Effects of sintering temperature on interfacial structure and interfacial resistance for all-solid-state rechargeable lithium batteries

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Abstract

Sintering processes yield a mutual diffusion region at the electrode/solid electrolyte interface, which is considered as a crucial problem for developing large-sized all-solid-state rechargeable lithium batteries with high power density. This work focuses on the interface between $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) and NASICON-structured Li^+ conductive glass ceramics solid electrolyte ($\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$: LATP sheet (AG-01)), and investigates the effects of sintering temperature on interfacial structure and interfacial resistance at the NMC/LATP sheet. Thin films of NMC were fabricated on the LATP sheets at 700 °C or 900 °C as a model system. We found that the thickness of the mutual diffusion region was almost the same, ca. 30 nm, in these two samples, but the NMC film prepared at 900 °C had three orders of magnitude larger interfacial resistance than the NMC film prepared at 700°C. Around the interface between the NMC film prepared at 900°C and the LATP sheet, Co in the NMC accumulates as a reduced valence and lithium-free impurity crystalline phase will be also formed. These two problems must contribute to drastic increasing of interfacial resistance. Formation of de-lithiated NMC around the interface and its thermal instability at higher temperature may be considerable reason to induce these problems.

1. Introduction

All-solid-state rechargeable lithium batteries using oxide solid electrolytes (Ox-SSBs) will be one of the candidates for next-generation rechargeable batteries with high energy density, safety, and long-life performance. Thin-film Ox-SSBs have been investigated by various researchers [1-3], and their excellent cycle stability (over 10,000 cycles) has been reported. Although such thin-film Ox-SSBs generally use a glass electrolyte, typically lithium phosphorus oxynitride glass electrolyte (LiPON) with lower Li^+ conductivity (ca. $2 \times 10^{-6} \text{ S cm}^{-1}$ at R.T. [4]), several kinds of oxide solid electrolytes with two to three orders of magnitude higher Li^+ conductivity (10^{-3} - $10^{-4} \text{ S cm}^{-1}$) than LiPON have been discovered ($\text{Li}_{0.34}\text{La}_{0.51}\text{TiO}_3$ [5], $\text{Li}_7\text{La}_3\text{Zr}_{12}\text{O}_{12}$ [6], $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5\text{-TiO}_2\text{-GeO}_2$ (NASICON-structured Li^+ conductive glass ceramics solid electrolyte (LATP) [7]). Now that, it is demanded to develop large-sized Ox-SSBs using such solid electrolytes with higher Li^+ conductivity especially for the applications to PHEV and EV.

Large-sized Ox-SSBs will apply an electrode-solid electrolyte composite as with conventional rechargeable lithium-ion batteries (LIBs) using liquid electrolyte. In case of the LIBs, liquid electrolytes penetrate into porous electrodes, and an electrode/electrolyte interface is automatically formed. On the other hand, in case of

the Ox-SSBs, both electrode and solid electrolyte are fragile and hard ceramics, thus they need a densification process to enlarge the electrode/solid electrolyte contact area. Those composites have been developed by heating processes such as co-sintering [8], spark plasma sintering [9, 10], fusion bonding using low-melting solid electrolyte [11], etc. However, one of the crucial problems to apply such a heating process is the formation of a mutual diffusion region at the interface. While the formation of a mutual diffusion region works as a driving force for solid-solid adhesion, this formation can retard interfacial Li^+ transfer reaction and then reduce the battery power density. Therefore, it is important to examine how mutual diffusion region formation provides resistive interface in detail.

Among the various kinds of electrodes and solid electrolytes, we focused on $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) as the electrode active material and LATP as the solid electrolyte. The NMC shows small volume change (less than 1%) during charge-discharge reactions [12], which is an appropriate feature for Ox-SSBs. Also, LATP is one of the highest Li^+ conductive solid electrolytes as mentioned above. Here, the NMC films were deposited by pulsed laser deposition (PLD) on mirror-polished LATP sheets at different temperatures, which were model systems of the sintered NMC/LATP interface.

