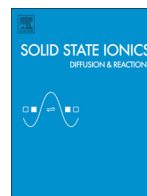




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Complex hydride for composite negative electrode—applicable to bulk-type all-solid-state Li-ion battery with wide temperature operation

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ABSTRACT

A composite negative electrode for use in bulk-type all-solid-state batteries was developed by combining the solid electrolyte $\text{Li}_4(\text{BH}_4)_3\text{I}$ (LiBH_4 doped with LiI), acetylene black (AB) (as a conductive additive), and lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO). Because of the highly deformable nature of the complex hydride, hand milling and subsequent uniaxial pressing were sufficient to ensure tight interfacial contact. As a result, the composite negative electrode allowed successful operation of a bulk-type all-solid-state battery from room temperature (23 °C) to 150 °C. The composite negative electrode was characterized via microstructural observation and using electrochemical techniques. In the prepared composite negative electrode, LTO, $\text{Li}_4(\text{BH}_4)_3\text{I}$, and AB were homogeneously dispersed and formed tightly contacted interfaces. At 150 °C, the battery exhibited high discharging capacities of 170 and 158 mAh g^{-1} for the 1st and 2nd cycles, respectively, which corresponded to LTO utilization ratios of 97% and 90%. Moreover, it retained 140 mAh g^{-1} at the 100th cycle, which equates to a 90% capacity retention ratio from the 2nd cycle. Furthermore, the battery was successfully operated at room temperature (23 °C), exhibiting discharging capacities of 122 mAh g^{-1} for the 1st cycle and 111 mAh g^{-1} for the 5th cycle (capacity retention ratio of 91%). At both temperatures, the coulombic efficiency was nearly 100%, indicating that the charge/discharge reactions proceeded without any significant side-reactions. This good performance is due to the small charge-transfer resistance at the LTO interface resulting from the tight contact between the constituents of the composite electrode, and suggests that LiI -doped LiBH_4 is a promising solid electrolyte for practical composite electrodes.

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1. Introduction

Li-ion batteries are both promising energy storage devices due to their high energy and power densities compared to other devices and a key technology for the development of electronic devices, including electric vehicles. To increase the scale of Li-ion batteries, however, their safety profiles must be improved; flammable organic solvents are commonly used and dendrite formation can cause short circuits [1]. In addition, temperature increases during battery operation often lead to remarkable capacity fading [2,3]. All-solid-state batteries, which use solid electrolytes instead of organic solvents, are one solution for avoiding the above-mentioned issues.

Fig. 1 shows a schematic illustration of a typical all-solid-state battery, in which a solid electrolyte layer is sandwiched between composite negative and positive electrode layers that comprise active materials, the solid electrolyte, and conductive additives when needed. To develop an all-solid-state battery, it is important to choose an appropriate solid electrolyte for each battery component; specifically, the solid electrolyte should have sufficient reducing and oxidizing abilities for the negative

and positive electrode layers, respectively. In addition to high Li-ion conductivity, it should also be highly deformable in order to increase the contact area between the constituents, and thereby minimize interfacial resistance. Over the past several decades, various inorganic solid electrolytes suitable for use in all-solid-state batteries have been developed, including perovskite-type [4,5], NASICON [6,7], LISICON [8,9], thio-LISICON [10,11], garnet-type [12,13], and glass-ceramic [14] materials.

The typical complex hydride solid electrolyte LiBH_4 undergoes a phase transition at 110 °C, and its high-temperature (HT) phase (space group: $P6_3mc$) [15] exhibits an ionic conductivity as high as $2.0 \times 10^{-3} \text{ S cm}^{-1}$ at this temperature [16–18]. In addition, the HT phase of LiBH_4 can be stabilized at lower temperatures by doping with a lithium halide (LiCl , LiBr , or LiI) [17–19]. In fact, when LiBH_4 is doped with LiI , i.e., $\text{Li}_4(\text{BH}_4)_3\text{I}$, the HT phase is stable even at room temperature, which results in a higher Li-ion conductivity ($2.0 \times 10^{-5} \text{ S cm}^{-1}$) than is possible without LiI ($2.0 \times 10^{-8} \text{ S cm}^{-1}$) [19]. In addition, the doped material is highly deformable, thermally stable up to 150 °C, highly stable toward lithium metal electrodes due to its high reducing ability, and electrochemically stable over the range of 0 to 5 V vs. Li/Li^+ . In recent years, a number of studies on the development of all-solid-state batteries employing complex hydride electrolytes have been reported. Takahashi et al. fabricated

