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Preparing Li-garnet electrodes with engineered structures by phase inversion and high shear compaction processes

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Abstract

Solid-state lithium batteries are promising for safety and energy density compared to traditional lithium-ion batteries. However, the large interfacial resistance between the electrode and electrolyte is a bottleneck to achieving high performance solid-state batteries. Engineered electrode structures with a porous scaffold of the solid electrolyte material are promising to lower the interfacial resistance, and provide a mechanical support for a thin solid electrolyte layer. In this work, two ceramic processing techniques are used to fabricate porous/dense bi-layer architectures based on a $Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$ (LLZO) Li-garnet material. Finger-like vertically aligned pores are created by the phase inversion (PI) process. A water bath pre-saturated with Li salt prevents Li loss during the PI solvent exchange step. Pore size and porosity can be optimized by adjusting the bath temperature. The high shear compaction (HSC) process was used to prepare LLZO tapes with 40, 60, and 80 vol.% poreformer. The porosity of the tapes after sintering is 39.5, 58.4, and 75.4%, respectively. Microtomography exhibits the porosity, pore shape and pore distribution of the tapes. A typical cathode material $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) is filled into the pores *via* vacuum infiltration, and a dense cathode layer is formed within the garnet scaffold.

Key word: Solid-state battery; Garnet; Porous scaffold; Infiltration; LLZO

Introduction

Lithium-ion batteries are widely used in portable devices and electric vehicles.[1] The inherent safety issues of conventional lithium-ion batteries, such as explosion, fire, and leakage of organic electrolyte, are significant.[2, 3] Solid-state batteries (SSBs), as the next-generation of battery technology, have gained extensive attention in recent years due to their high safety and potential compatibility with lithium metal anode.[4, 5] Garnet electrolytes show ionic conductivity greater than 1 mS cm^{-1} at room temperature,[6, 7] which is sufficiently high to support reasonable current densities in lithium metal battery configurations. Ceramic electrolytes exhibit poor interfacial contact with electrodes, however, and they are generally thick and brittle leading to high ohmic impedance and mechanical failure.[8, 9] The specific energy density is still low due to the high density of ceramics.[10] In addition, it is challenging to fabricate garnet electrolytes, such as Al-doped $Li_7La_3Zr_2O_{12}$ (LLZO), with thickness < 100 μm without any support,[11] which means the lithium-ion conduction pathway between the electrodes is long. The porous scaffold/dense electrolyte structure makes it feasible to have a thin (tens of microns) electrolyte, leading to lower ohmic impedance, as the thick porous scaffold can provide mechanical support.

Using a porous ceramic scaffold to support a thin ceramic electrolyte is a mature technique and has been widely applied in solid oxide fuel cells (SOFCs),[12, 13] filters,[14, 15] and SSBs.[16, 17, 18] To fabricate porous scaffold for SSBs, tape casting,[19, 20] freeze tape casting,[21, 22, 23, 24] templating,[25, 26] electrospinning,[27, 28, 29] 3D printing,[30, 31] etc., have been demonstrated. Most of these methods create porous structures with high tortuosity, leading to long lithium-ion diffusion pathways and challenges for infiltrating solid active material particles, and these methods may not scale well due to low throughput, complicated processing, or high cost.

The phase inversion (PI) process has been widely used in numerous chemical industries, biotechnology, environmental separation, and energy conversion and can fabricate large area porous scaffolds with low cost.[32, 33, 34] It has also been used to construct micro-channels of $Li_{0.34}La_{0.51}TiO_3$ for SSBs.[35] The PI process creates finger-like pores when the solvent in a slurry of ceramic particles, binder, and dispersant counter-diffuses with a non-solvent liquid placed in contact with the slurry surface. During the PI procedure, water is typically used as the non-solvent to induce phase separation. Water reacts with most battery materials, however, which is one reason why the PI process has not been widely applied in the battery community. The high shear compaction (HSC^{TM}) process is a ceramic tape fabrication technique developed by Ragan Technologies. It densifies powders and binders by compaction to form large-area thin tapes. HSC is capable of preparing tapes with high quality and excellent dimensional tolerance, without separation of the ceramic, poreformer, and binder phases. This process is commonly used in manufacturing production of ceramic substrates due to its low cost, high production throughput and good control of shrinkage.[36, 37]