2. Experimental

The NMC thin films were deposited by PLD using a fourth harmonic YAG laser (266 nm) with the repetition frequency of 10 Hz. Those NMC films were deposited for 1 hour at 1.15 J cm^{-2} under an O_2 atmosphere of 27 Pa. The laser was focused on a target located inside an evacuated chamber, where the target to substrate distances were 46 mm. The laser radiation angle against the target surface was 45° . The target was Li-rich NMC pellet ($\text{Li}/(\text{Ni}+\text{Co}+\text{Mn})=1.40$, $\text{Ni}:\text{Co}:\text{Mn}=1.00:1.00:1.00$; Toshima, Japan) to compensate for the lithium deficiency during the PLD deposition [13]. The substrates were 150 μm -thick LATP sheets (Ohara Inc., AG-01 composed of $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5-\text{TiO}_2-\text{GeO}_2$ [7]) or Pt ($t=100 \text{ nm}$)/Ti ($t=5 \text{ nm}$)-coated SiO_2 substrates prepared by RF magnetron sputtering. The latter substrate will be denoted as Pt- SiO_2 substrates in the description below. The substrate temperature was set to 700°C or 900°C , but the surface temperature of the substrate was 520°C and 670°C , respectively. The NNC films prepared at 700°C or 900°C will be denoted as NMC-700 and NMC-900, respectively. In case of the NMC films deposited on the LATP sheets, platinum (Pt) films were coated on the NMC films as current collector by RF magnetron sputtering and units of Pt films/NMC films/LATP sheets were prepared.

Electrochemical properties of the NMC films were measured by using a three-electrode cell. Figure 1 shows a schematic image of the electrochemical measurement cell, where Pt film/NMC film/LATP sheet is used as a unit. Working electrodes were NMC films and both reference and counter electrodes were Li metal immersed in a liquid electrolyte, 1 mol dm⁻³ LiClO₄ dissolved in propylene carbonate. A bare side of the LATP sheet was immersed in the liquid electrolyte, while the Pt film side was attached to a current collector. The LATP sheet is a liquid-tight sheet, and then the lithium extraction/insertion reactions at the NMC films/LATP sheets interface are measured by this cell configuration. In case of the NMC films deposited on the Pt-SiO₂ substrates, they were set in place of the unit of Pt film/NMC film/LATP sheet. Electrochemical measurements of those NMC films were investigated by cyclic

Figure 1. Schematic image of the electrochemical cell, where a unit of platinum film/NMC film/LATP sheet is used.

voltammetry (CV) and electrochemical impedance spectroscopy (EIS), where the electrode area was 0.636 cm² in any cases. The CVs were measured at a potential sweep rate of 1.0 mV s⁻¹ between 3.0 and 4.2 V vs. Li⁺/Li. Also, EIS measurements were conducted at 3.0 V and 4.0 V under equilibrium state with AC amplitude of 10 mV between 100 mHz to 200 kHz. All the electrochemical measurements were carried out at 25 °C in an Ar-filled glove box (dew point <-90 °C).

Grazing-incidence X-ray diffraction (XRD) measurements were performed by a step-scan method (**incidence angle: 1.0°, accumulation time: 10 sec/step, step width: 0.02°**) between 10° and 70° using a CuKα source (Rigaku Ultima IV). The interface region of the NMC films/LATP sheets were characterized by both energy-dispersed X-ray analysis (EDX) and electron energy loss spectroscopy (EELS). Here, the sample **was thinned to ca. 100 nm in thickness** by a focused ion beam (FIB) technique using a Ga ion beam. EDX line profiles in the vicinity of NMC films/LATP sheets interface were measured using scanning transmission electron microscopy (STEM) equipped with EDX (Topcon EM-002BF). Measurements of EELS around the NMC films/LATP sheets interface were conducted using a TEM (Hitachi HF3300) equipped with EELS system (Gatan GIF Quantum ER) at intervals of 10 nm. EELS images were obtained by subtracting the background intensity using power law fitting.

