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# 1 Oriented porous LLZO 3D structures obtained by 2 freeze casting for battery applications

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19

## 20 **Abstract**

21 All solid-state lithium batteries are, potentially, higher energy density

22 and safer alternatives to conventional lithium-ion batteries (LIBs). These are

23 particularly attractive characteristics for large-scale applications such as  
24 electric vehicles and grid energy storage systems. However, the thin film  
25 deposition techniques used to make current devices are not readily scalable,  
26 and result in low areal capacities, which translate to low practical energy  
27 densities. To overcome these deficiencies, it is necessary to design thicker  
28 electrodes similar to what are used in LIBs (30-100  $\mu\text{m}$ ), in which active  
29 material is composited with the ionic conductor and an electronically  
30 conducting additive, to overcome transport limitations. In this paper, we  
31 propose a method for making such an electrode, starting with a porous  
32 scaffold of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO), made by freeze casting, which is then  
33 infiltrated with active material  $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$  (NMC-622) and other  
34 components. The freeze casting technique results in the formation of  
35 oriented channels with low tortuosity, which run roughly parallel to the  
36 direction of current. The scaffolds were characterized with synchrotron X-ray  
37 micro-tomography for structural analysis, as well as synchrotron X-ray  
38 fluorescence to map the elemental distribution in the infiltrated composite. A  
39 hybrid half-cell was constructed and cycled as proof of principle, and showed  
40 good stability. In addition, a bilayer structure consisting of a porous layer  
41 combined with a dense LLZO film was successfully made as a prototype of an  
42 all solid-state battery. A mathematical model was established to propose  
43 optimized scaffold structures for battery performance.

## 44 Introduction

45 The widespread use of Li-ion batteries (LIBs) in electronic devices and  
46 electric vehicles has highlighted the need for both improved safety and  
47 energy density. The use of lithium metal as an anode can potentially  
48 increase both specific energy and energy density due to the high gravimetric  
49 capacity (3869 mAh/g) and low density (0.534 g/cm<sup>3</sup>).<sup>1-3</sup> Unfortunately, safety  
50 issues preclude its use in conventional battery configurations because of  
51 mossy lithium deposition or Li-dendrite induced cell shorting when Li metal is  
52 cycled in cells with flammable liquid electrolytic solutions.<sup>4</sup> To overcome this,  
53 solid state electrolytes have been proposed as safer alternatives to the  
54 liquids. In particular, solid-state garnet type ceramic electrolytes, such as  
55 cubic Al-substituted Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO), are promising, due to their kinetic  
56 stability against Li,<sup>5-8</sup> large potential window (0 ~ 6V), and ionic  
57 conductivities up to 1 mS/cm.<sup>9-15</sup> Although Li deposition or dendrite growth  
58 along the LLZO grain boundaries in polycrystalline dense films has recently  
59 been recognized as a source of shorting in cells, modifications of the LLZO/Li  
60 interface and cell architecture have successfully improved the stability and  
61 cycling behavior of symmetrical cells.<sup>11, 16-19</sup>

62 Another challenge, particularly if solid-state batteries are to be used  
63 for large-scale applications such as vehicles, has to do with the design of the  
64 electrodes and cells.<sup>20</sup> Most solid-state batteries are fabricated in thin film  
65 configurations to overcome the transport limitations of cathode materials.<sup>21-24</sup>  
66 Not only does this usually require the use of vacuum deposition techniques,

67which are costly and difficult to scale, but it also results in low cathode areal  
68capacity. For this reason, practical energy densities are low, in spite of the  
69use of metallic lithium anodes. Several attempts have been made to build  
70composite electrodes for solid-state batteries, in which the active material  
71and ionic conductor are combined to improve ionic transport. In some cases,  
72composites may be fabricated by cold-pressing the active material and  
73electrolyte together<sup>25-27</sup>. This is most easily accomplished with soft  
74electrolytes such as sulfides. The low compressibility of garnets, in contrast,  
75makes this an impractical approach. Instead, Fu *et al.* constructed a porous  
76garnet layer by including a sacrificial polymer, which was burned away to  
77create pores and then infiltrated these with other components to make a  
78composite.<sup>28</sup>

79 Sander *et al* recently demonstrated the advantages of low tortuosity  
80pores in battery electrodes using a magnetic alignment technique on thick  
81LiCoO<sub>2</sub> electrodes.<sup>29</sup> There was a noticeable increase of usable capacity of  
82the aligned LiCoO<sub>2</sub> electrodes with low tortuosity pores oriented in the  
83direction of transport, compared to those with isotropic porosity, when  
84cycled in half cells with liquid electrolytic solutions. To this end, McOwen *et*  
85*al.* 3D printed LLZO scaffolds by using LLZO inks, which allows good control  
86of the electrode structure.<sup>30</sup> The effect of tortuosity on the electrochemical  
87behavior of LLZO electrolytes has recently been described, with lower  
88tortuosity potentially providing a means for achieving higher critical current  
89densities and power densities in solid-state batteries<sup>31</sup>. Another attractive

90method for producing low-tortuosity pores in ceramics is that of freeze  
91casting.<sup>32</sup> There has already been a report on freeze-casting LLZO to make  
92ceramic/polymer composite electrolytes<sup>33</sup>. Here we report our preliminary  
93results using freeze casting to produce LLZO scaffolds with low tortuosity  
94pores, which were subsequently infiltrated with active material and used as  
95electrodes in hybrid half-cells. A prototype all solid-state cell was also  
96assembled. We used synchrotron radiation micro-computed tomography to  
97visualize the three-dimensional (3D) models of the porous LLZO scaffolds and  
98X-ray fluorescence to map distributions of the components. A simple  
99mathematical model is also presented to provide guidance on the design of  
100the porous scaffolds.

101

## 102**Experimental**

### 103**1. Preparation of porous LLZO scaffolds**

104 Sub-micron-sized commercial Al-doped LLZO powders were obtained  
105from MSE Supplies, Inc. for the freeze casting experiments. A slurry  
106containing 20 wt.% LLZO powder and 78 wt.% tert-butyl alcohol (TBA) was  
107mixed with 1 wt.% polyvinyl butyral (PVB) and 1 wt.% deionized water (to  
108adjust the freezing point). Afterwards, another 5 wt.%  $\text{Li}_2\text{CO}_3$  was added into  
109the slurry to compensate for Li loss during sintering. The mixture was ball-  
110milled with  $\text{ZrO}_2$  grinding media for 8 h to form a stable LLZO slurry at room  
111temperature. **Although water is known to cause slow decomposition of LLZO,**  
112**the amount of decomposed LLZO is negligible after several hours ball milling.**

