Preparation of thick-film $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrodes by aerosol deposition and its application to all-solid-state batteries

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Abstract

We prepared thick and dense- crystalline $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) composite films at room temperature that can work well as cathodes in all-solid-state battery cells. The thick films were fabricated by aerosol deposition using NMC powder ($D_{50}=10.61\text{ }\mu\text{m}$) as a source material. Commercially-obtained NMC powder did not form films at all on silicon wafer substrates, and cracking of the substrates was observed. However, a few tens of nanometer coating with amorphous niobium oxide resulted in the deposition of 7 μm -thick crystalline dense composite films. The films were successfully fabricated also on Li^+ -conductive glass-ceramic sheets with 150 μm in thickness, and all-solid-state batteries were fabricated. The solid-state battery provided a cathode-basis discharge capacity of 152 mAh g^{-1} (3.0-4.2 V, 0.025 C, 333 K) and repeated charge-discharge cycles for 20 cycles.

Introduction

Development of solid electrolytes with high ionic conductivity and reduction of interfacial resistance at the electrode-solid electrolyte interface are key hurdles to surmount in the design of better-performing solid-state batteries (SSBs). Lithium-ion conductive inorganic solid electrolytes used in the SSBs are roughly categorized as sulfide-based and oxide-based solid electrolytes, and presently the ionic conductivity at room temperature of $1 \times 10^{-2} \text{ S cm}^{-1}$ [1] and $1 \times 10^{-3} \text{ S cm}^{-1}$, [2,3] respectively, have been attained. Thus, practical lithium ionic conductivity in these solid electrolytes has reached comparable values to conventionally-used organic liquid electrolytes ($1 \times 10^{-2} \text{ S cm}^{-1}$, $t_{\text{Li}^+} \sim 0.3$). Also, several methods such as coating, [4] annealing, [5,6] and in-situ formation of the interface [7] have been proposed to reduce the interfacial resistivity, and some of these values have been demonstrated to be less than about $100 \Omega \text{ cm}^2$, on par with those observed for liquid electrolyte cells. [8]

Nevertheless, studies on SSBs toward high capacity are mainly limited to the SSBs using sulfide-based solid electrolytes (S-SSBs), while the SSBs using oxide-based solid electrolytes (Ox-SSBs) are typically thin-film format with low capacity. The difference of these SSBs arises from the convenience of electrode-solid electrolyte interface construction. Electrode active materials (LiCoO_2 , LiFePO_4 , etc) are common in these SSBs, but they are not, in general, soft materials. In comparison, the sulfide-based solid electrolytes are soft and have lower Young's

moduli than oxide-based solid electrolytes.^[9] Therefore, in case of the S-SSBs, mixing and cold pressing electrode powders with sulfide-based solid electrolyte powders realize well-adhered interfaces so that various kinds of combinations and/or volume ratios of electrode and solid electrolyte can be examined as SSBs.^[1,10,11] On the other hand, oxide-based solid electrolytes are fragile and are hard materials. Thus, the above-mentioned composite process tends to produce point contacts at the interface. This problem inevitably increases grain boundary resistance and reduces the number of electrochemically active sites at the interfaces, resulting in poor capacity battery cells. Alternatively, Ox-SSBs mostly adopt a thin-film format, where each electrode and solid electrolyte are piled up sequentially as layers by sputtering,^[5,12] pulsed laser deposition,^[13,14] sol-gel,^[15] etc. However, these methods require heating processes for the crystallization of electrode and/or solid electrolyte, and the mismatch of the thermal stabilities and their reactivities limit the combination between electrode and solid-electrolyte and then scaling-up of Ox-SSBs. Thus, it is highly desirable to find a novel method to develop dense electrode and oxide-based solid electrolyte composites at room temperature as with the sulfide-based solid electrolyte systems.

Aerosol deposition (AD) is a film fabrication technique using powder as a source material. The starting particles are ejected from a nozzle at high speed onto the substrate, and then the particles are fractured. This induces both deformation of the particle and enhancement of surface activity by the newly-formed surface, resulting in the densification of the films.^[16] A unique

feature of this technique is that crystalline films can be prepared at room temperature.^[17] Although this method has been already used to prepare several electrode **active materials** ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$,^[18] LiFePO_4 ,^[19] Si ^[20]) and solid electrolytes,^[21] there are no reports on the fabrication of dense composites that can be used effectively in Ox-SSBs. In this work, we will show that dense and thick composites composed of crystalline electrode material ($\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC)) and amorphous solid electrolyte (Li-Nb-O) are fabricated at room temperature by AD and that the composite works well in Ox-SSBs.

