Preparation of thick-film electrode-solid electrolyte composites on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and their electrochemical properties

Takeshi Kato^{1,2}, Shinya Iwasaki¹, Yosuke Ishii¹, Munekazu Motoyama^{1,2}, William C West³, Yuta Yamamoto⁴, and Yasutoshi Iriyama^{1,2}*

1. Department of Materials, Physics, and Energy Engineering
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 4648603, Japan
2. JST-ALCA, Chiyoda-ku, Tokyo 102-0076, Japan
3. Green Mobility Collaborative Research Center
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 4648603, Japan
4. High Voltage Electron Microscope Laboratory,
Institute of Materials and Systems for Sustainability
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 4648603, Japan

* corresponding author

E-mail: iriyama@numse.nagoya-u.ac.jp

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Abstract

We prepared up to 20 μm -thick $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC)- Li^+ conductive glass-ceramic solid electrolyte (LATP: $\sigma_{\text{Li}^+} \sim 10^{-3} \text{ S cm}^{-2}$ at 298 K) composite cathode films on $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) substrates by aerosol deposition (AD) and investigated their electrochemical properties as all-solid-state batteries. The resultant NMC/LATP interface in the composite film had a thin mutual diffusion layer ($\sim 5 \text{ nm}$) and a film had a porosity of ca. 0.15% in volume. The composite films were well adhered to the LLZ substrates even though the films were prepared at room temperature. All-solid-state batteries, consisting of Li/LLZ/NMC-LATP composite film (20 μm), repeated charge-discharge reactions for 90 cycles at 100° C at a 1/10 C rate (capacity retention: 99.97 % / cycle). Rate capability of this battery was improved by modifying both the LATP and electron conductive source amount in the composite film, and a battery with 16 μm -thick composite electrode delivered 60 mAh g^{-1} at 1 mA cm^{-2} .

Introduction

All-solid-state rechargeable lithium batteries (SSBs) using oxide-based solid electrolytes (Ox-SSBs) have been studied to realize safe and high energy density rechargeable batteries. Thin-film Ox-SSBs using a few micron- or submicron-order thin film electrodes prepared by sputtering [1], pulsed laser deposition [2], and sol-gel [3] have been widely examined. Also, thin-film Ox-SSBs have been already commercialized which are capable of over 10,000 charge-discharge cycles [4]. For further scaling-up of the Ox-SSBs, thicker films of electrode-solid electrolyte composites over 10 μm in thickness will be required. However, both the electrode and solid electrolyte materials used in the Ox-SSBs are hard and fragile materials. Thus their composite electrodes have rather poor contact to each other at the interfaces even after thorough mixing and cold pressing of those powders. Therefore, there are several reports to densify the composite electrodes, typically with heating processes. Kobayashi et al. applied a co-sintering process to prepare symmetrical SSBs using all phosphate-based materials, where $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) was used as both positive and negative electrodes and $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) as the solid electrolyte [5]. Aboulaich et al. applied a spark plasma sintering process to prepare thick-layered electrode (LVP or LiFePO_4) – solid electrolyte (LAGP) composite materials [6]. Ohta

et al. used a low melting point electrolyte of Li_3BO_3 , and developed a $\text{Li}/\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}/\text{LiCoO}_2\text{-Li}_3\text{BO}_3$ battery cell [7].

Our group has focused on aerosol deposition (AD) that can prepare crystalline ceramics films without heating [8]. The densification mechanism of the AD is different from the above-mentioned heating processes, and involves the formation of particle-to-particle bonding by way of the creation of activated surfaces (reactive free surfaces) from cracking or deformation of the source particles, followed by particle-to-particle adhesion to reduce overall surface energy [9,10]. This heating-free and binder-free process enables us to eliminate the mismatch of thermal stability of both electrodes and solid electrolytes, and reduces the likelihood of undesired side reactions (e.g. mutual diffusion layers) between the materials. In our past work, we prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC)-amorphous Li-Nb-O composite electrodes (7 μm in thickness) by AD and found that the composite films certainly work as electrode materials in an Ox-SSB [11]. However, because Li^+ conductivity in amorphous Li-Nb-O (ca. $10^{-7} \text{ S cm}^{-1}$ [12] at R.T.) is low, it is desirable to replace this material with a highly lithium-conductive solid electrolyte. Among the various kinds of oxide-based lithium-conductive solid electrolytes, Li-Al-Ti-P-O glass ceramics (LATP) manufactured by Ohara Inc. has the highest lithium conductivity ($10^{-3} \text{ S cm}^{-1}$ at 298 K)

[13]. In addition, glass ceramics can increase the toughness of the composite material because a large amount of grain boundaries can disperse the fracture energy and thus prevent the growth of the cracking [14]. This advantage will be fruitful to stabilize the charge-discharge reactions with inevitable volume changes of electrode active materials.