113 Moreover, during the sintering process, the decomposed LLZO is recovered  
114 through addition of extra  $\text{Li}_2\text{CO}_3$  and heating. A house-made freeze casting  
115 system was used to prepare samples at various temperatures as illustrated  
116 in Figure 1a. A PVC mold of 2 cm in diameter and 1.5 cm in height was  
117 attached to a liquid nitrogen cooling bed with a polished copper plate in  
118 between to ensure excellent thermal conductivity. The top surface of the  
119 slurry is still exposed to ambient temperature resulting in a temperature  
120 gradient from the bottom (cold) to the top (warm). To control the freezing  
121 rate, the temperature of the slurry was adjusted and monitored by an  
122 embedded heating element and thermocouple in the cooling bed. For this  
123 work, the cooling plate temperature was set at  $-20\text{ }^\circ\text{C}$  and  $-50\text{ }^\circ\text{C}$ . After the  
124 temperature stabilized, the LLZO slurry was poured into the mold and  
125 maintained at the desired temperature until fully frozen. Then the solidified  
126 TBA and LLZO was unmolded and transferred to a freeze drier at  $-40\text{ }^\circ\text{C}$  and  
127 kept under vacuum overnight to sublime the TBA crystals (Figure 1b). The  
128 removal of TBA through this process results in a porous green body structure  
129 (inset of Figure 1b). Some samples were also prepared using water as the  
130 solvent as follows: 15-30 wt. % LLZO, was mixed with 1 wt.% Darvan, 1 wt.%  
131 Poly(vinyl alcohol) (PVA) and the remainder deionized water, then ball milled  
132 overnight and frozen at a cooling rate about of  $\sim 20\text{ }^\circ\text{C}/\text{min}$ . One sample was  
133 also prepared substituting gelatin for PVA.

134 The scaffolds were then sintered at  $1050\text{ }^\circ\text{C}$  for 2 h in Ar atmosphere.  
135 Ambient air was avoided because a large amount of lithium was lost,

136resulting in decomposition of the LLZO and crumbling of the structure (SI,  
137Figure S1). The sintered scaffolds decreased in volume substantially (inset of  
138Figure 1b). The scaffolds were then encapsulated with epoxy (Allied High  
139Tech Products, Inc.) to avoid destroying the scaffold during the following  
140operations, which had an insignificant volume change after curing, and sliced  
141into thin sections using a diamond saw. The LLZO section with thickness of  
142200  $\mu\text{m}$  showed high optical transparency (Figure 1c). Freestanding porous  
143LLZO scaffold films were obtained after burning away the epoxy in dry air at  
144800  $^{\circ}\text{C}$  for 30 min.

## 1452. Preparation of dense/porous LLZO bilayer structures

146 The oriented scaffold becomes fragile and hard to handle after  
147sintering, especially when sliced thin. Adding PVDF binder into the NMC  
148slurry helps to keep the integrity of the composite electrode. Another  
149solution to avoid damage and fracture during assembly is to support the  
150porous layers with a dense layer to form a bilayer structure. In this study,  
151two types of dense LLZO structures with thicknesses of approximately 100  
152 $\mu\text{m}$  and 20  $\mu\text{m}$  were used for the proof of principle study and the prototype  
153half-cells, respectively. The thick dense films were fabricated using a tape  
154casting method. The LLZO slurry for the dense layer preparation was a  
155mixture of 30 wt.% LLZO powders, 3 wt.%  $\text{Li}_2\text{CO}_3$  (32 wt.% extra elemental Li  
156in LLZO), 3 wt.% PVA and 64 wt.% analytically pure isopropyl alcohol. The  
157slurry was introduced into a  $\text{ZrO}_2$  container and ball milled with  $\text{ZrO}_2$  milling  
158media using a SPEX 8000M mixer for 30 minutes to guarantee a stable



159suspension of LLZO. Then the slurry was tape cast onto conventional  
160household polyethylene membranes using a doctor blade, and dried at room  
161temperature. The dried LLZO film was peeled off the polyethylene  
162membrane, cut into pieces and cold pressed using a stainless-steel die.

163 The ultrathin LLZO dense films ( $\sim 20 \mu\text{m}$  thick) were fabricated  
164adopting a previously reported approach.<sup>34</sup> LLZO,  $\text{Li}_2\text{CO}_3$ , polyvinyl butyral  
165(binder), and benzyl butyl phthalate (plasticizer) were dissolved/dispersed in  
166an alcohol/acetone mixed solvent system by ball-milling for 48 h using 3 mm  
167 $\text{ZrO}_2$  beads. The suspension was formulated to result in  $\sim 55$  vol.%  
168LLZO/ $\text{Li}_2\text{CO}_3$  excluding the solvent. The amount of  $\text{Li}_2\text{CO}_3$  was selected to  
169equal 50 wt.% excess elemental Li in LLZO. The suspension was tape cast  
170onto a Mylar substrate and left to dry for several hours. The dried green  
171tapes were peeled off and punched to desired sizes for subsequent sintering.

172 The bilayer structure was prepared by co-sintering a LLZO porous  
173scaffold (after epoxy burnout) and a dense film (green) at  $1070^\circ\text{C}$  for 3 h in  
174Ar atmosphere between two pieces of alumina disks, each of which was 2  
175mm thick. No extra pressure was imposed onto the LLZO scaffold and film  
176besides the weight of the alumina disks. In order to prevent unwanted  
177diffusion and reaction with the alumina, graphite foils or Ni meshes were  
178placed between the LLZO and the disks.

### 1793. Active material infiltration and electrochemical testing

180 In this study, the NMC-622 particles (3-12  $\mu\text{m}$ ) provided by Umicore,  
181Inc. were introduced into the LLZO scaffolds as the active material. A slurry

182 was prepared by mixing 84 wt.% NMC-622, 8 wt.% carbon black, and 8 wt.%  
183 PVDF into N-methyl-2-pyrrolidone (NMP). During the stirring, several more  
184 drops of NMP were added to adjust the viscosity of the slurry. The slurry was  
185 then drop-cast onto the LLZO scaffolds. The success of the infiltration  
186 process of NMC particles could be readily indicated by a color change from  
187 natural ivory to black. It usually took several rounds of infiltration to fully fill  
188 the pores, as confirmed by scanning electron microscope (SEM) observation  
189 of the bottom surface of the infiltrated sample. The addition of polyaniline  
190 was also demonstrated in freeze cast structures (see SI, Figure S2e). A  
191 partially infiltrated sample was also prepared using smaller (submicron in  
192 diameter) NMC particles (SI, Figure S3). Smaller NMC particles were obtained  
193 by ball-milling the as-received NMC for 48 h in EtOH using 2 mm ZrO<sub>2</sub> beads  
194 which resulted in fracturing of secondary particles to primary particles. After  
195 infiltration, samples were kept in a vacuum oven at 80 °C overnight.

