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Preparation of thick-film electrode-solid electrolyte composites on $Li_7La_3Zr_2O_{12}$ and their electrochemical properties

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HIGHLIGHTS

- Electrode–solid electrolyte composite films up to 20 μm are prepared on $Li_7La_3Zr_2O_{12}$.
- Thickness of mutual diffusion layer in the composite is ca. 5 nm.
- All-solid-state battery has capacity retention of 99.97% per cycle at 100 ° C.
- The battery delivered discharge capacity even at 1 mA cm^{-2}.

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ABSTRACT

We prepared up to 20 μm-thick $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC)-Li^+ conductive glass–ceramic solid electrolyte (LATP: $\sigma_{Li^+} \sim 10^{-3}$ S cm^{-2} at 298 K) composite cathode films on $Li_7La_3Zr_2O_{12}$ (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 (~5 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}.

1. 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 $Li_3V_2(PO_4)_3$ (LVP) was used as both positive and negative electrodes and $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) as the solid electrolyte

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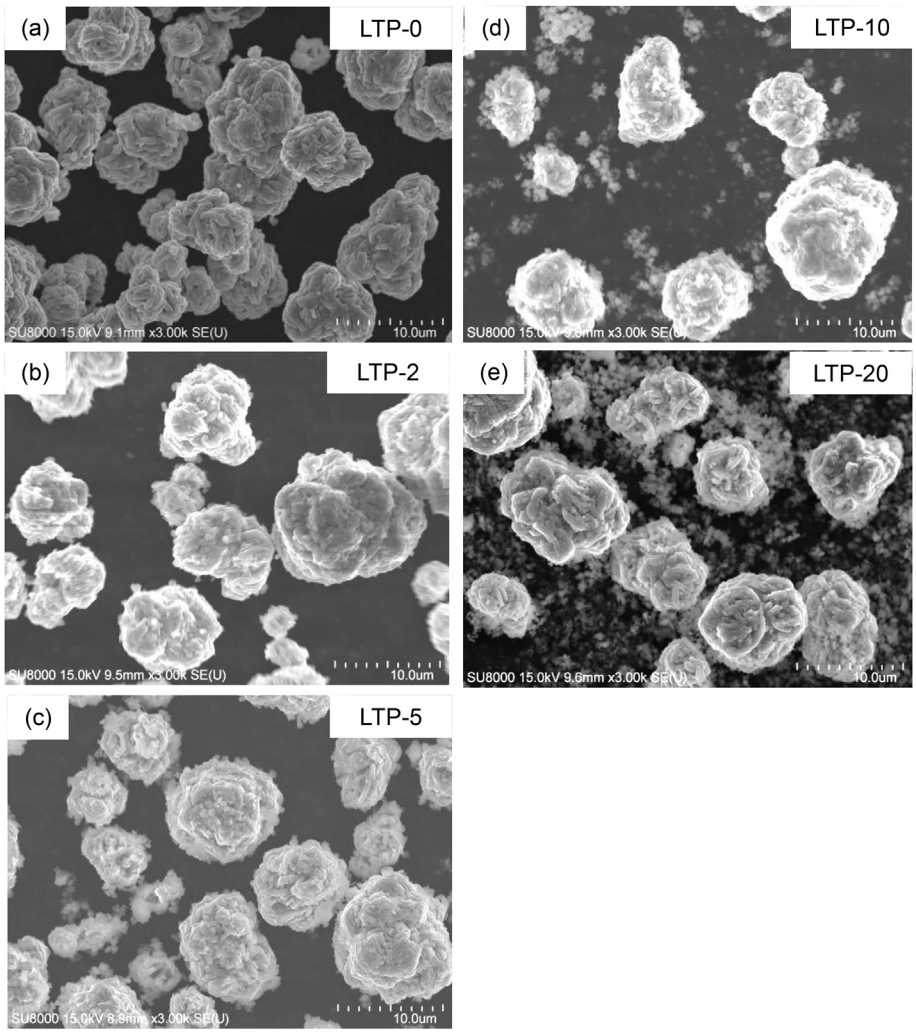

Fig. 1. SEM images of (a) NMC pristine powder (LTP-0) and the mixed powders of NMC and LATP with the weight ratios of (b) 100:2 (LTP-2), (c)100:5 (LTP-5), (d)100:10 (LTP-10), and (e)100:20 (LTP-20).

[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 $Li/Li_7La_3Zr_2O_{12}/LiCoO_2$–$Li_3BO_3$ 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 $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (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} 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} 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 1/10C 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}.

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 (D50 = 10.61 μm, Nihonkagaku, Japan) as the mother powder. This cathode powder was well mixed with LATP powder (D50 = 0.5 μm, Ohara Inc., Japan [13]) by a powder