Correction of the zero loss peak and the subtracting background were conducted by software (Gatan Digital Micrograph).

3. Results & Discussion

Figure 2(a) shows an XRD pattern of a Pt-SiO₂ substrate, and Figs. 2(b) and 2(c) show XRD patterns of NMC-700 and -900 on the Pt-SiO₂ substrates, respectively.

Figure 2. XRD patterns of a (a) Pt-SiO₂ substrate, (b) NMC-700 on Pt-SiO₂, (c) NMC-900 on Pt-SiO₂, (d) LATP sheet, (e) NMC-700 prepared on a LATP sheet, and (f) NMC-900 prepared on a LATP sheet. Peaks marked by † in Fig. 2(c) arise from the heating of the Pt-SiO₂ substrates. Also, peaks marked by * in Figs. 2(e) and 2(f) arise from the heating of the LATP sheet. A peak marked by an arrow in Fig. 2(f) indicates an impurity peak. JSPDS data of NMC are shown as lines at the bottom in Fig. 2.

A diffraction peak observed at 18.7° in both Figs. 2(b) and Fig. 2(c) was assigned to the 003 peak of the NMC [12]. Other peaks in Figs. 2(b) and 2(c) were in good agreement with the XRD pattern of a Pt-SiO₂ substrate shown in Fig. 2(a). Figures 2(d-f) show XRD patterns of a LATP sheet, a NMC-700 prepared on a LATP sheet, and a NMC-900 prepared on a LATP sheet, respectively. The diffraction peak at 18.7° assigned to 003 peak of the NMC was observed both in Figs. 2(e) and 2(f). Also, several small peaks newly appeared at $20\text{--}30^\circ$ (marked by *) in Figs. 2(e) and 2(f) in addition to peak shifts. These new peaks appeared also in the LATP sheets heated in the PLD chambers as with the fabrication conditions of NMC films (marked by * in Figs. S1 (a-c).) The shifted peaks appear clearly as signals in the difference line (Fig. S1(d)) between pristine LATP sheet (Fig. S1(a)) and LATP sheet after heating at 700°C (Fig. S1(b)). The difference line between LATP sheets after heating at 700°C and that at 900°C were flat (Fig. S1(e)), indicating that they are almost same structure. As will be shown later, ionic conductive properties of those heated LATP sheets were almost same. However, an impurity peak at 36.2° (marked by arrow in Fig. 2(f)) was not assigned to both the NMC-900 and the LATP sheet after heating. Thus, we can conclude that this impurity peak appears by a reaction between the NMC-900 and the LATP sheet.

Figure 3(a) shows the CVs of the NMC-700 and -900 deposited on the Pt-SiO₂

Figure 3. CVs of (a) NMC-700 and -900 deposited on Pt-SiO₂ substrates measured in liquid electrolytes and (b) NMC-700 and -900 deposited on LATP sheets. All the measurements were carried out at 298 K at a potential sweep rate of 1 mV s^{-1} .

substrates measured in liquid electrolyte. Redox peaks appeared at around 3.6-3.8 V in both the NMC films, which were in good agreement with the past report [14]. On the other hand, Fig. 3(b) shows the CVs of the NMC-700 and -900 deposited on the LATP sheets. It is clear that these two NMC films show quite different reactivity. The CV of the NMC-700 deposited on the LATP sheet was almost the same with that measured in the liquid electrolyte, while the NMC-900 deposited on the LATP sheet did not show any redox peaks. The NMC-700 deposited on the LATP sheet was annealed at 900°C in the PLD chamber as with the preparation conditions of the NMC-900, and

the resultant annealed NMC film also did not show clear redox peaks (Fig. S2). These results indicate that Li^+ extraction/insertion reactions of the NMC films deposited on the LATP sheets are strongly influenced on the sintering temperature.