196 The composite structures were then transferred to an Argon-filled  
197 glove box for assembly into coin cells. For the hybrid cells, Celgard 2400  
198 polypropylene membranes wet with 1 M LiPF<sub>6</sub> in ethylene carbonate : diethyl  
199 carbonate (1 : 1 vol%) were employed as separators, and Li foils (Alfa-Aesar)  
200 were used as the anodes. The coin cells were then galvanostatically cycled  
201 using a VMP3 multichannel potentiostat/galvanostat equipped with a  
202 frequency response analyzer between 2.5 and 4.7 V at a current density of  
203 0.3 mA/cm<sup>2</sup> (approximately a ten hour rate) after 12 hours rest. The  
204 impedance was measured from 1 mHz to 100 kHz every 10 cycles. The

205bilayer structures were also assembled into coin cells with lithium anodes,  
206without polymeric separators or liquid electrolyte. The open circuit voltage  
207was monitored for 12 h.

#### 2084. **Structure characterization**

209 The morphologies of the selected samples were examined using a  
210Hitachi TM-1000 tabletop scanning electron microscope (SEM). Filters were  
211applied to binarize the SEM images (SI, Figure S4) to enable measurement of  
212pore size and estimate porosity by calculating the dark area. X-ray powder  
213diffraction (XRD) patterns were acquired on a Bruker D2 PHASER  
214diffractometer with monochromatic Cu  $K_{\alpha}$  radiation to check the phase purity  
215of the samples.

216 Because of the fragility of the LLZO samples after sintering, the freeze  
217cast pellet was first mounted in epoxy prior to sample characterization. Both  
218the LLZO films and longitudinal sections were cut from the same sample.  
219Films were cut perpendicular to the TBA channel growing direction, while the  
220longitudinal sections were cut parallel to the channel direction. The  
221thicknesses of the films and the diameters of the longitudinal sections were  
222controlled to be 200-300  $\mu\text{m}$ . Then synchrotron micro computed tomography  
223(SR- $\mu\text{CT}$ ) experiments were performed at Hard X-ray Micro-Tomography  
224Beamline 8.3.2 of the Advanced Light Source (ALS) on the samples. Images  
225were collected over 180 degrees in 0.072 degree steps, with 24 keV X-rays.  
226Detection was accomplished with a 50 micrometer thick LuAG:Ce scintillator,  
227a 10x Olympus optical lens in an optical system from Optique Peter, and a

228PCO.edge sCMOS detector, with 500 ms exposure time. Dark field images  
229(with the X-ray shutter closed) were collected to subtract detector dark  
230counts, and bright field images were collected before and after the sample  
231scan to normalize for variations in the incident illumination. The voxel  
232dimension with this setup was approximately 0.64 microns. Tomographic  
233reconstruction was done with TomoPy<sup>35</sup> and Xi-CAM<sup>36</sup>. Visualization and  
234analysis was done with Avizo, from FEI.

235 The elemental distribution of the NMC particle-infiltrated LLZO  
236scaffolds was mapped using the synchrotron radiation based X-ray micro-  
237fluorescence (SR- $\mu$ XRF) technique, which was conducted at Beamline 12.3.2  
238of the ALS. The specimen cross-section along the thickness direction was  
239raster scanned using a micro-focused polychromatic X-ray beam (5 - 24  
240keV). At each scanning position the fluorescence signal was collected with a  
241silicon drift detector. In this study, the Zr K-edge and Mn K-edge intensities  
242were recorded, and thus the concentration distribution of these two elements  
243were obtained.

244

## 245 **Results and discussion**

246 The fracture surface of a green body made using TBA frozen at -20 °C  
247is shown in Figures 2a and b. The long channels exhibit clean and sharp  
248edges, with minimal bridging. After sintering, the structure shrank by about  
24935% in diameter and became fragile. The fracture surface of the sintered  
250scaffold in Figure 2c and d displays walls with high density and low thickness,

251 composed of grains about 2  $\mu\text{m}$  in diameter. The walls in the scaffold are  
252 only a few grains thick, and the pores are prismatic in shape and well faceted  
253 due to the directional growth behavior of the TBA.

254 The 3D image of the sintered scaffold was collected using SR- $\mu\text{CT}$ . A  
255 sub-volume with the size of 700  $\mu\text{m}$   $\times$  700  $\mu\text{m}$   $\times$  200  $\mu\text{m}$  of the LLZO film is  
256 shown in Figure 3a. A video of the reconstructed model is included in the  
257 supporting information, and one slice of the top view and left view from this  
258 video are shown in Figures 3b and c, respectively, indicating that the pore  
259 size is around 50  $\mu\text{m}$  and that the pores are uniformly distributed throughout  
260 the whole structure. Better contrast is obtained from the 3D model of a LLZO  
261 longitudinal section shown in Figure 3d. By rotating the image, it is found  
262 that the smooth and empty channels with the same orientation are present  
263 and there is no bridging over the length range of several hundred microns  
264 (Figures 3e and f), which by far exceeds the thickness of the scaffolds ( $\sim$ 100  
265  $\mu\text{m}$ ). Moreover, the shape and size of the channels remain comparatively  
266 unvaried throughout the thickness of the sample. The long-range bridge-free  
267 structure provides distinct advantages for the infiltration process compared  
268 to the slit-like or layer-stacked structures fabricated using water as the  
269 solvent for freeze casting (SI, Figure S2, S5).

270 The temperature of the cooling bed in the freeze cast apparatus is one  
271 of the key processing parameters for optimizing the pore size and porosity of  
272 the LLZO scaffold. A lower cooling temperature leads to more nucleation  
273 sites and higher solidification velocity, and thus finer TBA dendrites are

274formed, resulting in more, smaller pores than when the temperature is  
275higher. However, if the temperature is too low, the sample may crack; if it is  
276too high, the slurry will not freeze completely in a reasonable period of time.  
277The SEM images of the top cross sections of samples which are frozen at -20  
278and -50 °C are compared in Figure 4. Both samples were sintered before  
279taking the SEM photos. The average pore size of the sample processed at -20  
280°C is about 52 μm, twice as large as the one fabricated at -50 °C (~23 μm). A  
281statistical analysis of the white (LLZO scaffold) and black areas (pores)  
282indicates that the porosity of the -20 °C sample is 73 vol.% and the -50 °C  
283sample has a lower porosity of about 60 vol.%. The same trend was also  
284reported by Xu *et al.* in the freeze cast lead zirconate titanate (PZT)  
285system.<sup>37</sup> As the cooling bed temperature decreases, a higher volume  
286fraction of pore walls form, and pore size decreases.

287 After the initial sintering but prior to epoxy burned out, the excess  
288Li<sub>2</sub>CO<sub>3</sub> used to compensate for Li loss results in the formation of some  
289tetragonal LLZO, evidenced by the weak peak splitting observed in the XRD  
290pattern (Figure 5a). After the epoxy removal heat treatment, the tetragonal  
291LLZO signals disappear and the structure fully converts to cubic LLZO, with  
292traces of LiAlO<sub>2</sub> and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> impurities associated with Li loss due to the  
293high temperature exposure. Although increasing the amount of excess of  
294Li<sub>2</sub>CO<sub>3</sub> helps to compensate for the Li loss, it also accelerates the sintering  
295process and generates cracks in the bulk of LLZO scaffold, which is  
296undesirable.