Based on the above motivations, we prepared NMC-LATP composite positive electrode films up to 20 μm in thickness by the AD and combined them with LLZ substrates and Li metal negative electrodes. We show that a resultant Ox-SSB, Li/LLZ/NMC-LATP composite film, can repeatedly undergo charge-discharge reactions for 90 cycles at 1/10 C at 100° C (capacity retention: 99.97 % / cycle). Also, a battery cell with a small amount of RuO_2 as a conductive additive provided 40% capacity even at 1 mA cm^{-2} .

Experimental

The AD process uses powder materials for composite film fabrication [9,10]. As with our past work, we used commercially-available NMC powder ($D_{50}=10.61 \mu\text{m}$, Nihonkagaku, Japan) as the mother powder. This cathode powder was well mixed with LATP powder ($D_{50}=0.5 \mu\text{m}$, Ohara Inc., Japan [13]) by a powder mixing tool (NOB-MINI, Hosokawa Micron, Japan) with a rotating speed of 2000 rpm for 10

minutes in an Ar-filled glove box (dew point < -80° C). The mixing weight ratio of the NMC and the LATP powders was varied as 100:X (X = 0, 1, 2, 3, 4, 5, 10, 20, 100), which will be denoted as LTP-X below. The mixed powders were characterized by SEM, EDX, and XRD, where some of the particles were Ar-ion-milled to observe cross-sectional images. Also, LTP-100 was fired at 700 or 900° C in air for 2 hours to investigate the reactivity between the NMC and the LATP powder.

We used an AD system where all the carrier tubes and chambers were made from SUS 304 stainless steel. The starting powders, LTP-X, of 4-20 g were dried at 150° C for 1 hour and then introduced into the aerosol container. Then, the powders were injected toward the substrate inside the chamber through a nozzle (10 mm × 0.23 mm in area) by Ar gas (5N) with the flow rate of 10 L min⁻¹. When the particles hit with the substrate, they are crushed or deformed, which provides newly-formed activated surfaces, which serves one of the driving force for the particle-to-particle adhesion and further densification of the composite films [9,10]. During this process, the substrates were moved back and forth for 50 mm in length at a rate of 50 mm min⁻¹ for 40 times, and were not heated at all. The chamber was evacuated by vacuum pump to 3-5 Pa and the chamber pressure was kept at 8×10² Pa during the deposition. A schematic image of the AD apparatus is shown elsewhere [9,10]. Substrates used in

this study were Si/SiO₂ wafer ($t = 1$ mm) or LLZ ($t = 0.5$ mm, Toshiba, Japan). The resultant films were characterized by FE-SEM, EDX, FIB-SEM, cross-sectional TEM, and XRD, where some of the films were Ar-ion-milled as with the particles. Also, ICP measurements were carried out to investigate the amount of NMC in the films.

Composite films prepared by LTP-5 with the thickness of 4-20 μm were deposited on LLZ substrates where one side of the substrates was polished inside the glove box before the usage. Gold thin films were deposited on the resultant composite films by RF sputtering as current collectors. After polishing the opposite side of the LLZ substrates, **Li** metal films were deposited by vacuum deposition inside the glove box. Electrochemical properties of the resultant batteries comprising the Li/LLZ/NMC-LATP composite film were measured inside the glove box at 100° C. The batteries were pressed by spring with a pressure of 150 kPa during the charge-discharge reactions carried out by **constant current/constant voltage** (CC/CV) methods at 3.0-4.2 V, **where the batteries were maintained at each end voltage for 3-5 hours**. The charging current was maintained 50 $\mu\text{A cm}^{-2}$ while the discharging current was varied from 50, 100, 200, 500, and 1000 $\mu\text{A cm}^{-2}$.

Results and Discussion

Figure 1(a) shows a SEM image of LTP-0, that is, pristine NMC particles. The particles have a spherical shape with ca. 10 μm in diameter. Figures 1 (b-e) show the SEM images of LTP-2, -5, -10, and -20, respectively. Sub-micron-sized LATP particles are attached on the NMC particles. Almost all the LATP powder appeared to attach onto the NMC particles in cases of LTP-2 and LTP-5, while some of the LATP powders were disconnected from the NMC particles in cases of LTP-10 and LTP-20.