Figures 4(a) and 4(b) show the Nyquist plots of the NMC-700 and -900

Figure 4. Nyquist plots of (a) NMC-700 and (b) NMC-900 deposited on Pt-SiO₂ substrates measured in liquid electrolytes. Nyquist plots of (c) NMC-700 and (d) NMC-900 deposited on LATP sheets. Magnified spectra at higher frequency regions of Figs. 4(c) and 4(d) are shown in (e) and (f), respectively. All these measurements were carried out at 3.0 V and 4.0 V at 298 K. Measured data points at 10 Hz are shown as numbers.

deposited on the Pt-SiO₂ substrates in liquid electrolytes, respectively. At 3.0 V, these spectra showed half semicircular arc at higher frequency region assigned to the resistance of liquid electrolyte (400-500 Ω), followed by a straight line tilted against the real axis at lower frequency region. For both spectra, one semicircular arc newly appeared at 4.0V at middle frequency region, which was assigned to the interfacial resistance (R_{int}) at the NMC film/liquid electrolyte interface, and then tilted straight line at lower frequency region against the real axis because of the Li⁺ diffusion in the NMC films. The R_{int} of the NMC-900 was 315 Ω (200 $\Omega \text{ cm}^2$), which was slightly smaller than that of the NMC-700, 550 Ω (350 $\Omega \text{ cm}^2$). Figures 4(c) and 4(d) show the Nyquist plots of the NMC-700 and -900 deposited on the LATP sheets, respectively. Also, magnified images at higher frequency region of Figs. 4(c) and 4(d) are shown in Figs. 4(e) and 4(f), respectively. To examine the heating effects on the Li⁺ conductive properties in the LATP sheets, the LATP sheets with and without the heating in the PLD chamber as with fabrication conditions of the NMC films were combined with the Pt film and the EIS measurements were carried out using same cell configuration (Pt film/LATP sheet/liquid electrolyte). The Nyquist plots measured at both 3.0 V and 4.0 V showed almost same semicircles with the diameter of ca. 1000 Ω at higher frequency region (Figs. S3(a-f)). Therefore, we can conclude that semicircular arc ($R \sim 1000 \Omega$) at

higher frequency region in Figs. 4(e) and 4(f) arise from the cell resistance composed of the resistances by liquid electrolyte, LATP sheet, and liquid electrolyte/LATP sheet interfacial Li^+ transfer reaction. Although some of X-ray diffractions peaks newly appeared by the heating of the LATP sheets as mentioned above, Li^+ conductive properties look to be unchanged by the heating. At 4.0 V, the NMC-700 deposited on the LATP sheet displayed another semicircle at middle frequency region as shown in Fig. 4(e). This semicircle is assigned to the R_{int} at the NMC-700/LATP sheet interface, and the value, 495Ω ($315 \Omega \text{ cm}^2$), was comparable with that measured in the liquid electrolyte. The NMC-900 deposited on the LATP sheet also displayed a new semicircle at 4.0 V as shown in Fig. 4(d), but the R_{int} was estimated to be 179000Ω ($114,000 \Omega \text{ cm}^2$), three-order larger value than that of the NMC-700 deposited on the LATP sheet. These huge differences on the R_{int} must provide drastic differences of the reactivities in their CVs. The Nyquist plots at 3.0 V of the Pt films/LATP sheets after the heating showed tilted straight line against the real axis at lower frequency region (Figs. S3(b) and S3(c)). Thus, the capacitive semicircular arc observed at lower frequency region at 3.0V in Figs. 4(c) and 4(d) do not mean the increased grain boundary resistance in the LATP sheet by the heating but originate from the formation of NMC/LATP interface. Tiny amount of Li^+ transfer reaction may take place due to

the formation of mutual diffusion region and/or reacted phase as will shown in later.

