, after charging to 0.03 mAh g^{-1} , the color of only the outer part of the LLTO TDSE turned black, indicating the charging reaction occurred from outside the sintered disk. In addition, the Pt current collector is thin film ($\sim 60 \text{ nm}$) and there are pores. Thus, not only the edge but also the current collector side may play as the initial reaction site. Based on this consideration, we propose the reaction mechanism for LLTO TDSE at the first charging process, as shown in Fig. 4(d). Firstly, since the electronic conductivity of $\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$ was extremely low, electrons can provide from only the current collector; the reaction occurred at the triple-phase boundary between LLTO, electrolyte, and the current collector, where Ti^{4+} reduction phase forms around this interface. This limited reaction

site causes the localization of currents in this area, resulting in high overpotential. During the charging process, the formed Ti^{3+} enhances the electronic conduction through LLTO, and the reaction site gradually increases due to the chemical diffusion of Li through LLTO. Here, the outer part can directly contact to the liquid electrolyte. On the other hand, the inside of LLTO Li migration through the LLTO is slower than that of the outside, because the Li ion conductivity of LLTO is much lower than that of the liquid electrolyte. As a result, the Li insertion reaction proceeds homogeneously in the diameter direction. Finally, all surfaces of LLTO TDSE become the reaction surface, and the overpotential caused by low electronic conductivity completely disappears. Thus, the high overpotential at the initial stage for the Li insertion may be improved by enhancing the electronic conductivity of LLTO TDSE. So far, we investigated the effect of Mn substitution for Ti to improve the electronic conductivity and demonstrate these electrode properties.

3.2 Mn substitution for Ti site to enhance the electronic conductivity

To enhance electronic conductivity, we investigated Mn substitution for Ti site in $\text{Li}_{0.33}\text{La}_{0.557+1/3x}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$. Here, to compensate for the Mn^{3+} , the amount of La^{3+} was controlled. **Figures 5(a)** and **5(b)** show the XRD patterns of Mn-substituted LLTO and the correlation between the amount of Mn substitution and lattice constants (a and c) calculated by Rietveld refinement. Although the perovskite peak can be observed in all XRD patterns, the peak intensity of $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ as the impurity phase increases with an increase in Mn substitution amount. Additionally, c increases as the Mn substitution amount increases despite

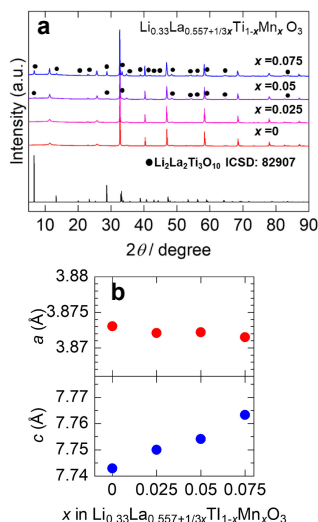


Fig. 5. (a) XRD patterns of $\text{Li}_{0.33}\text{La}_{0.557+1/3x}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ and (b) the correlation between the amount of Mn substitution and lattice constants.

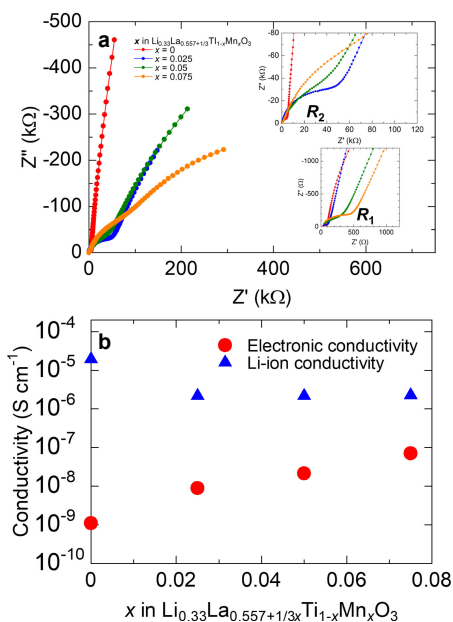


Fig. 6. (a) The Nyquist plots of $\text{Li}_{0.33}\text{La}_{0.557+1/3x}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ TDSEs at 25 °C. (b) The correlation between the amount of Mn substitution and electron/Li-ion conductivity of $\text{Li}_{0.33}\text{La}_{0.557+1/3x}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ sintered disks.

of no change in a . This change may be attributed to be Jahn–Teller effect of substituted Mn^{3+} at the B-site, indicating that Ti has been partially replaced by Mn in LLTO.