In this work, LLZO scaffold electrodes with engineered structures were fabricated by PI and HSC processes, and incorporated into bi-layer architectures. HSC has not been reported previously to fabricate battery components. Large area porous tapes with vertically aligned finger-like pores were fabricated by the PI process, and the intended cubic phase was obtained after sintering when using a water bath that was saturated with Li_2CO_3. The porosity of HSC tapes was adjusted and the highest porosity of 75.4% was achieved. Pores in both tapes were successfully filled with $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC) cathode material, with good contact between the cathode and the scaffold.

Experimental

Preparing dense tapes by tape casting

Commercial Al-doped LLZO powder (Ampcera, USA) was used in this study. Dense tapes were prepared by tape casting with solvent-based binder (Polymer Innovation Inc., USA).[38] Briefly, LLZO powder (5 g), Li_2CO_3 (0.3 g) and MgO (0.1 g) were mixed in a Teflon bottle with 30 g ZrO_2 balls. MgO acts as a sintering aid and limits the LLZO grain growth. Toluene solvent (4.5 g) and DS002 dispersant (0.1 g, Polymer Innovations, Inc., USA) were added subsequently. The mixture was ball milled overnight. MSB1-13 binder (2 g, Polymer Innovations, Inc., USA) was then added and the suspension was ball milled for another 4 h. After tape casting onto Si-coated Mylar substrates, the tapes were dried naturally and peeled off the substrate.

Preparing porous tapes by phase inversion

LLZO powder (5 g), Li_2CO_3 (0.3 g) and MgO (0.1 g) were mixed in a Teflon bottle with 30 g ZrO_2 balls. N-Methyl-2-pyrrolidone solvent (NMP, 4.5 g) and polyvinylpyrrolidone dispersant (PVP, 0.05 g) were added. After ball milling for 4 h, polyethersulfone (PESF, 0.322 g) was added into the suspension, followed by 2 h ball milling. PL008 (0.1 g, Polymer Innovation Inc., USA) was added to improve wetting on the Mylar casting substrate, followed by 30 min ball milling.

The prepared LLZO suspension was tape cast on Si-coated Mylar substrate and soaked immediately in a water bath with de-ionized (DI) water or Li_2CO_3-saturated water. After solvent exchange completed, the tape was removed from the water bath and dried overnight in ambient air. The phase inversion process is illustrated in Figure 1(a). Bi-layer structures were prepared by casting the LLZO slurry onto a dry pre-formed electrolyte tape, followed by phase inversion. Lamination or hot pressing are not needed to achieve good bonding between the porous and dense layers.

Preparing porous tapes by high shear compaction

HSC tapes were prepared by Ragan Technologies, whose full-scale continuous process is illustrated in Figure 1(b). Samples were prepared with lab-scale procedures that mimic the full-scale process. LLZO slurry was prepared with LLZO (5 g), Li_2CO_3 (0.3 g), MgO (0.1 g), 12.3 wt.% commercial binder, and polymethyl methacrylate (PMMA, Sunjin Chemical Co. Ltd, South Korea) poreformer (40, 60, 80 vol%). Water was used as the solvent. The size of PMMA is ~60 µm and the thickness of the tape is about 200 µm. HSC tapes were laminated with dense tapes at 100 °C and 100 MPa for 15 min to make bi-layer structures.

Sintering

Tapes were cut into the desired shape and size and debinded at 700 °C for 1 h in air with heating rate of 1 °C min^{-1}. They were sandwiched between two thin Al_2O_3 sheets to prevent warping during debinding. The debinded tapes were sintered at 1125 °C for 5 h in Ar atmosphere with heating and cooling rate of 5 °C min^{-1}. During sintering, graphite sheets were inserted between the tapes and Al_2O_3 sheets to prevent reaction.

Cathode infiltration

NMC (MTI corporation, USA) was dispersed in N-Methyl-2-pyrrolidone (NMP, Sigma Aldrich, USA) solvent and ball milled for 48 h to obtain submicron-scale particles. The NMC suspension was drop cast on bi-layer structures and infiltrated under vacuum. The tapes were dried under vacuum at 60 °C for 5 h to evaporate the NMP solvent.

