



Short communication

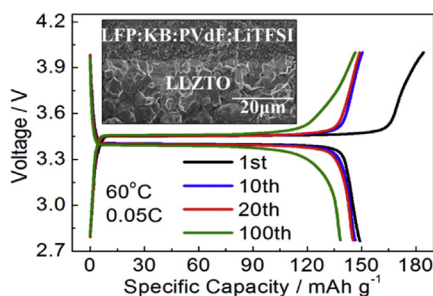
All solid state lithium batteries based on lamellar garnet-type ceramic electrolytes

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HIGHLIGHTS

- All solid state batteries were constructed with a mild and convenient approach.
- Dense and highly conducting garnet electrolytes were used as supports of the cells.
- Composite cathodes with highly conducting ionic and electronic networks were built.
- The solid state batteries showed good performance at 60 °C.
- Further elevated temperature like 100 °C led to greatly improved cell performance.

GRAPHICAL ABSTRACT



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ABSTRACT

All solid-state lithium batteries are constructed by using highly conducting Ta-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZTO) as the solid electrolytes as well as the supports, coated with composite cathodes consisting of poly(vinylidene fluoride) (PVdF):LiTFSI, Ketjen Black, and carbon-coated LiFePO_4 on one side and attached with Li anode on the other side. At 60 °C, the batteries show the first discharge capacity of 150 mAh g^{-1} at 0.05 C and 93% capacity retention after 100 cycles. As the current density increases from 0.05 C to 1 C, the specific capacity decreases from 150 mAh g^{-1} to 100 mAh g^{-1} . Further elevated temperature up to 100 °C leads to further improved performance, i.e. 126 mAh g^{-1} at 1 C and 99% capacity retention after 100 cycles. This good performance can be attributed to the highly conducting ceramic electrolytes, the optimum electronic and ionic conducting networks in the composite cathodes, and closely contacted cathode/LLZTO interface. These results indicate that the present strategy is promising for development of high-performance solid-state Li-ion batteries operated at medium temperature.

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1. Introduction

Development of large-scale storage grids and electric vehicles calls for the lithium batteries to be safer as well as with greater energy density than the currently commercialized lithium-ion batteries [1]. Under such circumstance, the rechargeable solid state lithium batteries have attracted much attention [2–5]. Using

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solid state electrolytes instead of combustible liquid counterparts not only can relieve the safe hazard, but can allow incorporation of lithium metal anodes and high-voltage cathodes into the batteries as well, which may greatly enhance the energy density of batteries [6–9]. However, to fulfil potential of the solid state batteries, two key problems have to be solved, that is, the availability of a stable and highly ionic-conducting solid electrolyte and reduction of the large resistance resulting from solid–solid interfaces between electrolytes and cathodes.

Recently, the garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) ceramics which were first reported by Murugan et al. showed promising properties for using as the solid state electrolytes [10]. With optimization of element substitution, their ionic conductivities can be as high as $10^{-3} \text{ S cm}^{-1}$ at room temperature [11–14]. Moreover, they are chemically stable against the lithium metal and have electrochemical window above 5 V [12,15]. In conjunction with the highly conducting solid electrolytes, the low resistive electrolyte/cathode interfaces are crucial to obtain high-performance batteries. Thin-film growth techniques such as sputtering and pulsed laser deposition were often used to grow cathode layers on ceramic electrolyte supports [16,17]. Through careful control of the composition at the interfaces, the battery performance could be greatly improved. However, such configuration limits achievement of the high capacity owing to the small amount of electrode materials available by the growth [18]. In contrast, bulk synthesis techniques are considered as powerful tools to prepare high-energy batteries [19]. In this case, composite cathodes consisting of active electrodes (e.g. LiCoO_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$) combined with Li^+ or e^- conducting particles (e.g. LLZO, Li_3BO_3 , Ag) were sintered together with the LLZO electrolytes at 700–900 °C, aiming to build good ionic and electronic conducting networks in the cathodes as well as closely connected electrolyte/cathode interfaces [20–25]. However, the used temperature range (i.e. below 900 °C) on one hand is difficult to fabricate dense and thus highly conducting electrolyte membranes, on the other hand is apt to cause phase transition of crystalline cathodes and/or reactions between cathodes and electrolytes. Therefore, it is suggested that combination of sufficient high-temperature prepared ceramic electrolytes with low-temperature processed electrolyte/cathode interfaces might be necessary to obtain high-performance solid-state batteries [26].