Figures 6(a) and 6(b) show the Nyquist plots of Mn-substituted LLTO and the correlation between the amount of Mn substitution and Li-ionic/electronic conductivity. In the Nyquist plots, two semicircles are corresponding to bulk and grain boundary resistance. According to the equivalent circuit shown in Fig. 2(a), total Li-ion conductivities were estimated. As shown in Fig. 6(b), Li-ion conductivity decreased to 2.2×10^{-6} S cm^{-1} as the Mn

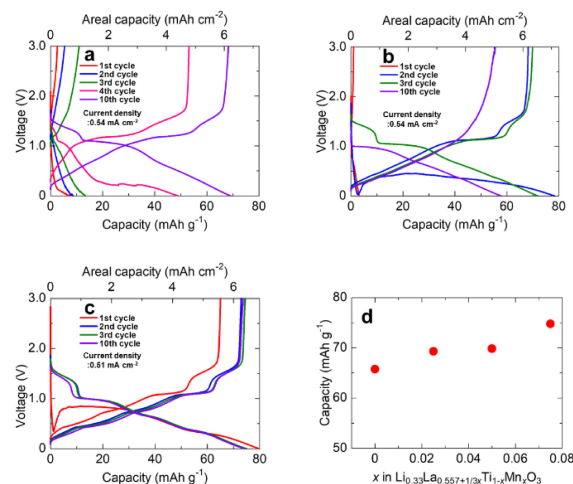


Fig. 7. The charge–discharge curves for sintered disks of $\text{Li}_{0.33}\text{La}_{0.557+1/3x}\text{Ti}_{1-x}\text{Mn}_x\text{O}_3$ sintered disks (a) $x = 0.025$, (b) $x = 0.05$, (c) $x = 0.075$, (d) correlation between the amount of Mn substitution and the highest discharge capacity through 10 cycles.

substitution increased. On the other hand, the electronic conductivity increased with an increase in Mn substitution, and the highest electrical conductivity for $x = 0.075$ of 7.1×10^{-8} S cm^{-1} was obtained. These results show a good agreement with the previous report.²⁸⁾

A charge–discharge test was conducted to reveal the effect of Mn-substitution on electrode property. Figures 7(a)–7(c) shows the charge–discharge curves of Mn-substituted LLTO. The diameter of LLTO sintered disk used in the charging/discharging test was 7.78, 7.83 and 7.93 mm, respectively. Although the compositions with $x = 0.025$ and 0.05 exhibited a low capacity of less than 10 mAh g^{-1} in the first cycle, $x = 0.075$ exhibits the highest capacity of 75 mAh g^{-1} . This may be attributed to an increase in electronic conductivity. As shown in Fig. 4(d), the charging reaction occurred around the triple-phase boundary in LLTO sintered anode immediately after the start of charging due to the low electronic conductivity of LLTO without Mn substitution. Consequently, it was shown that enhanced electronic conductivity improved the first Li insertion reaction for LLTO TDSEs.

Figure 7(d) shows the relationship between the Mn substitution amount and the highest discharge capacity through 10 cycles. The discharge capacity increases with an increase in the Mn substitution amount, indicating that the Mn substitution effectively improves the discharge capacity of LLTO TDSE. The improved electronic conductivity by Mn substitution may enhance the capacity. However, the new plateau can be observed when the Mn substitution amount increases. Figure 8 shows the dQ/dV curves for LLTO and Mn-substituted LLTO ($x = 0.075$). Although the peak intensity for Mn-substituted LLTO above 1 V decreased, a new peak around 0.7 and 0.4 V was observed. This new redox peak may be assigned to the Ti^{4+} redox in $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$. Thus, not only the change in bulk property by Mn substitution for LLTO but also impurity phases like $\text{Li}_2\text{La}_2\text{Ti}_3\text{O}_{10}$ would affect the enhanced

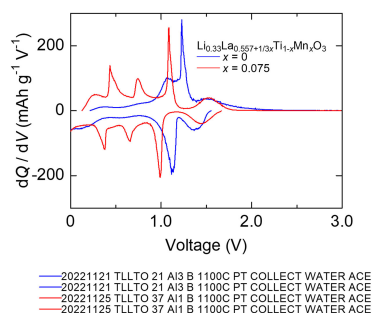


Fig. 8. The dQ/dV curves for LLTO and Mn-substituted LLTO.

discharge capacity. The detailed mechanisms will be reported in the future.

4. Conclusion

In this study, we investigated the electrochemical properties of the LLTO thickly and densely sintered electrode (TDSE) as the anode for Li-ion batteries. We found that the LLTO TDSE exhibited high overpotential and low capacity during the first cycle charging, attributed to low electronic conductivity of $1.1 \times 10^{-9} \text{ S cm}^{-1}$. Furthermore, we investigated the effects of Mn substitution on enhancing the electronic conductivity of LLTO. Mn substitution increased electronic conductivity to $7.1 \times 10^{-8} \text{ S cm}^{-1}$ despite a decrease in Li-ion conductivity, and this enhanced electronic conductivity improved the overpotential and capacity during the first cycle. In addition, we have demonstrated that Mn-substitution improved the discharge capacity. Thus, it was found that controlling the electronic conductivity with the partial substitution of other elements effectively improves the initial Li insertion reaction for LLTO TDSEs.

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