Characterization

The cross section and surface of tapes were observed using a tabletop scanning electron microscope (SEM, JSM-7500F, JOEL). Tapes were mounted in epoxy, cut, and dry polished with aluminum oxide sandpapers (320, 600, 1000, and 1400 grit) to obtain a flat cross section. The crystal structure of sintered tapes was characterized by x-ray diffraction (XRD, D2 Phaser, Bruker), with 10° min^{-1} scanning speed at 0.02° step size. The concentration of chemical elements in the samples was measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 5300 DV, Perkin Elmer). Microtomography was conducted at the Advanced Light Source (ALS) Beamline 8.3.2 at Lawrence Berkeley National Laboratory, with pixel size of 0.65 μm. Images were collected over 180° in 0.072° steps, with 24 keV X-ray. The dark field images were collected to deduct detector dark counts with the X-ray shutter closed, and the bright field images were collected before and after the sample scan to normalize for variations in the incident illumination. The 3D reconstructions were performed with TomoPy, and images were visualized and analyzed with Avizo software. Energy dispersive X-ray spectroscopy (EDS) analysis used the secondary electron detector of a field-emission scanning electron microscope (FESEM, Zeiss Gemini Ultra-55) with a beam energy of 20 kV.

Results and discussion

Phase inversion

During the PI process, solvent exchange was initially carried out at ~0 °C for 30 min, with DI water as the non-solvent. Rapid exchange of water and NMP occurs between the interface, causing the precipitation of PESF along with the LLZO powder because of its limited solubility in water. During this process, Li^+/H^+-exchange caused severe de-lithiation of the LLZO slurry in the water bath.[39, 40]. After sintering at 1125 °C for 5 h, only the Li-deficient $La_2Zr_2O_7$ phase is detected by XRD (Figure S1). Severe Li loss was observed even if extra Li^+ source (Li_2CO_3) was added into the LLZO slurry. To overcome this issue, the DI water was replaced with Li_2CO_3 saturated water and this effectively prevented the Li^+/H^+-exchange. Also, the Li salt in the residual water is retained in the LLZO tape after drying, and can compensate for subsequent Li loss during sintering. The ICP-OES data are shown in Table S1, as well as their fitting in Figure S2. The normalized stoichiometry of Li:Al:La:Zr by La-content is 7.08:0.24:3:2.17. As a reference, the stoichiometry of the LLZO green powder is 6.52:0.21:3:2.20. Li is rich because extra Li source is added to the PI slurry and water bath. During sintering, MgO acts as a sintering aid and is not doped into the LLZO unit cell. The XRD pattern of the sintered tape shows cubic LLZO phase with a tiny peak at 27.8°, which is unsure what belongs to (Figure S1). The lattice parameter is calculated to be 12.991 Å, which is a little higher than the dense tapes.[38] The expand lattice parameter could be ascribed to the extra Li in the tape.

PI introduces vertical and finger-like pores (Figure 2a). The depth of the pores is ~120 µm and the pores do not completely penetrate to the bottom of the tape. There is a dense layer with a thickness of 20 to 30 µm at the bottom. A magnified image for a typical pore is shown in Figure 2b. Microtomography was used to characterize the pore shape and distribution. Vertical pore shape was confirmed throughout the imaging volume (Figure 2c). The average porosity of the sintered tape prepared at 0 °C is ~37% and the porosity changes along the thickness (Z coordinate). It is ~30% at the top surface and increases in the bulk, then suddenly decreases to zero at the dense bottom layer. The average pore area has a similar distribution. An illustration of the average pore shape derived from the pore area curve is shown in the inset of Figure 2d. The pore is largest in the middle, necks gradually at the top, and pinches off suddenly at the bottom.

The porosity and pore size can be adjusted by changing the water bath temperature. Higher bath temperature increases the solvent exchange kinetics and limits the growth of pores. As the temperature rises from 0 °C to 50 °C, the porosity and pore size decrease gradually, as seen in the tomography xyz slices and average porosity data in Figure 3. The porosity ranges from 10% to 37% when PI is carried out at 50 °C and 0 °C, respectively.