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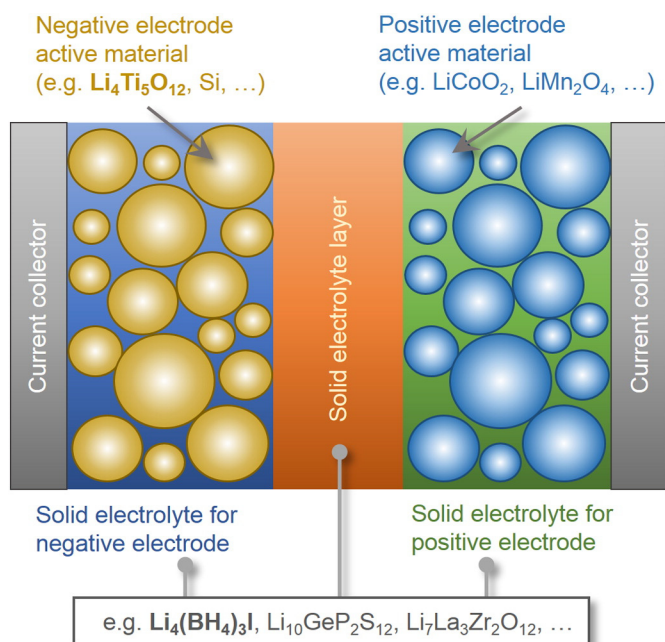


Fig. 1. Schematic illustration of a typical bulk-type all-solid-state battery configuration.

a bulk-type all-solid-state battery with a LiBH_4 solid electrolyte and a LiCoO_2 positive electrode [20,21]. In their study, the LiCoO_2 surface was coated with Li_3PO_4 in order to avoid the reductive decomposition of the LiCoO_2 and enable repeated charge/discharge cycling at 120°C . The initial discharge capacity was 89 mAh g^{-1} , and the capacity retention ratio at the 30th cycle was 97%. Unemoto et al. incorporated a LiBH_4 solid electrolyte into a bulk-type all-solid-state lithium-sulfur battery [22]. They realized discharge capacities as high as 1140 and 730 mAh g^{-1} for the initial and 45th discharges, respectively. Sveinbjörnsson et al. assembled an all-solid-state battery using a thin-film lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) electrode and LiBH_4 -LiI solid electrolyte [23]. The use of the LiBH_4 -LiI solid electrolyte allowed low temperature operation (60°C). Because LTO has a low redox potential of 1.55 V (vs. Li/Li^+), it forms a stable interface with the LiBH_4 -LiI electrolyte; therefore, in contrast to the LiCoO_2 positive electrode, no surface coating was necessary. This all-solid-state battery exhibited a high initial discharge capacity of 142 mAh g^{-1} , corresponding to an LTO utilization ratio of 81%. As demonstrated by these studies, complex hydride electrolytes should be considered as appropriate components for incorporation into composite negative electrodes intended for use in bulk-type all-solid-state batteries.

Herein, we describe the fabrication of a composite electrode that uses a $\text{Li}_4(\text{BH}_4)_3\text{I}$ solid electrolyte and an LTO electrode, and examine its performance over a wide temperature range (23 to 150°C). LTO undergoes extremely small volume changes during battery operation (less than 0.2%), and allows good cycle life for practical Li-ion batteries [24]. In general, LTO is used as a negative electrode active material, as described in Fig. 1. In the present study, however, we examined the performance of an LTO composite electrode by combining it with lithium metal electrode prior to the assembly of a practical rechargeable battery with LiCoO_2 or other high-voltage positive electrodes. Because lithium metal has lower redox potential, LTO functions as a positive electrode. The system performance is discussed based on the microstructure and the electrochemical analysis results.

