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Development of complex hydride-based all-solid-state lithium ion battery applying low melting point electrolyte

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HIGHLIGHTS

- All-solid-state battery with oxide and complex hydride electrolyte was developed.
- Low melting point $LiBH_4+2LiNH_2$ reduced contact resistance among these electrolytes.
- Repeated operation was demonstrated at 150 °C due to the reduced contact resistance.
- Our battery realized a discharge capacity of 114 mAh g^{-1}.

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ABSTRACT

A thermally durable all-solid-state lithium ion battery composed of a complex hydride, oxide electrolytes, and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ active material is developed. This battery exhibits a discharge capacity of 56 mAh g^{-1}, and the tenth capacity retention ratio is 29% at 150 °C owing to the large contact resistance between the electrolyte layer and the composite positive electrode layer. This large contact resistance is reduced by introducing an adhesive layer comprised of a mixture of $LiBH_4$ and $LiNH_2$ that is easily melted by thermal treatment and fills the voids and pores at the interface between the two layers. As a result, repeated charge-discharge cycles are successfully demonstrated at 150 °C with a high discharge capacity and discharge capacity retention ratio. The first discharge capacity is enhanced to 114 mAh g^{-1} and the capacity retention ratio at the tenth cycle is improved to 71%. These results demonstrate that using an adhesive layer is an effective measure to reduce the contact resistance and thereby enhance the performance of the battery.

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1. Introduction

The all-solid-state lithium ion battery is considered a promising candidate for next-generation energy storage devices for electric vehicles, smart grids, and wearable devices [1,2]. Although conventional lithium ion batteries have excellent properties such as high volumetric and gravimetric energy densities as well as high power density, using volatile and flammable electrolyte solvents causes safety issues which are currently problematic for the lithium ion batteries [3]. In addition, insufficient thermal stability of the electrolytes limits the battery operating temperature (the volatile and decomposition temperature of an electrolyte based on $LiPF_6$ is about 90 °C [4]). One of the measures to overcome such issues is to use a non-volatile and thermally stable solid-state electrolyte instead of the electrolyte solutions [1].

Among the solid-state electrolytes discovered thus far, a complex hydride, typically a high-temperature phase of $LiBH_4$, is considered as a candidate for solid-state electrolytes because it allows for assemblies of thermally durable all-solid-state batteries [5–9]. Complex hydride electrolytes possess excellent properties including high temperature durability (pyrolysis unlikely occur at temperatures lower than 320 °C), high electrochemical stability (electrochemical potential window is 0–5 V *vs.* Li/Li^+), and high compatibility with lithium metal electrodes (forming an interface with a negligibly small interfacial resistance) [10–12]. $LiBH_4$ undergoes a phase transition from an orthorhombic structure to a

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hexagonal structure at 118 °C [10,13,14]. Then, the hexagonal $LiBH_4$ phase realizes a high lithium ionic conductivity of 2×10^{-3} S cm^{-1} at 120 °C. Researchers have recently taken advantage of these characteristics and incorporated the complex hydride electrolyte into all-solid-state lithium ion batteries [5–9]. Charge and discharge of the battery have been successfully demonstrated with a composite electrode with TiS_2 [5], S [6], and $Li_4Ti_5O_{12}$ [7] as an active material and $LiBH_4$ as a solid electrolyte. In addition, fast lithium ionic conduction at reduced temperatures is achieved by doping lithium halides including LiCl, LiBr, and LiI to stabilize the high-temperature phase of $LiBH_4$ [15]. Notably, $Li_4(BH_4)_3I$ (LBHI) has a high lithium ionic conductivity of 2×10^{-5} S cm^{-1} at 25 °C [15].

Complex hydrides have high reducing ability. Although the class of the materials allows for establishing a stable interface with metallic lithium electrodes, this high reducing ability rather invites a reductive decomposition of high voltage positive electrodes including $LiCoO_2$ (LCO). Takamura et al. developed a thin-film-type all-solid-state battery comprised of a LCO thin film positive electrode, $LiBH_4$ electrolyte, and lithium negative electrode. They reported that the cell resistance becomes more than 10^4 Ω due to the reductive decomposition of delithiated LCO by contacting with $LiBH_4$ [8]. To avoid this decomposition, a thin Li_3PO_4 interlayer with a 25-nm thickness is introduced between the LCO and a complex hydride electrolyte to protect LCO from direct contact with hydride electrolyte, and as a result, cell resistance is successfully reduced. The cell resistance was only 90 Ω, and the discharge capacity retention ratio is 97% after 30 cycles [8,9]. Their report suggests that repeated battery operation can be assured if direct contact between positive electrode active material and $LiBH_4$ electrolyte is prevented by introducing a solid oxide electrolyte.

From the viewpoint of energy density and battery capacity, a bulk-type battery configuration with a composite electrode comprised of mixtures of active material particles of a few dozen micrometers and electrolyte is preferable to the thin-film-type battery [16]. Considering this, we develop a bulk-type battery, as shown in Fig. 1. The positive electrode layer is composed of a solid oxide electrolyte, Li_3BO_3 doped with TiO_2 (LBO-TiO), and a $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) positive electrode active material. LBHI is used as an electrolyte layer. LBO-TiO is introduced in the composite layer to avoid direct contact between NMC and LBHI. LBHI and a Li metal are utilized for the electrolyte layer and negative electrode, respectively.