297 As the NMC particles are comparable in size to the pore size obtained  
298 at  $-50\text{ }^{\circ}\text{C}$ , the infiltration would be challenging. Only a few point contacts  
299 would be formed between LLZO and NMC, which is harmful to the cell  
300 performance. Thus, the scaffold made at  $-20\text{ }^{\circ}\text{C}$  is preferable for cell testing.  
301 The bottom view of the LLZO scaffold freeze cast at  $-20\text{ }^{\circ}\text{C}$  infiltrated with  
302 NMC particles, PVDF, and carbon suggests that a fraction of the pores are not  
303 completely filled (Figure 5b). A scaffold about 8 mm in diameter and 1 mm in  
304 thickness was infiltrated using the same process and contains 7.9 mg NMC-  
305 622, corresponding to active material loading of  $15.7\text{ mg/cm}^2$  or about  $3.14$   
306  $\text{mAh/cm}^2$  (based on the practical specific capacity of  $200\text{ mAh/g}$ ), similar to  
307 loadings used in commercial lithium-ion batteries. It was then incorporated  
308 into a hybrid cell with Celgard separator, electrolytic solution, and Li anode,  
309 and was cycled at a current density of  $0.3\text{ mA/cm}^2$  between 4.7 and 2.5V  
310 (approximately C/10). The charge and discharge profiles of every tenth cycle  
311 as a function of cycle number are shown in Figure 6a, together with  
312 Coulombic efficiency and capacity for each cycle (Figure 6b). The initial  
313 capacity of NMC-622 is similar to that of previously reported values, which is  
314 around  $200\text{ mAh/g}$  when charged to over 4.5 V.<sup>38,39</sup> The areal capacity is also  
315 comparable to the reported high areal loading liquid Li/NMC-622 cell of about  
316  $3\text{ mAh/cm}^2$  with current density of  $0.5\text{ mA/cm}^2$ .<sup>40,41</sup> There is some capacity  
317 fading observed, but it is similar to what is seen in conventional NMC half-  
318 cells cycled under similar conditions.<sup>42</sup> The fading can be attributed to the  
319 increased interfacial impedance (Figure 6c) caused by the formation of a

320resistive cathode/electrolyte film and surface reconstruction to rock salt,  
321similar to what is seen in the conventional cells. This has been documented  
322in many reports using surface sensitive characteristic techniques<sup>39,42-46</sup>. These  
323results can be taken as proof of principle that infiltrated scaffolds of LLZO  
324can be used as cathodes in cells, although further optimization is required.

325        Although the specific area loading of the active material NMC  
326demonstrated in this example, 15.7 mg/cm<sup>2</sup>, is fairly high, the pores are not  
327completely filled using the drop casting method. The density of NMC-622  
328provided by the manufacturer is about 2 g/cm<sup>3</sup>. From the SEM images, the  
329porosity of the LLZO scaffold is estimated to be approximately 70% of the  
330total volume. Therefore, only 11% of the pore volume is filled by NMC-622.  
331Thinner scaffolds, similar to what is used in lithium ion batteries (about 1/10  
332of this thickness or ~100 μm) would be easier to infiltrate and would most  
333likely perform better, particularly if a completely solid state configuration is  
334used. Work on making thinner scaffolds and optimizing the infiltration  
335process is currently underway in our laboratories.

336        The ultimate goal is to use the scaffolds in a totally solid state  
337configuration. To this end, we built bilayer structures, in which a dense LLZO  
338layer is stacked with a porous scaffold and sintered together (Figure 7a). In  
339other words, the dense LLZO layer is employed in this configuration to play  
340the role that both the separator and liquid electrolytic solution play in a  
341hybrid cell. From the XRD patterns in Figure 7b, fewer impurities are formed  
342in the scaffold upon sintering in a bilayer configuration than those shown in



343Figure 5a, because the dense layer acts as an additional source of lithium.  
344Figure 7c and d show the fracture surfaces of the bilayer structures with 100  
345 $\mu\text{m}$  and 20  $\mu\text{m}$  thick dense layers fabricated by the two different approaches  
346explained in the experimental section, respectively. In both structures, the  
347porous scaffold is about 150  $\mu\text{m}$  thick. A smooth fracture surface will be  
348formed if the scaffold and dense layer are well connected, which is important  
349for ion transfer. Combining the results from the SEM photos and the fracture  
350surfaces, it appears that the connections are partly formed, but there are still  
351some gaps between scaffold and dense layer, which may be caused by  
352different shrinkage rates of the two parts during the sintering procedure. The  
353overall differences in shrinkage rates can be caused by the difference in  
354porosities and additive concentrations. In addition, once a local connection is  
355formed, the area around will be pinned (SI, Figure S6b), and the uneven  
356shrinkage may result in gaps between the layers and even pinholes in the  
357dense layer (SI, Figure S6c). It can also be seen that the channels in the  
358scaffold are oriented slightly off the normal direction of the interface.

359 After the active material NMC-622 was infiltrated into the scaffold, the  
360cross section morphology of the bilayer structure was first observed in SEM  
361in backscattered electron (BSE) mode (Figure 7e), and then the elemental  
362distribution was mapped using the SR- $\mu\text{XRF}$  method, focusing on the Mn K-  
363edge signals arising from the NMC and the Zr K-edge signals from LLZO  
364(Figure 7f). The Mn signal is primarily located in the areas where Zr is absent  
365and almost fills these spaces, even though many of the NMC particles cannot

366be seen in the corresponding SEM images. From the map as well as the SEM  
367images, a thin layer of NMC particles are observed on top of the scaffold  
368after infiltration, indicating some heterogeneity in the distribution. A cell with  
369a lithium foil anode and bilayer with the 20  $\mu\text{m}$  thick dense layer as separator  
370was assembled and the open circuit voltage (OCV) monitored over a period  
371of about twelve hours (SI, Figure S7). Initially, the OCV was close to 0V,  
372indicating shorting of the cell. However, the potential rose to 2V over 2  
373hours, and then reached 2.8 V after 12 hours, the expected potential for a Li/  
374NMC cell in the discharged state. This indicates that there was a soft short  
375that could have been caused by pinholes in the dense film, which allowed  
376some carbon particles to cross over and caused initial voltage instability (SI,  
377Figure S8). Although thicker dense layers might mitigate the soft short  
378problem, this would come at the cost of higher cell resistance and reduced  
379energy density due to the weight of the excess LLZO. Therefore, it remains a  
380particular challenge when very thin dense layers are used in solid-state  
381configurations along with extremely fine particles of carbon. The tri-layer  
382LLZO reported by G. T. Hitz *et al.* offers a successful example for densifying  
383multi-layer LLZO structures through laminating green LLZO layers as porous-  
384dense-porous sandwich structures<sup>47</sup>. This method decreases the difference in  
385shrinkage rates between the scaffolds and dense layers and also balances  
386the stresses on both sides. However, for the porous structure made by freeze  
387casting in the current study, the bulk scaffold needed to be sliced into thin  
388sections, and the fragile ceramic structure needed to be stabilized. Thus

389sintering the structure for a short time was required. We are currently  
390exploring making trilayers and using a related technique, which yields  
391thinner structures (freeze tape casting), and which will simplify this process.