In order to estimate the coverage ratio of LATP on the NMC in these mixed powders, both cross-sectional SEM observations and EDX analyses were conducted. Figure 2(a) shows cross-sectional SEM and EDX mapping images for Mn-K (NMC region) and P-K (LATP region) of LTP-5. Here, the coverage ratio by LATP was estimated through image analysis as follows. These two EDX mapping images were overlapped into one picture. We considered the length of outer perimeter of the Mn-K region as surface area of NMC (L_{NMC}). Also, the total length of the overlap region between the Mn-K and P-K peaks was considered as the covered area by LATP (L_{LATP}). Then, the coverage ratio was estimated as $L_{\text{LATP}}/L_{\text{NMC}}$. This measurement was carried out for 5 particles in each mixed powder. The variation of these coverage ratios in the mixed powders is summarized in Fig. 2(b), where the average value is shown on each sample. The coverage ratio tended to increase with increasing LATP weight ratio until

LTP-5, where the coverage ratio reached 68% for LTP-5. This coverage ratio was maintained even in cases of LTP-10 and LTP-20, where additional amounts of LATP particles were not attached as shown in Figs. 1(d) and 1(e).

Figure 3(a) shows cross-sectional SEM images of the composite films fabricated on Si/SiO₂ wafers using LTP-2, -5, -10, and -20. Although LTP-0 did not form a film on the Si/SiO₂ wafer as previously reported [11], LTP-X ($1 \leq X$) successfully yielded films. The thickness of the composite films tended to increase with increasing LATP weight ratio in the starting powders. Figure 3(b) summarizes the variations of both thicknesses of composite films and NMC content (volume and weight percentage) in the composite films against the LATP weight ratio in the starting powders. Here, the NMC amount in each film was estimated from the Ni amount measured by ICP, and both the volume and weight contents were calculated from the total weight of the film and densities (NMC: 4.76 g cm⁻³, LATP: 3.06 g cm⁻³). The film thicknesses tended to increase with increasing the LATP weight ratio, while the NMC content in the film tended to decrease. The NMC content in the starting powders was higher than that in the films. For example, the NMC weight ratio in LTP-5 was 93% (5/105), which reduced to 79% in the film. As with our previous results using Nb-O coated NMC powders [11], particle surface region of the starting powder will tend to be incorporated

into the film preferentially, resulting in the increasing of the LATP content in the composite film. Also, the numbers denoted in Fig. 3(b) indicates relative density percentages of the films, where each value was estimated from division of apparent density against theoretical density estimated from deposition area, apparent film thickness measured from SEM image, and densities of NCM and LATP. The values prepared by LTP-1, -3, and -5 provides almost 100%, but those look to reduce in cases of the films prepared by LTP-10 (~90%) and -20 (~80%). This means that there may be a limitation of densification at larger amount of LATP.

Figures 4 (a-d) show the XRD patterns of composite films on Si/SiO₂ wafers using LTP-1, -5, -10, and -20, respectively. Also, Figures 4(e-f) show the XRD patterns of the pristine NMC and the LATP, respectively. All the diffraction peaks from the films are assigned to NMC and LATP except for the substrate peak of Si/SiO₂ wafer at 52.9° and 55.6°. This demonstrates that crystalline NMC and LATP glass ceramics composite films were prepared on Si/SiO₂ wafers at room temperature as evidenced by a lack of any unindexed peaks associated with any possible reaction products. In these patterns, the diffraction intensity is normalized by the 003 peak of NMC at 18.7°, and the diffraction peak intensity from LATP appears to increase with increasing the LATP amount in the starting powders. This trend is consistent with the

variations of the NMC amount in the films shown in Fig. 3(b). Also, Figures 4(g-i) show the XRD patterns of LTP-100, and those after thermal treatment at 700°C and 900°C in air, respectively. As shown in those patterns, once LTP-100 were heated over 700°C, new peaks appeared at around 23.0°, 30.3°, 35.7°, 43.3°, and 63.2° probably because of the formation of a mutual diffusion layer between NMC and LATP. Because the AD process does not need any heating for densification of the film, those side reactions will be virtually eliminated, and then the resultant AD films do not show those new peaks.