Figure 5(a) shows the cross-sectional TEM image around the NMC-700/LATP sheet interface and spatially-resolved EELS mapping image of Co-L edge. The thickness of the NMC-700 was estimated to be 115 nm. The Co-L edge spectra were collected with an interval of 10 nm across the interface at the numbered positions, 1-10, shown in the right side of the EELS mapping image. Also, measurements of Mn-L edge spectra were carried out at the same points. Figures 5(b) and 5(c) show the EELS

Figure 5. (a) TEM image around the NMC-700/LATP sheet interface and EELS mapping image of Co-L edge obtained by spatially-resolved EELS analysis. EELS of the (b) Co-L edge and (c) Mn-L edge measured at the numbered positions in Fig. 5(a). (d) TEM image around the NMC-900/LATP sheet interface and EELS mapping image of Co-L edge. EELS of the (e) Co-L edge and (f) Mn-L edge measured at the numbered positions in Fig. 5(d).

spectra of the Co-L edge and Mn-L edge spectra measured at those numbered positions in Fig. 5(a). Both elements have two peaks assigned to L3- and L2-edges [15]. Similar measurements were carried out for the NMC-900/LATP sheet interface. Figure 5(d) shows the cross-sectional TEM image around the NMC-900/LATP sheet interface and **spatially-resolved EELS mapping image** of Co-L edge. Also, both Co- and Mn-L edge spectra measured at numbered positions in Fig. 5(d) are summarized in Figs. 5(e) and 5(f), respectively. In both NMC films, the Co-L edge spectra shifted to lower energy loss in the vicinity of the interface, indicating that valence state of Co around the interface region is lower than that inside the NMC films. It has been reported that the integrated intensity ratio of these two L edge peaks, L3-edge/L2-edge, in these two elements corresponds to the valence state of Co and Mn [15]. Therefore, it is possible to analyze the valence-state distribution around the interface of these two elements. The L3-edge/L2-edge for Co and Mn will be denoted as L3/L2-Co, and L3/L2-Mn, respectively, in later description. Increasing of the L3/L2 value corresponds to more reduced valence in both elements.

Figure 6(a) shows the EDX line profile of O, P, Ti, Mn, Ni, and Co around the NMC-700/LATP sheet interface and the TEM image of the measured area is displayed in the inset. **The atom percentage of each element against total amount of these six**

elements is shown in the vertical axis. The thickness of the NMC-900 was 95 nm, which was slightly thinner than that of the NMC-700. This may be induced by the reduced adhesion probability at a higher deposition temperature. The atomic percentage of Ni, Co, and Mn in the NMC-700 was uniform and even, which was an expected trend for ideal NMC. Also, the atomic percentages of Ti and P in the LATP sheet were uniform. A mutual diffusion region was detected around the

Figure 6. (a) EDX line profile of O, P, Ti, Mn, Ni, and Co around the NMC-700/LATP sheet interface. The inset shows a TEM image of the measured area. Variations of (b) L3/L2-Co and (c) L3/L2-Mn are shown corresponding to the EDX line profile.

NMC-700/LATP sheet interface, where gradation of the atomic percentage of these elements except for O was observed. The thickness of the mutual diffusion region was estimated to be 30 nm from Fig. 6 (a). Variations of L3/L2-Co and L3/L2-Mn corresponding to the EDX line profile are summarized in Figs. 6(b) and 6(c), respectively, where reported valence-state variations of Co and Mn against the L3/L2-Co and L3/L2-Mn are displayed as a gray-colored band in them [15]. Valences of Co and Mn in the NMC have been reported to be +3 and +4 [16], respectively, and then it is reasonable that the L3/L2-Co and L3/L2-Mn in the NMC-700 is located in the band of the $\text{Co}^{2+}/\text{Co}^{3+}$ mixture and Mn^{4+} , respectively. Although the L3/L2-Mn in the mutual diffusion region was still located in the Mn^{4+} band, the L3/L2-Co appeared at a higher value than that of the $\text{Co}^{2+}/\text{Co}^{3+}$ band, suggesting that the average Co valence was further reduced in the mutual diffusion region as compared with that inside the NMC-700. However, this situation does not increase interfacial resistance so much.