Experimental

Pristine NMC powder (D50=10.61 μm) was purchased from Nihonkagaku, Japan. The powder was coated by niobium ethoxide (purity: 99.95 %, Aldrich) distilled by anhydrous ethanol (Kanto Kagaku, Japan) as 1:8 in weight ratio using a tumbling fluidized bed granulating-coating machine (MP-25, Powlex, Japan) with the coating rate of 2 g min⁻¹ by compressed air. The coating thickness was controlled by **total coating amount to a tested powder** so that the theoretical coating thickness becomes 10, 20, 30, and 40 nm in Nb_2O_5 equivalent, which will be denoted as NMC-10, -20, -30, and -40, respectively, described later. Pristine NMC powder without coating will be denoted as NMC-0. These powders were heated at 673 K in air just before the usage to remove organic elements derived from the coating substance, but X-ray diffraction (XRD) and differential

scanning calorimetric analyses revealed that the resultant coating layer of a Nb-O maintained an amorphous state. Both the pristine and the coated powders were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDX). As shown in supplemental figure 1, Nb-O layer was coated on the particle surface uniformly. Also, the molar ratio of Li, Ni, Co, Mn, and Nb of the NMC-30 was measured by inductively coupled plasma spectroscopy (ICP) measurements. The work functions of NMC-0, SUS304, and coating layers (Si-O and Nb-O) were measured in air by photoelectron yield spectroscopy (AC-2, AC-3, Riken Keiki, Co., LTD).

The AD system setup was a general one as described in detail elsewhere.^[22] All the carrier tubes were made from SUS 304. The coated or uncoated NMC powders of 20 g were introduced in aerosol container. The chamber was evacuated by vacuum pump to 3-5 Pa and the chamber pressure was kept at $4-8 \times 10^{-3}$ Pa during the deposition. Substrates were set inside the deposition chamber, and the substrate was not heated at all during the deposition. The powder was injected into the chamber by Ar (5N) with the flow rate of 10 L min^{-1} (at 100 kPa). The ejected powder from the nozzle ($10 \text{ mm} \times 0.23 \text{ mm}$ in area) was sprayed on the substrate and then films were deposited. The substrates were moved back and forth for 50 mm in length during the deposition at a rate of 50 mm min^{-1} for 40 times (40 min.). Substrate species were SUS304 (thickness (t) = 100 μm), Si/SiO₂ wafer ($t = 1 \text{ mm}$), and NASICON-structured Li⁺ conductive

glass-ceramic sheet (LATP-sheet: Ohara Inc. Japan, 150 μm in thickness).^[3] The resultant films were characterized by XRD, SEM, EDX, cross-sectional TEM, selected area electron diffraction (SAED), and ICP measurements.

Films of the NMC-30 were deposited on one side of the LATP-sheet and then a platinum current collector ($t = 100\text{ nm}$) was deposited on it by R.F. magnetron sputtering. The opposite side of the LATP-sheet was covered by lithium phosphorus oxynitride glass electrolyte (LiPON^[23]) with 2.5 μm in thickness by R.F. magnetron sputtering with the deposition rate of 0.1 $\mu\text{m h}^{-1}$. Deposition conditions of the LiPON films were same with the past report.^[6] After that, a lithium metal anode was deposited on the LiPON film by vacuum evaporation in an Ar-filled glove box, and then an Ox-SSB, Li/LiPON/LATP-sheet/NMC-composite-film/Pt, was prepared. Charge-discharge tests of the resultant batteries were carried out by 5 or 10 $\mu\text{A cm}^{-2}$ at 298 or 333 K in an Ar-filled glove box.

Results and Discussion

Figures 1(a)-(e) show the cross-sectional SEM images of the cathode films prepared by NMC-0, -10, -20, -30, and -40. Cathode films were formed successfully by using Nb-O coated NMC powders in all cases. The mean thickness of the films gradually increased with the increasing Nb-O coating thickness. Figure 1(f) shows the XRD patterns of the cathode films.

Except for the diffraction peak at 53° from the substrate, all the diffraction peaks were assigned to NMC.^[24] On the other hand, the NMC-0 did not form a cathode film at all. Clearly, the presence of a Nb-O layer on NMC powder is an important variable in cathode film deposition by AD.