2. Experimental

The $\text{Li}_4(\text{BH}_4)_3\text{I}$ solid electrolyte was synthesized from LiBH_4 (>95%, Sigma-Aldrich) and LiI (99.999%, Sigma-Aldrich) using a high-energy mechanical milling technique. All of the operations described below

were performed under argon. First, the powders were mixed in a 3:1 molar ratio for 30 min in an agate mortar, and then the mixture was transferred into a stainless-steel vessel with 20 stainless-steel balls (diameter: 7 mm). Mechanical ball milling was performed in a planetary ball mill (P-7, Fritsch) at a rotation rate of 400 rpm for 5 h under Ar. LTO (>99%, Sigma-Aldrich) was used as the active material. Acetylene black (AB), used as the conductive additive, was dried in a vacuum oven at 120°C for more than 1 h before use. The LTO composite electrode was prepared by mixing LTO, $\text{Li}_4(\text{BH}_4)_3\text{I}$, and AB in a 32:61:7 wt.% ratio in an agate mortar for 30 min. To form the electrode-electrolyte composite pellet, the powders of each (9.5 and 53 mg, respectively) were transferred to a die (8 mm in diameter) and uniaxially pressed at 240 MPa and room temperature. The thicknesses of the electrode and electrolyte layers were approximately 0.1 and 0.7 mm, respectively. A lithium foil was then used as the negative electrode. The experimental configuration for the battery tests is described elsewhere [22]. The battery tests were performed using a Solartron 1470 CellTest system (Solartron Analytical) at C-rates of 0.2 C (current density: $200\text{ }\mu\text{A cm}^{-2}$) at 150°C and 0.02 C (current density: $20\text{ }\mu\text{A cm}^{-2}$) at 23°C (room temperature) in the potential range of 1.0–2.0 V.

Electrochemical impedance measurements were obtained using a chemical impedance meter (Model 3532-80, Hioki E. E. Corp.) at room temperature in the frequency range of 10 MHz to 4 Hz. Prior to each impedance analysis, the cell was charged to a 50% state of charge (SOC).

The microstructure and elemental distribution of the composite electrode were evaluated via scanning electron microscopy (SEM, Hitachi S-4800) and energy dispersive X-ray spectroscopy (EDS, Horiba EX-350), respectively. For these analyses, the composite was prepared in the ratio $\text{LTO}:\text{Li}_4(\text{BH}_4)_3\text{I}:\text{AB} = 74:22:4\text{ wt.}\%$ to avoid possible damage to the sample during electron beam irradiation. SEM analysis revealed that the constituents were filled successfully at this mixing ratio (see Fig. 3(a)), and no remarkable differences were observed in the microstructure compared to that of the electrode used for the electrochemical analyses (see Fig. S-1 in the Supplementary Information). An LTO composite pellet was also prepared using the foregoing procedure at a thickness of 0.1 mm and attached to a piece of indium foil (0.2 mm thick) for handling. The cross-sectional surface was obtained via ion milling (Hitachi E-3500).

3. Results and discussion

3.1. Microstructure of the composite electrode

Successful, stable battery operation and enhanced electrode utilization ratios require a homogeneous distribution of the LTO, $\text{Li}_4(\text{BH}_4)_3\text{I}$, and AB constituents in the composite electrode layer, including the formation of tight interfaces. As expected, homogeneous distributions of the LTO, $\text{Li}_4(\text{BH}_4)_3\text{I}$, and AB were observed in the cross-sectional SEM image of the composite electrode, as displayed in Fig. 2(a). Although a few pores were observed, which most likely formed during the pellet fabrication process, the composite electrode pellet showed good filling of the constituents. The elemental distributions from the same area as used for the SEM observation revealed homogeneous distributions of iodine and titanium over the entire composite electrode (Fig. 2(b) and (c)). These results demonstrate that the solid electrolyte and the LTO active material were uniformly mixed.

A higher resolution image of the surface (Fig. 3(a)) shows particles of various sizes observed in rather bright contrast. Both the large particles in the left and lower right portions of the image and the small particles distributed between them are considered to be LTO. The deviation of the particle size is attributed to the original size distribution of the commercially available LTO powder. The spaces between the small LTO particles observed in darker contrast are assumed to be filled by the solid electrolyte, because no charging of the edge effect was observed, indicating that the spaces are not pores. The elemental analysis for the indicated area in Fig. 3(a) revealed the presence of titanium,

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