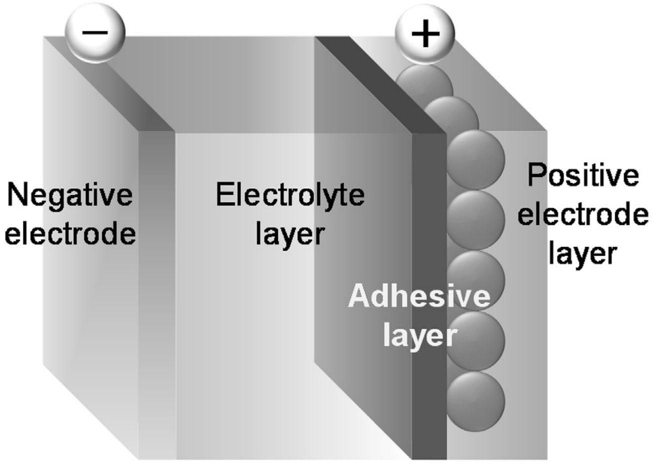

Fig. 1. A schematic illustration of our battery design. A composite positive electrode layer is comprised of an NMC active material with an LBO-TiO solid oxide electrolyte. An adhesive layer $LiBH_4+xLiNH_2$ ($x = 1$ or 2) is placed between the composite positive electrode and LBHI electrolyte layers. Lithium metal is used as a negative electrode.

Although thin-film type battery reported by Takamura et al. can make a tight interface between electrolyte and positive electrode because of flat surface of LCO electrode and Li_3PO_4 interlayer, this composite positive electrode is expected to have a rough surface and hardly make a tight interface with a complex hydride electrolyte. Thus, a $LiBH_4+xLiNH_2$ ($x = 1, 2$) adhesive layer is introduced between positive electrode layer and LBHI based solid electrolyte layer to make tight interface and reduce contact resistance. Since the $LiBH_4+xLiNH_2$ system can melt in temperature range as low as 50–80 °C [17] and exhibits the high lithium ion conductivity of $>1 \times 10^{-4}$ S cm^{-1} at room temperature [6,18], open pores and cracks near the interface is expected to be filled by $LiBH_4+xLiNH_2$ when melted, leading to a low contact resistance. In this study, we study on low melting point electrolyte $LiBH_4+xLiNH_2$ as an adhesive layer to reduce the contact resistance between solid oxide and complex hydride electrolytes in bulk-type all-solid-state lithium ion battery.

2. Experimental

2.1. Preparation of solid state electrolyte powder

LBHI was prepared using a mechanical ball milling method [5]. In an Ar-filled glove box, $LiBH_4$ (>95%, Sigma-Aldrich) and LiI (99.999%, Sigma-Aldrich) were mixed in a 3:1 molar ratio for 30 min in an agate mortar with an agate pestle. The obtained mixture was then transferred into a stainless steel vessel with 20 stainless steel balls (diameter: 7 mm) and sealed to make sure that the vessel was air-proof. Mechanical ball milling was carried out with planetary ball milling equipment (P-7, FRITSCH) at a rotation rate of 400 rpm for 5 h.

$LiBH_4+xLiNH_2$ ($x = 1,2$) for use as an adhesive layer was also prepared by mechanical ball milling. $LiBH_4$ and $LiNH_2$ (95%, Sigma-Aldrich) as starting materials were mixed in 1:1 and 1:2 molar ratios to obtain $LiBH_4+LiNH_2$ and $LiBH_4+2LiNH_2$, respectively.

$Li_7La_3Zr_2O_{12}$ (LLZ, TOSHIMA Manufacturing) was used as received. Synthetic routes, crystal structure analysis, and the thermodynamic study of LBO and LBO-TiO_2 are described in the Supporting Information, Figs. S1 and S2.

2.2. Evaluation of electrochemical property and microstructure of solid-state electrolyte

To form a pellet of complex hydride electrolyte (LBHI or $LiBH_4+xLiNH_2$), the powder was transferred to a die (8 mm in diameter) and uniaxially pressed at 300 MPa at room temperature in Ar filled grove box. To form an electrolyte pellet of LLZ, the powder was transferred to a die (10 mm in diameter) and uniaxially pressed at 200 MPa at room temperature. The obtained LLZ pellet was sintered at 1200 °C for 6 h in a powder bed of LLZ in ambient atmosphere.

The conductivity of the electrolyte pellet was evaluated by electrochemical impedance measurement using a chemical impedance meter (Model 3532-80, Hioki E. E. Corp.) with a two-probe ac technique. For this measurement, symmetric cells were assembled as shown in Fig. 2(a).

Li and In metals were used for assemblies of the symmetric cells and utilized the complex hydrides (LBHI and $LiBH_4+xLiNH_2$) and solid oxide (LLZ), respectively. The conductivities of these cells were determined by Eq. (1),

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