In addition to the presence of a Nb-O layer, particle size has been recognized as an important factor to prepare dense films by AD, and large-sized particles over a few micrometers in diameter tend to physically etch the substrate and then films are not formed.^[16,25] The NMC-0 follows this tendency, but a few tens of nm-coating by a Nb-O layer on NMC powder changes the cathode film deposition mechanism. Figure 1(g) summarizes the molar percentage of Li, Ni, Co, Mn, and Nb in the films prepared by NMC-10, -20, -30, and -40. Data of the NMC-30 is also shown as a reference. Because NMC-30 is just covered with a Nb-O layer on pristine NMC powder, the molar ratio of Ni, Co, Mn, and Li in all the starting powders is same and is estimated from the ICP data of the NMC-30 in Fig 1(g). The molar percentage of Ni, Co, and Mn is 16.3, 16.4, and 16.4, respectively, which means that their ratio is even (0.33: 0.33: 0.33) in all the starting powders. In the same manner, molar ratio of Li/(Ni+Co+Mn) in the starting powder is calculated to be 1.02, indicating that lithium is slightly rich as compared with the stoichiometry, 1.00. A noted trend is that molar ratio of Ni:Co:Mn varied to (0.32:0.33:0.35) in all the films. Fuchita *et al.* has pointed out local plasma formation and sputtering during the AD process by a fracture of electrostatically charged particle,^[25] where the electrostatic charge is produced by the friction

between the particle and the carrier pipe during the transfer. The sputtering ratio is generally influenced by the bonding energy, and its order in the NMC will be $\text{Ni} > \text{Co} > \text{Mn}$ because these elements occupy same crystallographic positions with nearly equivalent ionic radii^[26] and their valences are +2, +3, and +4, respectively.^[27] Therefore, the variation toward uneven molar ratio of the transition metals in the films ($\text{Ni} < \text{Co} < \text{Mn}$) can be explained by the preferential removal of the elements with higher sputtering ratio. Also, we found that an amorphous Si-O coating (20 nm in thickness) does not assist the film preparation. The work function of SUS304 (carrier pipe), NMC-0, Si-O coating layer, and Nb-O coating layer was 4.9, 5.4, 5.4 and 6.2 eV, respectively. Thus, a Nb-O coating layer may facilitate electrostatic charge to the Nb-O coated powders, leading to the enhancement of local sputtering and the surface activities. These composite films were formed even on polycarbonate substrates with a melting point of 500 K, demonstrating that the substrate temperature is kept less than 500 K during the AD process.

Figure 2(a) shows the cross-sectional TEM image of the film prepared on SUS304 substrate by the NMC-30. The film has a dense structure. The SAED patterns observed from this TEM image is shown in Figure 2(b). All the patterns are assigned to NMC, which is consistent with XRD analysis. Figure 2(c) shows the EDX mapping measured in Figure 2(a). Oxygen was recognized uniformly in the image. Also, Co, Mn, and Ni show common distribution, where it is assigned to NMC grains. It is interesting to note that Nb fills the voids of the NMC grains and

forms 3D nano-networks. High resolution TEM image observed around a void of NMC grains is shown in Figure 2(d). The SAED patterns reveal that the void (A : Nb region) is an amorphous state, while the NMC region (B) is a crystalline phase. The molar ratio of Nb/(Ni+Co+Mn) in the NMC-30 is calculated to be 1.22×10^{-2} , which increased to 8.55×10^{-2} in the film prepared by the NMC-30. Also, this value tended to increase in proportion with the coating thickness and varied from 3.80×10^{-2} (film by the NMC-10) to 10.2×10^{-2} (film by the NMC-40). These results indicate that the surface region in the starting powders is preferentially incorporated into the films. In addition, the molar ratio of Li/(Ni+Co+Mn) has increased from 1.07 (film by the NMC-10) to 1.12 (film by the NMC-40), where these values exceed 1.02 measured in the starting powders. Thus, we can expect that an excess amount of lithium present at the amorphous region that forms amorphous Li-Nb-O, known as a lithium-ion conductive solid electrolyte.^[28] Because the starting powder is slightly lithium-rich against stoichiometry as mentioned above, surface excess lithium on the starting powder may be the lithium source of Li-Nb-O formation.

Films prepared by the NMC-10, -20, -30, and -40 were deposited on SUS304 substrates and their electrochemical properties were investigated in a solution of 1 mol dm^{-3} LiClO₄ dissolved in propylene carbonate at 298 K. Figure 3 shows the charge-discharge curves of the 1st cycle of these films, where current density of $100 \text{ } \mu\text{A cm}^{-2}$ was supplied in all cases. The capacity of the film is calculated from total weight of the composite film including amorphous Li-Nb-O. A gradual

increase of the discharge capacity with increasing the thickness of a Nb-O layer is probably because of the difference of C-rate due to the difference in film thickness as shown in Figure 1(a). On the other hand, the film prepared by the NMC-40 was thicker than that of the NMC-30, but the former film had smaller capacity. The composite films do not include any kinds of conductive additives. The film prepared by the NMC-40 has a larger amount of Li-Nb-O from ICP analysis, and an excess amount of Li-Nb-O probably increases the less conductive or isolated cathode region in the films, resulting in the lower capacity.