Figure 5(a) shows the cross-sectional FE-SEM image of the composite film prepared by LTP-5 fabricated on a Si/SiO₂ wafer, and Figure 5(b) shows the EDX mapping image for Si-K, Mn-K, and P-K of the film. Signals from Si-K represent the Si/SiO₂ wafer region. Comparing the FE-SEM with the EDX mapping images, it is clear that black and white contrast regions in Fig. 5(a) correspond to P-K (LATP) and Mn-K (NMC), respectively. Both NMC and LATP appear to be dispersed uniformly at the submicron scale, and a dense composite film is formed. Three-dimensional reconstructed image of the LATP region in the composite electrode is displayed in Fig. 5 (c), where each sliced image was measured repeatedly by FIB-SEM. The LATP region does not present as the layered state but instead forms a three-dimensional

network. The total volume amount of voids over the 20 nm in diameter was estimated to be ca. 0.15% [15]. Figure 6 shows a TEM image around a NMC/LATP interface in the composite film prepared by LTP-5, and EDX line profiles of Ni-K, Mn-K, Co-K, O-K, P-K, and Ti-K are overlapped on the image. EDX signals from Ni-K, Mn-K, and Co-K appear almost constant and the gradual slope of these signals is observed ca. 5 nm around the interface. Even if this region is considered as a mutual diffusion layer between NMC and LATP, its thickness is approximately one order of magnitude smaller value than that of other SSBs (LiCoO₂/LLZ: ~80 nm [16], LiCoO₂/Li₂S-P₂S₅ : ~20 nm [17], LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂/LATP: ~20 nm [18]). This thinner mutual diffusion layer is consistent with the XRD data.

The electrochemical properties of the composite films prepared by LTP-5 were investigated using Ox-SSBs as Li/LLZ/NMC-LATP composite films. Figure 7(a) shows the cross-sectional SEM image around the LLZ/NMC-LATP composite film interface. The composite film with thickness of 20 μm was densely formed even on the LLZ substrate. Figure 7(b) shows the charge-discharge curves of this Ox-SSB measured by CC/CV modes at 100 °C. The charge current density was maintained at 50 μA cm⁻² (C rate: ca. 1/10 C), and the discharge current density was varied from 50-1000 μA cm⁻². The charging curve after 2 cycles followed almost the same profile

even after discharging at higher current densities. A specific discharge capacity of 135 mAh g⁻¹, based on the weight of NMC in the composite film, was obtained at 50 μA cm⁻² and this value decreased with the increasing of current densities, and decreased to 17 mAh g⁻¹ at 1000 μA cm⁻². Figure 7(c) summarizes the cycle performance of this Ox-SSB. Here, initial 11 cycles were carried out at different current densities as shown in Fig. 7(b), and later the charge-discharge reactions were repeated for 79 cycles at a constant discharge current density of 50 μA cm⁻². The Ox-SSB maintained 97% of the first cycle after 90 cycles (capacity retention: 99.97 % / cycle), indicating that this Ox-SSB undergoes stable charge-discharge reactions. One reason for this stable reaction will be due to the usage of NMC as an electrode material well known to undergo quite small volume change [19]. Of course, tiny amount of volume change can still provide serious stress inside the composite electrode. However, this composite material uses glass-ceramics as the solid electrolyte and it is expected that glass-ceramics can prevent the crack growth because nano-sized crystalline particles distribute the strain energy and reduce the crack growth. Thus, fabrication of composite electrodes using glass-ceramics may play an important role to stabilize the battery reactions.

Figure 8 summarizes the variation of specific discharge capacity and electrode utilization (%) at a given current density of Ox-SSBs with different thickness of composite films (4, 7, and 20 μm) prepared by LTP-5. Here, 100% utilization was set to 150 mAh g^{-1} [20]. Three kinds of resistance terms, that is, Li/LLZ interfacial resistance, resistance of LLZ substrate, and LLZ/composite film interfacial resistance, will contribute in the same manner in these batteries. On the other hand, the resistance by both Li^+ diffusion in NMC and interfacial resistance at the NMC/LATP interface in the composite film should increase with reducing film thickness because the reaction rate at each NMC grain becomes high with reducing the film thickness. The electrode utilization increased with reducing the film thickness, indicating that those two resistances do not determine rate capability in these cases. This will be given by a thin mutual diffusion layer at the NMC/LATP interface due to the room temperature densification by the AD process. Therefore, the most probable resistance correlates with Li^+ transport and electron conduction in the composite film. In fact, we preliminarily prepared a composite film (16 μm in thickness) using LTP-10 with an addition of small amount of RuO_2 as an electronically conductive component, and found that the electrode utilization increased up to ca. 40% (60 mA g^{-1}) at 1 mA cm^{-2} , though the electrode capacity was not fully utilized even at $50 \mu\text{A cm}^{-2}$. This result clearly

indicates that we need to design three-dimensional electrode-solid electrolyte composites including both Li^+ transport and electronic conductivity in the film. The amount of LATP can be controlled by controlling the LATP mixing amount as shown in Fig. 3(b). Also, there must be several other methods and materials to enhance electronic conductivity in the composite films. These two factors will further improve the rate capability of these batteries.

