



Toward practical all-solid-state lithium-ion batteries with high energy density and safety: Comparative study for electrodes fabricated by dry- and slurry-mixing processes



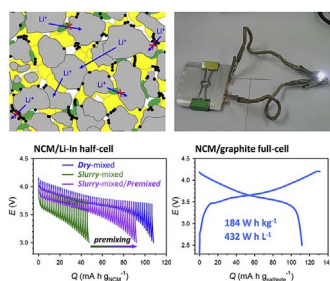
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HIGHLIGHTS

- Slurry-mixed electrodes using polymeric binders suffer from poor ionic contacts.
- Premixing of active materials and SEs significantly increases the capacity.
- Pouch-type ASLBs with high energy density ($184 \text{ W h kg}_{\text{cell}}^{-1}$) are fabricated.
- Excellent safety for pouch-type ASLBs is demonstrated by cutting and heating tests.

GRAPHICAL ABSTRACT



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ABSTRACT

Owing to their potential for greater safety, higher energy density, and scalable fabrication, bulk-type all-solid-state lithium-ion batteries (ASLBs) employing deformable sulfide superionic conductors are considered highly promising for applications in battery electric vehicles. While fabrication of sheet-type electrodes is imperative from the practical point of view, reports on relevant research are scarce. This might be attributable to issues that complicate the slurry-based fabrication process and/or issues with ionic contacts and percolation. In this work, we systematically investigate the electrochemical performance of conventional dry-mixed electrodes and wet-slurry fabricated electrodes for ASLBs, by varying the different fractions of solid electrolytes and the mass loading. This information calls for a need to develop well-designed electrodes with better ionic contacts and to improve the ionic conductivity of solid electrolytes. As a scalable proof-of-concept to achieve better ionic contacts, a premixing process for active materials and solid electrolytes is demonstrated to significantly improve electrochemical performance. Pouch-type $80 \times 60 \text{ mm}^2$ all-solid-state $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ /graphite full-cells fabricated by the slurry process show high cell-based energy density (184 W h kg^{-1} and 432 W h L^{-1}). For the first time, their excellent safety is also demonstrated by simple tests (cutting with scissors and heating at 110°C).

1. Introduction

Since the first commercialization of rechargeable lithium-ion batteries (LIBs) in the early 1990s, their use has been widespread for applications involving portable electronic devices [1,2]. Furthermore,

extensive progress in LIB technologies in recent years has accelerated the transition from gasoline-engine-powered vehicles to battery electric vehicles (BEVs). This transition is expected to enable reduction of air pollution, enhancement of energy efficiency, and lower dependency on limited fossil fuels [1,2]. Compared with the applications for portable

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electronic devices, batteries for BEVs must satisfy much more challenging requirements such as high energy density, long cycle life, safety, and wide ranges of operating temperature [1,3,4]. One of the most critical hurdles in the use of LIBs has been safety. Several recent accidents involved fire or explosions of LIBs in smart phones and BEVs, caused by flammable liquid electrolytes (LEs) [5–10]. Such events have made customers aware of the importance of battery safety. In this regard, all-solid-state lithium-ion batteries (ASLBs), which employ non-flammable solidified electrolytes, are considered a promising alternative to conventional LIBs [6,11–15].

In particular, it is the bulk-type ASLBs based on composite-structured electrodes and electrolyte layers that have the most advantages for BEV applications [6,11,13,16–18]. Bulk-type ASLBs are similar to the already-commercialized LIBs in that both are based on composite-structured electrodes. This implies that high energy density could be achieved by fabricating thick electrodes via a scalable wet-slurry process. In selecting appropriate solid electrolyte (SE) materials for bulk-type ASLBs, high ionic conductivity would be the most important criterion. Conventional LEs exhibit a Li-ion conductivity of $\sim 1 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature but have a low transference number (0.2–0.4) [6,19]. Because a SE is a single-ion conductor, a SE with an ionic conductivity one order of magnitude lower ($1 \times 10^{-3} \text{ S cm}^{-1}$) than that of LEs may result in electrochemical performance comparable to that of conventional LIBs [20]. Furthermore, an ionic conductivity two orders of magnitude lower ($1 \times 10^{-4} \text{ S cm}^{-1}$) than that of LEs would be a minimum requirement for SEs in bulk-type ASLBs that could operate at room temperature at moderately low C-rates (e.g., 0.1C) [16,21,22]. Various SEs showing ionic conductivity higher than $1 \times 10^{-4} \text{ S cm}^{-1}$ include oxides (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) [23,24], sulfides (e.g., $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$) [11,17,25], and hydrides, (e.g., $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$) [26]. Although oxide SEs are attractive in terms of processability under ambient conditions with good electrochemical stability, it is extremely challenging to form favorable two dimensional (2D) contacts with active materials because of their brittleness [27]. Thus, a sintering process at elevated temperature is inevitable to wet oxide SEs on active materials [6,27,28]; however, this causes undesirable side reactions, resulting in extremely poor electrochemical performance. To date, the performance of bulk-type ASLBs employing oxide SEs has been reported at elevated temperatures or at room temperature and at extremely low C-rates [28–30]. Alternatively, hybrid bulk-type all-solid-state Li- or Na-ion batteries based on oxide SEs were fabricated by addition of dry or gel polymer electrolytes and/or LE additives [12,31–34].