392 A number of technical questions arise for this approach. The oriented  
393low-tortuosity channels in the freeze cast scaffolds should be advantageous  
394because they minimize ion diffusion distances, but it is not clear what the  
395optimized channel sizes, wall thicknesses, and porosities should be. To  
396attempt to answer these questions, we established a simple model for semi-  
397quantitative estimations of these parameters. For the model, the geometric  
398configuration of the porous scaffold shown in Figure 8a was assumed. The  
399channels are assumed to run through the thickness of the scaffold and have  
400smooth walls, have the same constant diameter, and are uniformly  
401distributed with no bridges to form a regular hexagonal honeycomb. The top  
402view in Figure 8b shows the various parameters such as the pore diameter  
403( $d_p$ ), wall thickness ( $d_w$ ), porosity, and number density of the pores. Taking  
404the number density of the pores as  $N$  (per unit area), the side length  $a$   
405(distance between centers of adjacent pores) of the regular hexagonal base  
406is calculated to be:

$$407 \quad a = \left( \frac{2}{\sqrt{3}} \frac{1}{N} \right)^{1/2} \quad (1)$$

408 For a scaffold with the porosity  $P$ , the diameter of the pores  $d_p$  and the  
409wall thickness  $d_w$  are:

410 
$$d_p = \left( \frac{4P}{\pi N} \right)^{1/2} = \left( \frac{2\sqrt{3}P}{\pi} \right)^{1/2} \cdot a \quad (2)$$

411and

412 
$$d_w = a - d_p = \left[ 1 - \left( \frac{2\sqrt{3}P}{\pi} \right)^{1/2} \right] \cdot a \quad (3)$$

413respectively. It is self-evident that for higher porosities in the structure, more  
 414active material can be infiltrated into the channels resulting in higher areal  
 415capacity. However, Equation (3) suggests that the porosity cannot be close  
 416to 100%. Even when the wall thickness is infinitesimally small, LLZO will be  
 417left at the corners of the hexagons shown in Figure 8b to maintain the

418integrity of the scaffold, and a theoretically maximal porosity,  $P_{max} = \frac{\pi}{2\sqrt{3}} = 91\%$   
 419, will be obtained.

420 When using this type of scaffold structure with active material  
 421infiltrated into the channels, which run approximately parallel to the current  
 422direction, the lithium diffusion path length is shortened and effective  
 423NMC/LLZO contact area is increased, compared to the case in which dense  
 424LLZO films are employed. A semi-quantitative evaluation of the improved  
 425performance is estimated. Considering that Li ions diffuse in LLZO and in the  
 426active material at different rates, we can define a constant K as the

427diffusivity ratio:  $K = \frac{D_{LLZO}}{D_{cathode}}$ . From Einstein's random walk theory<sup>48</sup>, we know

428 that in a certain period of time the Li ion diffusion distance in LLZO and in the  
 429 active material follow a square root relationship. In other words, in the same  
 430 period of time, Li ions will migrate the length  $L_{NMC}$  in NMC as  $\sqrt{K} \cdot L_{NMC}$  in  
 431 LLZO. The equivalent Li ion diffusion path in the porous/dense bilayer  
 432 structure  $L_{bilayer}$ , assuming that the channels are all fully infiltrated by active  
 433 materials, and that Li ions need to first diffuse from NMC to LLZO and then  
 434 migrate through LLZO, is expressed as:

$$435 \quad L_{bilayer} = \int_0^{t_s} \int_0^{\frac{1}{2}d_p} \int_0^{2\pi} \left[ \sqrt{K} \left( \frac{1}{2}d_p - r \right) + t \right] \cdot r d\theta dr dt, \quad (4)$$

436 where  $r$ ,  $\theta$  and  $t$  define a cylindrical coordinate system, and  $t_s$  denotes the  
 437 thickness of the scaffold. Combining Equations (1), (2) and (4),  $L_{bilayer}$  is  
 438 expressed as:

$$439 \quad L_{bilayer} = \frac{1}{24} \pi \left( \sqrt{K} d_p^3 t_s + 3 t_s^2 d_p^2 \right). \quad (5)$$

440 It is called the equivalent diffusion path because the diffusivity difference  
 441 between Li-in-NMC and Li-in-LLZO is considered, and the diffusion path  
 442 length in NMC is normalized by calculating its equivalent length in LLZO.

443 To consider a cell in which only a dense LLZO film and a dense layer of  
 444 active material are used, assuming the thickness of LLZO film and amount of  
 445 NMC active material are the same as used in the bilayer structure, the  
 446 thickness of the active material layer is  $t_a = P \cdot t_s$ , and in this situation the total  
 447 equivalent diffusion path length  $L_{dense}$  is calculated to be:

448 
$$L_{dense} = \int_{t_s}^{t_s+t_s} \int_0^{\frac{1}{2}(d_p+d_w)} \int_0^{2\pi} (t_s + \sqrt{K}t) \cdot r d\theta dr dt = \frac{1}{8} \pi d_p^2 t_s^2 (2\sqrt{K} + \sqrt{K}P + 2)$$
 (6)

449 To compare the equivalent diffusion path lengths of porous and dense  
 450 LLZO films, the  $L_{bilayer}$  to  $L_{dense}$  ratio is computed to be

451 
$$\frac{L_{dense}}{L_{bilayer}} = \frac{3t_s(\sqrt{K}P + 2 + 2\sqrt{K})}{\sqrt{K}d_p + 3t_s}$$
 (7)

452 In most cases, the pore diameter  $d_p$  is much smaller than thickness of  
 453 the scaffold  $t_s$ . Thus, the ratio is approximated to be:

454 
$$\frac{L_{dense}}{L_{bilayer}} = 2\sqrt{K} + 2 + \sqrt{K}P$$
 (8)

455 From this point of view, the higher the porosity is in the porous  
 456 structure, the better the performance that can be obtained, and the faster  
 457 the diffusion is in LLZO compared to the active materials, the more  
 458 enhancement can be achieved. With NMC particles infiltrated in the LLZO  
 459 scaffold,  $K$  can be estimated to be about 10, according to the reported Li ion  
 460 diffusivity around  $10^{-10}$  cm<sup>2</sup>/s in NMC<sup>49</sup> and  $10^{-9}$  cm<sup>2</sup>/s in LLZO<sup>50</sup>. Since porosity  
 461  $P$  ranges between 0 and 0.91, the equivalent diffusion path length of the  
 462 bilayer structure is 88% to 91% shorter than that of the dense LLZO for Li  
 463 ions. Although there is considerable variation for the literature values of Li  
 464 ion diffusivities in LLZO<sup>50-53</sup> and NMC<sup>49, 54-56</sup> it is still true that the equivalent  
 465 diffusion path length of the bilayer structure is much shorter than that of the  
 466 dense LLZO configuration.