Similar analyses were carried out for the NMC-900 deposited on the LATP sheet, which are summarized in Figure 7. Figure 7(a) shows the EDX line profile around the NMC-900/LATP sheet. As with the NMC-700/LATP interface, a mutual diffusion region with the thickness of ca. 30 nm was observed around the interface. An interesting feature in Fig. 7(a) was the presence of a Co-rich region with ca. 20 nm

in thickness around the interface. Both the L3/L2-Co and the L3/L2-Mn corresponding to the EDX line profile are summarized in Figs. 7(b) and 7(c), respectively. The L3/L2-Mn was located around the band of Mn^{4+} and the valence change was not observed. On the other hand, the L3/L2-Co was located in the $\text{Co}^{2+}/\text{Co}^{3+}$ band inside the NMC-900, which shifted toward a higher value in the Co-rich region and further higher value in the mutual diffusion region.

Figure 7. (a) EDX line profile of O, P, Ti, Mn, Ni, and Co around the NMC-900/LATP sheet interface. The inset shows a TEM image of the measured area. Variations of (b) L3/L2-Co and (c) L3/L2-Mn are shown corresponding to the EDX line profile.

Here, the question is how Co was reduced and accumulated in the NMC around the interface. These phenomena may be triggered by space-charge effect. When the NMC and the LATP contact each other, electrochemical potential of Li^+ must be even. Work function of the LATP sheet estimated by the photoelectron yield spectroscopy (AC-2, AC-3, Riken Keiki, Co., LTD) was 5.45 eV, which was slightly higher than that of the NMC (5.40 eV). Therefore, space-charge region in the NMC will be higher voltage, which will promote Li^+ transfer from the NMC toward the LATP sheet. Because the NMC is mixed conductor, de-lithiated NMC will be formed uniformly at an equilibrium state. However, such de-lithiated NMC is thermally unstable and release oxygen at lower temperature than that of the pristine one [17]. This oxygen release will provide lower-valence Co. It is suggested that Co^{2+} occupy lithium sites in the surface-degraded LiCoO_2 [18]. Thus, Co^{2+} may diffuse through de-lithiated lithium layers toward the LATP sheet and then accumulate around the interface, which must be resistive for Li^+ transfer around the interface.

When powders of the NMC and the LATP are mixed by 1:1 in volume and then heated in a furnace under air atmosphere at 700°C, the strongest diffraction peak by a formation of reacted phase appeared at 36.1° (Figs. S4 (a-e)), which further shifted to 35.7° by increasing the heating temperature up-to 900°C [19], indicating that reacted

phases change gradually with increasing the sintering temperature. Several lithium-free Co-rich compounds such as MnCo_2O_4 (Fig. S4(f)), Co_3O_4 (Fig. S4(g)), and NiCo_2O_4 (Fig. S4(h)) look to be candidates by comparing with JCPDS data. In the magnified TEM image observed at the mutual diffusion region in both the NMC-700/LATP sheet (Fig. S5(a)) and the NMC-900/LATP sheet (Fig. S5(b)) interfaces, LATP side was amorphous state while lattice images were observed clearly in the NMC-side. Also, the EELS analysis revealed the presence of reduced-valence Co and Mn^{4+} in the Co-rich region. From these results, an impurity X-ray diffraction peak at 36.2° will originate from Co-rich region and a suggested material is MnCo_2O_4 [20]. Such lithium-free crystalline compound formed around the interface must be also resistive for Li^+ transfer around the interface.