In contrast, deformability of sulfide SE materials allows the formation of 2D contacts with active materials using a simple pressing process at room temperature, without the use of Li-ion conducting organic additives [6,16,27]. Moreover, extremely high ionic conductivities ($\sim 10^{-2} \text{ S cm}^{-1}$) were achieved for several state-of-the-art sulfide materials (e.g., $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [11], $\text{Li}_7\text{P}_3\text{S}_{11}$ [25], and $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ [17]). Because of their aforementioned critical merits, sulfide SEs are considered to be the most appropriate candidates for making practical bulk-type ASLBs. However, as sulfide SE materials react with water in atmospheric air, generating harmful H_2S gases [6,16,35], manufacturing process in a dry room would be required. Or development of phosphorus-free materials, which is stable in atmosphere, would be imperative for practical applications [16,22,35–37]. Also, the problem of limited electrochemical stability for sulfide SE materials should be addressed by interfacial engineering [38–44].

In most previous reports, composite electrodes for bulk-type ASLBs using sulfide SEs were fabricated by mixing particulate active materials, SEs, and carbon additives in dry condition, followed by cold-pressing [6,11,16,17]. However, the resulting pelletized electrodes were too mechanically unstable to be scaled up [21,43]. Thus, addition of small amounts of polymeric binders is necessary to provide mechanical flexibility and good adhesion between particles and current collectors. In turn, a scalable wet-slurry process using solvent to dissolve

polymeric binders should be employed, which allows fabrication of large sheet-type electrodes. The available solvents are restricted to nonpolar or less polar ones such as xylene and toluene, due to severe reactivity of sulfide materials with common polar solvents [21,45]. Moreover, the more complicated homogenization of three components in the polymer-binder-dissolved wet-slurry for ASLB electrodes (active materials, SEs, and carbon additives) is contrasted by the need for only two components for LIB electrodes (active materials and carbon additives) [21]. Overall, the fabrication of sheet-type electrodes for ASLBs by the slurry method is much more complicated than that for well-optimized LIB electrodes. There are only a few reports regarding sheet-type electrodes for ASLBs to date [21,43,46–49], which led our group to investigate fabrication of bulk-type ASLBs using sulfide SEs from a practical point of view.

Herein, we make a comparative investigation of the electrochemical performance of conventional dry-mixed electrodes without polymeric binders, and sheet-type electrodes fabricated using a wet-slurry process with polymeric binders, in various combinations of electrode composition and mass loading. A controlled premixing process for active materials and SEs is introduced as a scalable method to enhance utilization of the active materials in all-solid-state cells. Finally, high cell-based energy density (184 W h kg^{-1} and 432 W h L^{-1}), and excellent safety for $80 \times 60 \text{ mm}^2$ pouch-type $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}$ (NCM622)/graphite all-solid-state full-cells are highlighted.

2. Experimental

2.1. Preparation of materials

Argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$ SE powders were prepared by mechanical-milling and subsequent heat-treatment under inert atmosphere. After a stoichiometric mixture of Li_2S (99.9%, Alfa Aesar), P_2S_5 (99%, Sigma Aldrich), and LiCl (99.99%, Sigma Aldrich) was ball-milled at 600 rpm for 10 h at room temperature in a ZrO_2 vial with ZrO_2 balls using a planetary ball mill (Pulverisette 7 PL; Fritsch GmbH). The resulting powders were heat-treated at 550°C for 5 h in a sealed quartz tube. The premixing process was carried out by milling a mixture of NCM622 and SE powders with ZrO_2 balls at 1000 rpm for 6 min using Thinky Mixer. LiNbO_3 (1.4 wt%) was coated on NCM622 powder using the wet-chemical method, before using the electrodes [16]. The uniform LiNbO_3 coating was confirmed by the field-emission scanning electron microscopy (FESEM) image and the corresponding energy dispersive X-ray spectroscopy (EDXS) elemental maps (Fig. S1).

Materials Characterization: The FESEM images were obtained using an S-4800 (Hitachi). Cross-sectional surfaces of the electrodes were prepared by polishing at 5 kV for 13 h with an Ar ion beam (JEOL, SM-0910). The FESEM images and the corresponding EDXS elemental maps of cross-sectioned electrodes were obtained using a JSM-7000F (JEOL). For the XRD measurements, samples were sealed with a beryllium window and mounted on a D8-Bruker Advance diffractometer (Cu K_α radiation: 1.54056 \AA) at 40 mA and 40 kV.

2.2. Electrochemical characterization

The Li-ion conductivity of the $\text{Li}_6\text{PS}_5\text{Cl}$ SE pelletized under 370 MPa was measured using an AC (alternating current) impedance method with a Ti/SE/Ti Li-ion blocking cell. The dry-mixed electrodes were obtained by manual mixing of active materials (NCM622), SE powders ($\text{Li}_6\text{PS}_5\text{Cl}$), and carbon additives (Super C65) with the target compositions. The wet-slurry fabricated electrodes were obtained by the following procedure. Slurries were prepared by mixing targeted amounts of SE powders, active materials (NCM622 or graphite powders), nitrile-butadiene rubber (NBR), and carbon additives (only for cathode) in anhydrous xylene. The Raman and Fourier-transform infrared (FTIR) spectra for NBR are provided in Fig. S2, where the characteristic peaks match well with the functional groups for NBR. After the as-prepared

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