467 In practice, this will be highly dependent upon how intimately the  
 468 active material and LLZO contact each other, and will require careful  
 469 optimization of the fabrication parameters. Thus a dimensionless quantity,  
 470  $A_{contact}$ , which is defined as the contact area per unit LLZO film cross-sectional  
 471 area, is calculated by summing up the contribution from two parts - the base  
 472  $A_b$  and the side-walls  $A_w$ :

$$473 \quad A_{contact} = A_b + A_w = \frac{1}{4} N \pi d_p^2 + N \pi d_p t_s \quad (9)$$

474 Substituting Equations (2) and (3) into (9), we get:

$$475 \quad A_{contact} = P + \frac{4Pt_s}{d_p} \quad (10)$$

476 From Equation (10), it is apparent that the diameter of the channels  
 477 should be as small as possible to increase contact area, but also that the  
 478 porosity should be as high as possible. To decrease the channel diameter,  
 479 lower cooling temperatures and higher solidification rates in the freeze  
 480 casting experiment are preferred. However, as revealed in the experimental  
 481 study, higher freezing rates also decrease the wall thickness. Moreover, the  
 482 wall thickness thinning rate is usually slower than the channel diameter  
 483 shrinking rate, resulting in lower porosity, which is not desirable in terms of  
 484 battery capacity, diffusion path length, and contact area. Therefore, it is not  
 485 useful to tune the microstructure by changing the cooling rate only. To  
 486 obtain small pore diameter and high porosity simultaneously, the LLZO slurry  
 487 mass loading has to be decreased as well.

488 It must be emphasized that the model presented above primarily  
489considers the Li ion diffusion path length. However, in reality, more factors  
490may need to be taken into account. Charge transfer occurs at the  
491cathode/LLZO interface during cell cycling and the kinetics will have a strong  
492impact on the performance of the cell. Besides contact area, the selection  
493and matchup of the morphology and size of the active material particles with  
494respect to the pores in the LLZO films are equally important. Large active  
495material particles are more difficult to infiltrate into the pores and channels  
496and may result in relatively fewer points of contact between active material  
497and LLZO than if smaller particles are used. However, if small particles are  
498infiltrated into pores much larger than their diameters, there will also be  
499particle-to-particle charge transfer resistance. Moreover, volume changes  
500during redox processes will affect the amount of contact among all the  
501components in the composite, and, thus the electrochemistry.

502

### 503**Conclusion:**

504 Here we propose a novel configuration for thick composite electrodes  
505in solid-state batteries utilizing a freeze casting approach to make ionically  
506conductive porous scaffolds, which are then infiltrated with active material  
507and other components. To illustrate the principle, we prepared scaffolds  
508using LLZO and TBA as the solvent. By changing the cooling bed  
509temperature and thus the solidification rate, the porosities and channel  
510diameters can be varied. Sintering then strengthens the structure and



511densifies the pore walls. 3D models of the LLZO scaffolds and longitudinal  
512sections were examined using monochromatic SR- $\mu$ CT, and show that the  
513low-tortuosity channels are uniformly distributed parallel to the thickness of  
514the scaffold, with pore diameters almost constant from top to bottom. The  
515open and oriented channels with few bridges make it possible for large  
516commercial cathode particles to be infiltrated into the structure readily. As  
517an example, a composite NMC622/LLZO electrode was successfully cycled in  
518a hybrid cell configuration. Bilayer structures were also fabricated by co-  
519sintering a dense layer and a porous layer together. SR- $\mu$ XRF shows that the  
520porous layer was successfully infiltrated with active material. It was possible  
521to read an open circuit potential on a totally solid state half cell consisting of  
522a lithium anode and the infiltrated bilayer structure. Theoretical calculations  
523were performed to model the porosity of the scaffolds, indicating that the  
524porosity cannot exceed 91%. Higher porosity results in higher energy density  
525and should result in improved rate capability, by offering shorter diffusion  
526path lengths and larger contact areas. However, smaller channel diameters  
527result in increased contact area between the ionic conductor and active  
528material, which also benefits performance. While lowering the temperature  
529of the freeze casting experiment results in smaller pore sizes, it also  
530decreases porosity. With these design considerations in mind, it is suggested  
531that the loading of LLZO in slurries for freeze casting experiments should be  
532lowered to meet the simultaneous goals of increased porosity and smaller  
533pores.

534

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549

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- 735

## 736 **Figure captions**

737 Fig. 1 Schematics of (a) the freeze casting apparatus and (b) formation of the  
738 porous green body by freeze drying. Insets are the bulk scaffold before and  
739 after sintering, with rulers serving as scale bars. (c) shows slices cut from the  
740 sintered scaffold mounted in epoxy. A 200  $\mu\text{m}$  thick slice is transparent, as  
741 displayed in the lower part of (c).

742 Fig. 2 SEM images of the fractured LLZO scaffolds (a-b) before and (c-d) after  
743 sintering.

744 Fig. 3 The 3D reconstructed structure from the SR- $\mu\text{CT}$  data of (a) the LLZO  
745 film and (b) longitudinal section. The cross sections for the film are shown in  
746 (b) top and (c) left views. (e) and (f) are the top and left views of the LLZO  
747 longitudinal section.

748 Fig. 4 SEM top views of the sintered LLZO scaffolds, frozen at  $-20\text{ }^{\circ}\text{C}$  and  $-50$   
749  $^{\circ}\text{C}$ , respectively, at low and high magnifications.

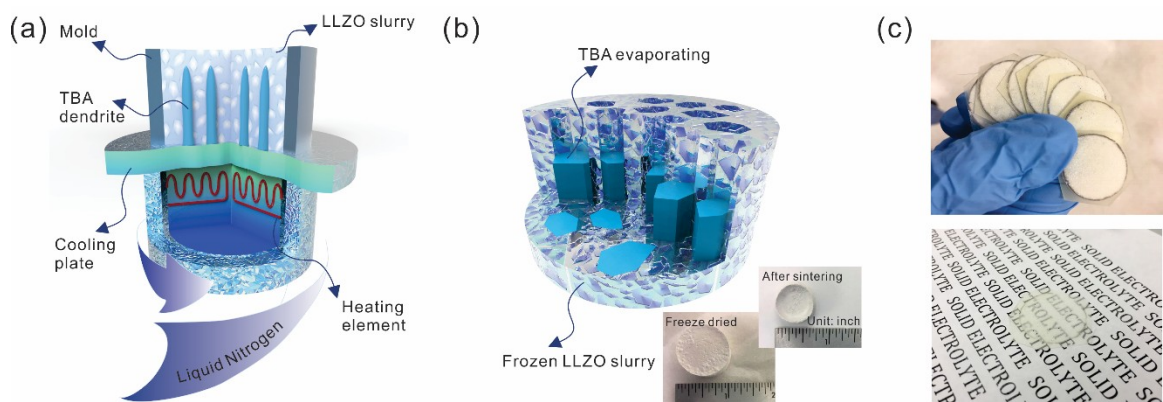
750 Fig. 5 (a) XRD pattern of the scaffold after sintering and after epoxy removal,  
751 respectively. The LLZO XRD peaks are indicated in the lower part. (b) is the  
752 SEM image of the scaffold flipped over after drop casting of NMC particles  
753 from the other side.