Bi-layer structures were fabricated by casting the PI layer on top of a pre-formed tape cast electrolyte layer. The bi-layer structure was co-sintered successfully, with excellent adhesion between the layers and full densification of the electrolyte layer (Figure S3). The pores at the top surface are small, 3 to 7 µm (Figure S3b), and the grain size on the electrolyte surface is roughly 5 to 10 µm. While it is interesting to demonstrate the fabrication of a bi-layer structure with this approach, the additional electrolyte layer appears unnecessary, as the bottom layer of the PI structure is already dense.

High shear compaction

The HSC tape with 40 vol.% PMMA was sintered at 1125 °C for 5 h and pure cubic phase was obtained except a tiny peak at 27.8°, similar to the PI tape (Figure S1). The ICP-OES data in Table S1 show the stoichiometry of Li:Al:La:Zr is 6.97:0.26:3:2.23. Less Li in the HSC tape than the PI tape could be due to no extra Li_2CO_3 used to saturate the water solvent during the tape preparing. The lattice parameter is calculated to be 12.962 Å, which is similar to the dense tapes.[38] The sintered tape is ~150 µm thick and contains round pores diameter ranging from 30 to 60 µm (Figure 4a). In contrast to the pore shape in the PI tape, the HSC pores are nearly spherical and only slightly elongated in the x-y plane, presumably due to deformation during compaction or anisotropic shrinkage during sintering (Figure 4b). The average porosity of the sintered tape is 39.5%, close to the volume loading of PMMA (40 vol.%) in the green tape. The porosity distributes uniformly along the Z direction and the average pore area also distributes uniformly (Figure 4c).

The porosity of the sintered HSC tapes can be adjusted by changing the PMMA loading in the green tapes (Figure 5). Microtomography analysis indicates the porosity of the three tapes prepared with 40, 60, and 80 vol.% PMMA is 39.5, 58.4, and 75.4%, respectively. The microstructure of bi-layers assembled by laminating tape-cast electrolytes to the HSC layers is shown in Figure S4. The bi-layer structure provides excellent adhesion between the layers and good densification of the scaffold and the approximately 25 µm thick electrolyte layer. In contrast to the PI structure, there are large open pores on the HSC top surface (Figure S4d), which is beneficial for cathode filling. The grain size is around 5 to 10 µm, similar to the PI tape.

Ionic conductivity and NMC filling

The ionic conductivity of the LLZO scaffolds was measured using the sample geometries shown in Figure 6(a). As the sintered PI structure (solvent exchanged at 0 °C) is dense on the bottom and has very small pore size (3-7 µm) on the top, silver paste was directly cast on both sides as the electrical contact for EIS analysis. HSC tapes have larger pores (30 to 60 µm) on both sides and silver paste could fill the pores when the paste is wet. Therefore, a thin (~20 µm) and dense LLZO layer was laminated on both side of the porous tapes to have dense/porous/dense tri-layer structure after sintering. An image of the tri-layer structure prepared from HSC tape with 60 vol% PMMA is shown in Figure S5. As shown in Figure 6(b), the first semicircle is ascribed to the bulk conductivity and the second semicircle is ascribed to the grain boundary conductivity. The effective ionic conductivity based on total geometric area of the PI tape with 37% porosity is $6.4\text{x}10^{-5}$ S cm^{-1}, and $1.0\text{x}10^{-4}$, $6.2\text{x}10^{-5}$, and $1.2\text{x}10^{-5}$ S cm^{-1} for the HSC tapes with 40, 60, and 80 vol% PMMA respectively. These values are not normalized by the porosity. For comparison, thin dense electrolyte layers prepared with the same powder provide ~$2\text{x}10^{-4}$ S cm^{-1}. As expected, the porosity decreases the effective conductivity.