In this work, we used the $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) ceramics in thickness of 0.1 cm as the solid electrolytes. They were sintered by the hot-pressing technique with the relative density of 99.6% and ionic conductivity of $1.6 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature (as presented in Fig. S1). The composite cathodes composed of carbon-coated LiFePO_4 (LFP), Ketjen black (KB), LiTFSI in PVdF were coated on one side of the LLZTO ceramic, and the Li anodes were attached on the other side by high pressure. It is worth noting that LiTFSI in PVdF may also be a good kind of polymer electrolyte [27–30]. In terms of building electrolyte/cathode interface, such configuration not only allows the high-temperature sintering which is necessary for obtaining the highly conducting electrolyte part but also allows construction of closely contacted electrolyte/cathode interfaces at low temperatures with the help of PVdF. Moreover, the composite cathodes have good conduction networks for both ions and electrons, the LLZTO/PVdF:LiTFSI interfaces can endure the volume changes during charge and discharge cycles. In the following discussion, we denote the solid state batteries as LFP:KB:PVdF:LiTFSI/LLZTO/Li. The performance of solid-state lithium ion batteries based on garnet electrolytes and the relevant mechanism are discussed.

2. Experimental

Detailed description of LLZTO powders and dense ceramics can

be found in Ref. [31] and Fig. S1. Composite cathodes consisted of poly(vinylidene fluoride) (PVdF) (Alfa Aesar), $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ (LiTFSI) (99.95%, Sigma–Aldrich), carbon-coated LiFePO_4 (LFP) and Ketjen black (KB). The PVdF polymers were dissolved in N-methyl-2 pyrrolidone (NMP) and stirred for 24 h, which were followed by addition of LiTFSI, LFP and KB in an agate mortar and ground for 1 h. The LiTFSI was prebaked at 80 °C in vacuum for 48 h. The obtained slurries were coated on one side of the LLZTO ceramic membrane by blades, then dried in an oven at 80 °C for 2 h to remove NMP. After being pressed with stainless-steel plate, the cathodes were dried in a vacuum oven at 80 °C again for 12 h to remove the trace amount of NMP and moisture. The typical mass of each cathode was approximately 2 mg. The weight ratio between LFP, KB, PVdF is fixed at 7.5:1.5:1.0 according to the conventional liquid-electrolyte-based lithium ion batteries and the mass ratio of LiTFSI to LFP is varied from 0%, 25%, 50%, 75% and 100% for comparison. Li anodes were attached on the other side by high pressure in an Ar-filled glove box with oxygen and moisture levels below 0.1 ppm. Finally, each laminated all-solid-state battery was assembled in a Swagelok-type or coin cell. The stainless steel (SS) foils instead of Al foils were chosen as current collectors in order to avoid the reaction between the Al and the PVdF:LiTFSI. The current density is normalized to the mass of LFP as well as the area of electrode, i.e. 1 C being 170 mA g^{-1} or $200 \mu\text{A cm}^{-2}$.

Surface and cross-section morphologies of the LLZTO ceramics and the cathodes were tested by scanning electron microscopy (SEM, FEI Magellan 400). Galvanostatic charge and discharge behaviors of the batteries were investigated using an Arbin battery cycler with the potential ranging from 4.0 to 2.76 V at 25, 60 and 100 °C. Before the tests, the cells were firstly rested in a thermostatic oven for 6 h to reach the set temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed in a frequency range of 1 MHz to 0.1 Hz with an amplitude of 10 mV using an Autolab instrument.

3. Results and discussion

Scanning electron microscope (SEM) image of a typical interface between the composite cathodes and the LLZTO electrolyte is shown in Fig. 1a. It can be clearly seen that the cathode in thickness of approximately $17 \mu\text{m}$ is tightly coated on the LLZTO ceramic and

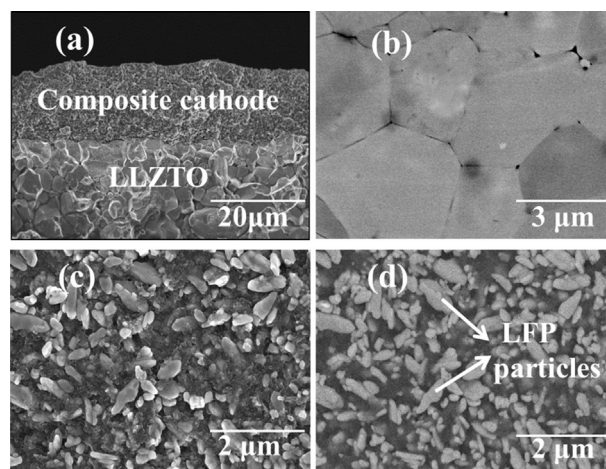


Fig. 1. (a) A typical scanning electron microscope (SEM) of the interface between the composite cathodes and the LLZTO electrolyte; (b) SEM image for the surface of LLZTO ceramic electrolyte; (c) and (d) display the SEM images of the composite cathodes which were measured in the second-electron and the back-scatter-electron mode, respectively. The oval-shaped LFP particles can be identified.

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