754 Fig. 6 (a) The cycling curves, (b) capacity and columbic efficiency, and (c)  
755 impedance curves of the hybrid cell from the 1<sup>st</sup> to the 90<sup>th</sup> cycle.

756 Fig. 7 (a) Schematic of the bilayer fabrication. Inset shows a bilayer structure  
757 on graphite, with carbon left on the top surface after sintering. The porous  
758 scaffold and dense film XRD patterns are displayed in (b). Fractured bilayer

759structure with (c) thick and (d) thin dense films are presented. The SEM  
760backscattered electron image (e) and its synchrotron radiation X-ray  
761fluorescence maps (f) of the infiltrated bilayer structure indicate well-  
762distributed NMC particles in areas where LLZO is absent.

763Fig. 8 (a) The 3D model and (b) top view of the simplified honeycomb  
764structure of the porous LLZO scaffold.



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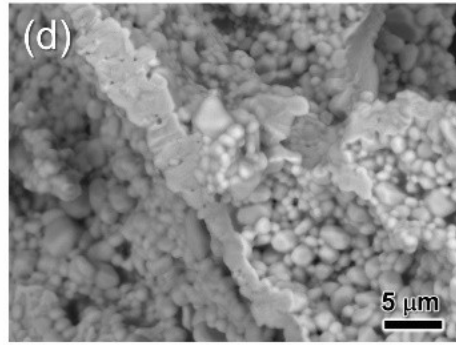
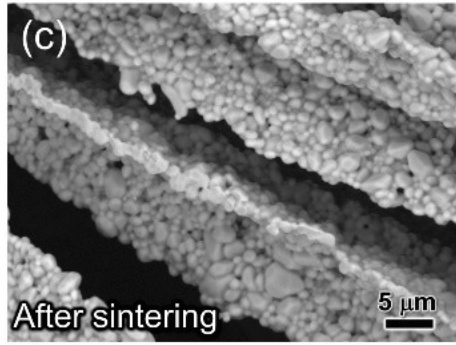
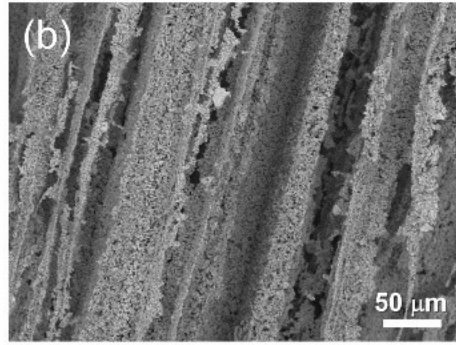
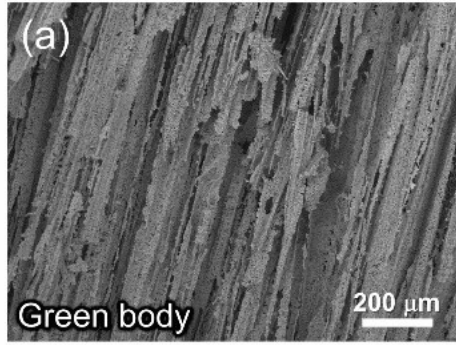
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**Figure 1**



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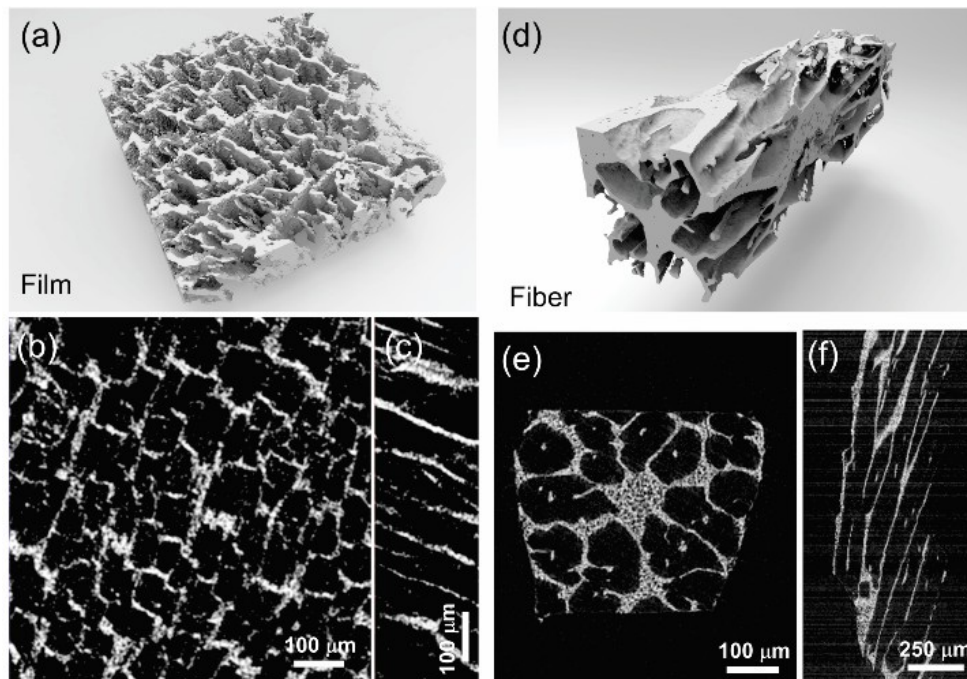
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**Figure 2**