Conclusion

We prepared $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2\text{-Li}^+$ conductive glass-ceramics solid electrolyte (LATP: $\sigma_{\text{Li}^+} \sim 10^{-3} \text{ S cm}^{-2}$ at 298 K) dense composite films by aerosol deposition (AD) and revealed that an all-solid-state battery comprised of Li/LLZ/NMC-LATP composite film (20 μm in thickness) undergo repeatable and stable charge-discharge reactions for 90 cycles at 100° C with a 1/10 C rate. These stable charge-discharge reactions with thick composite cathode films are ascribed to the incorporation of glass-ceramics solid electrolyte in the composite films in addition to the usage of NMC with small volume change during the charge-discharge reactions. Also, the resultant NMC/LATP interface in a composite film had a thin mutual

diffusion layer (~5 nm) and the film had small amount of porosity (ca. 0.15% in volume) in addition to well-adhesion to the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) substrate. The electrode utilization of the composite film improved by reducing the film thickness at a given current density, indicating that resistances due to lithium diffusivity in NMC and Li^+ transfer at the NMC/LATP interface **did not determine rate capability**. Further improvements of this battery cell design will be afforded by optimizing the configuration of Li^+ and electron conduction in the composite film. The AD that can realize heat-free ceramics densification will provide new possibilities and ideas for the scaling-up of all-solid-state batteries using oxide-based solid electrolytes.

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Figure Captions

Figure 1 SEM images of (a) NMC pristine powder (LTP-0) and the mixed powders of NMC and LATP with the weight ratios of (b) 100:2 (LTP-2), (c) 100:5 (LTP-5), (d) 100:10 (LTP-10), and (e) 100:20 (LTP-20).

Figure 2 (a) Cross-sectional SEM image of LTP-5 and the EDX mapping of Mn and P, and (b) estimated LATP coverage ratio on the NMC particles against the LATP weight ratios in the mixed powder.

Figure 3 (a) Cross-sectional SEM image of the composite films formed on Si/SiO₂ wafers by LTP-2, LTP-5, LTP-10, and LTP-20. (b) Relationships between the NMC-LATP weight percentage in the starting powders on both the film thickness (left axis) and the NMC content in the films (right axis; open circles are volume % and open triangles are weight %). Numbers in Fig. 3(b) mean the relative density % of each composite film.

Figure 4 XRD patterns of the NMC-LATP composite films on Si/SiO₂ wafers prepared by (a) LTP-1, (b) LTP-5, (c) LTP-10, (d) LTP-20, as well as powders of (e) pristine NMC (LTP-0), (f) pristine LATP, (g) mixed powder of NMC and LATP (1:1 in weight ratio; LTP-100), (h) LTP-100 after heating at 700 °C, and (i) LTP-100 after heating at 900 °C.

Figure 5 (a) Cross-sectional SEM images of a NMC-LATP composite film on Si/SiO₂ wafer by LTP-5. (b) EDX mapping of Mn (yellow), P (purple), and Si (Pink) of the composite film prepared by LTP-5. (c) Three-dimensional reconstructed image (20×20 μm² in area) of the LATP region in NMC-LATP composite film prepared by LTP-5.

Figure 6 TEM image around a NMC/LATP interface in the NMC-LATP composite film prepared by LTP-5, and EDX line profiles of Ni-K, Mn-K, Co-K, O-K, P-K, and Ti-K overlapped on the image.

Figure 7 (a) Cross-sectional SEM image around the LLZ/NMC-LATP composite film prepared by LTP-5. (b) Charge-discharge curves of an all-solid-state battery, Li/LLZ/NMC-LATP composite film prepared by LTP-5, measured at 100 °C. The charge current density was maintained at 50 μA cm⁻², and the discharge current density was varied from 50-1000 μA cm⁻². (c) Specific discharge capacity versus cycle number for the all-solid-state battery cell.

Figure 8 Variation of specific discharge capacity and electrode utilization (%) at a given current density (50-1000 μA cm⁻²) of the all-solid-state battery, Li/LLZ/NMC-LATP composite film prepared by LTP-5, with different thickness of composite films (4, 7, and 20 μm).