High interfacial resistance between the solid electrolyte and the cathode lowers the performance of SSBs. Infiltrating cathode material into a LLZO scaffold is a useful approach to lower the electrolyte/cathode resistance. Here, a proof-of-concept was carried out by infiltrating NMC into the PI and HSC porous scaffolds. The NMC was ball milled to reduce the particle size sufficiently to penetrate into the pores. NMC is clearly observed inside the bi-layer structures with PI and HSC porous layers (Figure 7). EDS mapping shows the elemental distribution of Zr, Ni, Mn, and Co for the HSC tape, demonstrating the successful infiltration of the NMC into the scaffold. A layer of NMC with the thickness of several hundred nanometers covers the LLZO scaffold with good contact. Even locations at the buried interface of the scaffold and electrolyte were covered by NMC, confirming the connectivity of the pores. Multiple cycles of infiltration are needed to load more NMC cathode, as the pores are not filled completely after the one-cycle infiltration demonstrated here. XRD patterns (Figure 7(e)) of the PI and HSC tapes with NMC infiltration match the cubic LLZO and NMC phases, indicating no reaction between LLZO and NMC after drying at 60 °C. In addition, no reaction between LLZO and the solvent NMP was detected. Bi-layer structures prepared with 40 and 60 vol.% PMMA were also successfully infiltrated with NMC (Figure S6).

Conclusions

Finger-like vertically aligned pore tapes and highly porous tapes were prepared by PI and HSC processes, respectively. Bi-layer structures with dense electrolyte and porous scaffold layers were also prepared. A Li_2CO_3-saturated water bath is effective to inhibit Li loss during PI solvent exchange. The porosity of the PI tapes can be increased to ~37% by lowering the water bath temperature to 0 °C. The PI pore size is larger at the middle and smaller at the top and bottom. The PI porous/dense bi-layer structure was prepared without lamination or hot press; thus the vertical pores can be preserved without damage. In addition, the unique architecture of PI tapes makes it possible to prepare an integrated electrolyte without merging a separate dense layer, as the finger-like pores do not penetrate the whole layer. Future optimization will focus on increasing the total porosity and penetration of the pores through the top surface. HSC tapes were prepared with 40, 60, and 80 vol.% PMMA and the highest porosity achieved after sintering was 75.4%. The porous/dense bi-layer structure, prepared through lamination, provides a thin densified electrolyte supported on a highly porous scaffold. A typical cathode material, NMC, was successfully infiltrated into PI and HSC pores, with good contact between NMC and LLZO. This demonstrates the possibility of cathode filling for full cell assembly in the future.

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usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

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Figure captions

Figure 1. Schematic of porous structure formation. (a) PI and (b) HSC processes.

Figure 2. PI microstructure. SEM images of (a) a fracture section of the sintered tape prepared by PI with Li^+ saturated water and (b) high magnification; (c) 3D microtomography pore distribution (d) and corresponding porosity and average pore area distribution along the z direction. Color map is used to distinguish pore size range, from large (light blue) to small (pink). The schematic pore shape based on the average pore size distribution along z direction is shown as an inset in (d).

Figure 3. Microtomography analysis of sintered PI tapes prepared at various inversion temperatures. (a) Image slices of PI tapes prepared at 0 °C, 22 °C, 40 °C and 50 °C. The darker areas are pores. (b) The relationship of average porosity with water bath temperature.

Figure 4. HSC microstructure. (a) SEM image of a fracture section of the sintered tape prepared with 40 vol.% PMMA; (b) Microtomography 3D pore distribution (c) and corresponding porosity and average pore area distribution along z direction. Color map is used to distinguish pore size range, from large (light blue) to small (pink).

Figure 5. Microtomography analysis of sintered HSC tapes with various poreformer loadings. (a) Image slices of HSC tapes prepared with 40 vol%, 60 vol%, and 80 vol% PMMA. (b) The relationship of the sintered porosity with PMMA loading in the green tape. The darker areas are pores.

Figure 6. Measurement of ionic conductivity. (a) Schematic of the ionic conductivity sample geometry for the PI and HSC tapes; (b) Impedance spectroscopy of the sintered PI porous tape (0 °C) and HSC-40, 60, and 80 dense/porous/dense tri-layer tapes at room temperature, converted to Ohm cm.

Figure 7. NMC filled into sintered porous/dense bi-layer structures. (a, b) PI (0 °C) and (c, d) HSC (80 vol.% PMMA) tapes, (e) XRD patterns of the PI and HSC tapes with NMC filling. EDS mapping of Zr and Co corresponds to image (d) at the same magnification.