At the sintering process of NMC/LATP, thickness of mutual diffusion region is desirable to be reduced well. However, at a higher sintering temperature, reduced-valence Co is accumulated and impurity lithium-free crystalline phase will be also formed around the interface in the NMC-side additionally. These two problems will retard Li^+ transfer around the interface and then contribute to critical increasing of the R_{int} . Because the R_{int} at the NMC-700/LATP sheet was comparable with that in the liquid electrolyte, a strategy to overcome these two problems will be to apply a

lower-temperature sintering process or a room-temperature densification process [19].

4. Conclusions

Sintering effects of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) with NASICON-structured Li^+ conductive glass ceramics solid electrolyte (LATP) were investigated using model systems, where NMC films were deposited on the LATP sheets at 700°C (NMC-700) or 900°C (NMC-900). The NMC-900 deposited on the LATP sheet showed ca. three orders of magnitude larger interfacial resistance (R_{int}) than that of the NMC-700 deposited on the LATP sheet, though the thickness of the mutual diffusion region was ca. 30 nm in both cases. Around the NMC-900/LATP interface, Co in the NMC accumulate as a reduced valence and lithium-free crystalline phase will be also formed. These two problems must contribute to drastic increasing of the R_{int} . Formation of de-lithiated NMC from the interface and its thermal instability at higher temperature may be considerable reason to induce these problems.

5. Acknowledgement

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Figure Captions

Figure 1. Schematic image of the electrochemical cell, where a unit of platinum film/NMC film/LATP sheet is used.

Figure 2. XRD patterns of a (a) Pt-SiO₂ substrate, (b) NMC-700 on Pt-SiO₂, (c) NMC-900 on Pt-SiO₂, (d) LATP sheet, (e) NMC-700 prepared on a LATP sheet, and (f) NMC-900 prepared on a LATP sheet. Peaks marked by † in Fig. 2(c) arise from the heating of the Pt-SiO₂ substrates. Also, peaks marked by * in Figs. 2(e) and 2(f) arise from the heating of the LATP sheet. A peak marked by an arrow in Fig. 2(f) indicates an impurity peak. JSPDS data of NMC are shown as lines at the bottom in Fig. 2.

Figure 3. CVs of (a) NMC-700 and -900 deposited on Pt-SiO₂ substrates measured in liquid electrolytes and (b) NMC-700 and -900 deposited on LATP sheets. All the measurements were carried out at 298 K at a potential sweep rate of 1 mV s⁻¹.

Figure 4. Nyquist plots of (a) NMC-700 and (b) NMC-900 deposited on Pt-SiO₂ substrates measured in liquid electrolytes. Nyquist plots of (c) NMC-700 and (d) NMC-900 deposited on LATP sheets. Magnified spectra at higher frequency regions

of Figs. 4(c) and 4(d) are shown in (e) and (f), respectively. All these measurements were carried out at 3.0 V and 4.0 V at 298 K. Measured data points at 10^n Hz are shown as numbers.

Figure 5. (a) TEM image around the NMC-700/LATP sheet interface and EELS mapping image of Co-L edge obtained by spatially-resolved EELS analysis. EELS of the (b) Co-L edge and (c) Mn-L edge measured at the numbered positions in Fig. 5(a). (d) TEM image around the NMC-900/LATP sheet interface and EELS mapping image of Co-L edge. EELS of the (e) Co-L edge and (f) Mn-L edge measured at the numbered positions in Fig. 5(d).

Figure 6. (a) EDX line profile of O, P, Ti, Mn, Ni, and Co around the NMC-700/LATP sheet interface. The inset shows a TEM image of the measured area. Variations of (b) L3/L2-Co and (c) L3/L2-Mn are shown corresponding to the EDX line profile.

Figure 7. (a) EDX line profile of O, P, Ti, Mn, Ni, and Co around the NMC-900/LATP sheet interface. The inset shows a TEM image of the measured area.

Variations of (b) L3/L2-Co and (c) L3/L2-Mn are shown corresponding to the EDX line profile.