The film prepared by the NMC-30 was thick and delivered the largest capacity among the films in the liquid electrolyte, and then the film (~7 μm in thickness) prepared by the NMC-30 was tested as Ox-SSBs. The film was formed on the LATP-sheet as shown in the inset SEM image of Figure 4(a). Figure 4(a) shows the initial charge-discharge curves of an Ox-SSB, Li/LiPON/LATP-sheet/NMC-composite-film by the NMC-30/Pt at 5 $\mu\text{A cm}^{-2}$ (0.025 C) at 298 K and 333 K. The LiPON was used to prevent the direct reaction between the LATP sheet and Li metal.^[7] The gravimetric capacity is calculated from *total weight of the composite film*. The discharge capacity was 87 mAh g⁻¹ at 298 K, which increased to 138 mAh g⁻¹ at 333 K. The amount of NMC in this composite film was estimated to be 91% from ICP analysis supposing that all the Nb included in the films formed crystalline LiNbO₃. This indicates that the NMC in this film supplies a discharge capacity of 152 mAh g⁻¹, almost consistent with the value reported in liquid electrolyte.^[29]

Figure 4(b) shows the cycle performance of the Ox-SSB at 333 K at $10 \mu\text{A cm}^{-2}$. Charge-discharge reactions were repeated for over 20 cycles. Although the Ox-SSB did not deliver sufficient capacity at $100 \mu\text{A cm}^{-2}$ as with in liquid electrolyte, this will arise from the difference of texture between the thick-film electrode and the LATP-sheet or liquid electrolyte producing interfacial resistivity. Further improvement of three-dimensional electrode-solid electrolyte composite fabrication is currently examined.

Conclusion

Dense composite films of crystalline NMC electrode with 3D-nano-network amorphous solid-electrolyte, Li-Nb-O, were prepared by the AD at room temperature. Amorphous Nb-O coating on NMC powder is an important parameter for the dense composite-film formation. The resultant composite film works well as an electrode material in an Ox-SSB. This heating-free densification process will enable other kinds of combinations of electrode-solid electrolyte materials in Ox-SSBs, which will be useful for the scale-up of the Ox-SSBs. In the current stage, we have succeeded in preparing LiCoO_2 dense films with $50 \mu\text{m}$ in thickness on Si wafers (supplemental figure 2) just by repeating the deposition cycles.

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Figure Captions

Figure 1. (a-e) Cross sectional SEM images of the films deposited on Si wafer by aerosol deposition.

The starting powders were (a) NMC-0, (b)NMC-10, (c)NMC-20, (d)NMC-30, and (e)NMC-40. (f)

XRD patterns of these films. Diffraction data of both the Si wafer and pristine NMC powder are

shown as a reference. (f) Molar percentage of Li (black), Mn (blue), Co(green), Ni(red), and

Nb(purple) in these films and the NMC-30 measured by ICP. The numbers in the Figure 1(f) mean

the precise values of each element.

Figure 2. (a) Cross-sectional TEM image of the film prepared by the NMC-30 on stainless steel

substrate. (b) SAED pattern measured in Fig. 2(a). (c) EDX mapping data of Nb, O, Co, Mn, Ni in

Fig. 2(a). (d) Magnified TEM image measured around Nb (A) and NMC (B) regions and their

SAED patterns.

Figure 3. Initial charge-discharge curves of the films prepared on stainless steel substrate by

NMC-10, -20, -30, and -40 in 1 mol dm⁻³ LiClO₄ dissolved in propylene carbonate at 298 K. $I =$

100 $\mu\text{A cm}^{-2}$.

Figure 4. (a) Initial charge-discharge curves of all-solid-state battery

(Li/LiPON/LATP-sheet/NMC-composite-film by the NMC-30/Pt) at 298 K (blue) and 333 K (red).

$I = 5 \mu\text{A cm}^{-2}$. The inset shows the cross-sectional SEM image around the composite film

electrode/LATP-sheet interface. (b) Cycle performances of the above all-solid-state battery at 333

K. $I = 10 \mu\text{A cm}^{-2}$.

Iwasaki et al. Fig. 1