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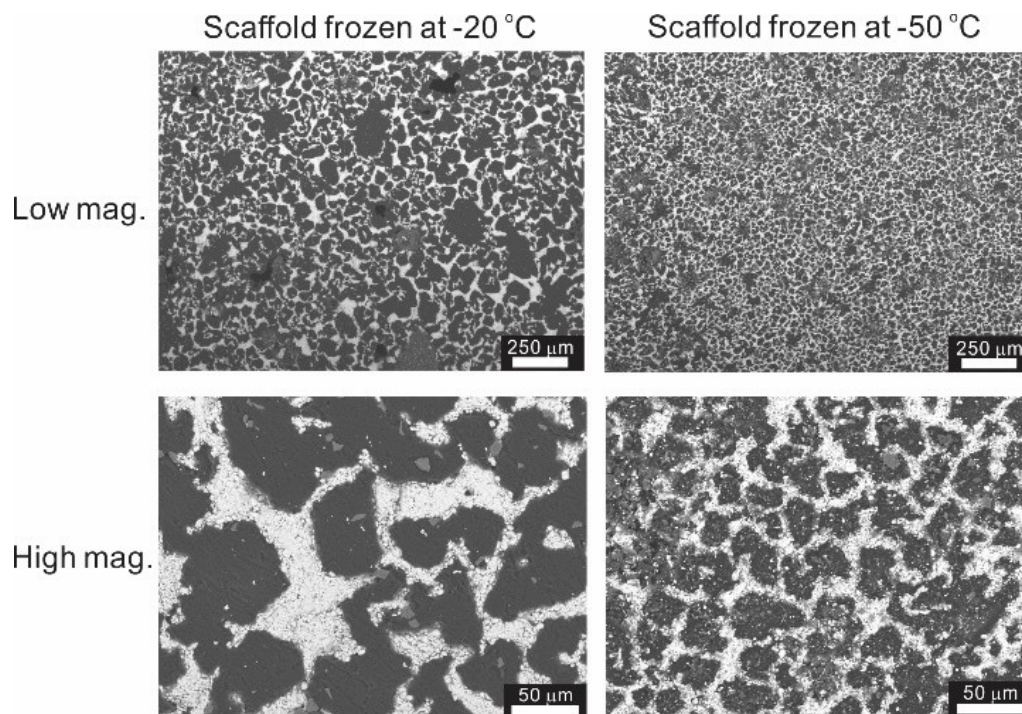
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**Figure 3**



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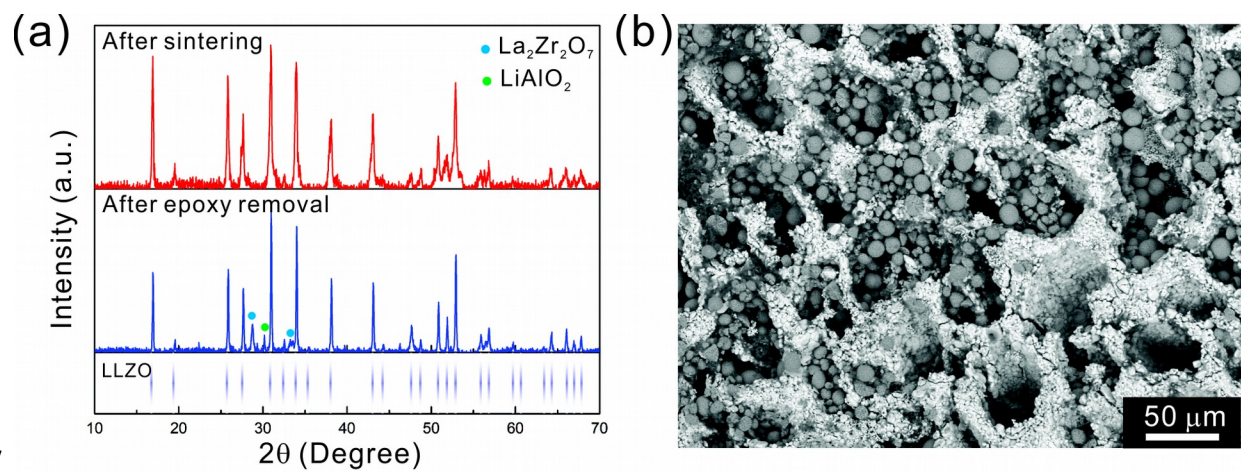
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**Figure 4**



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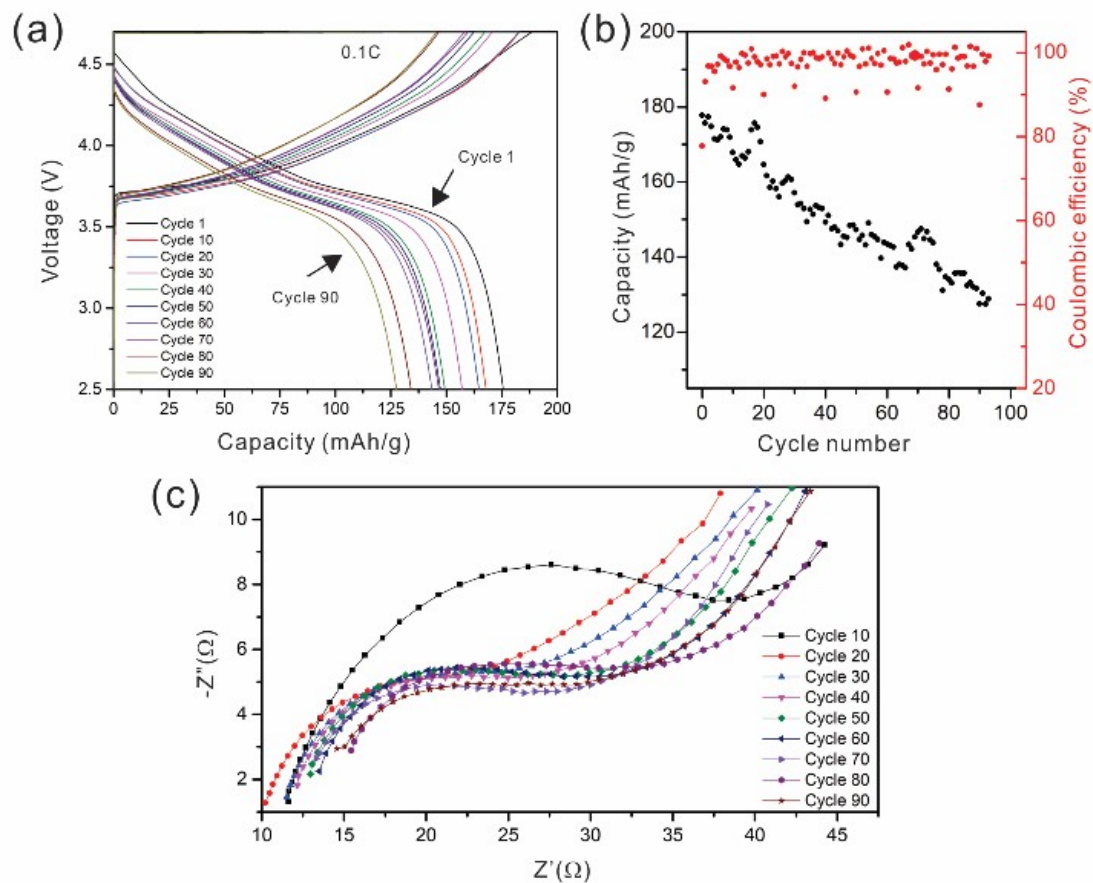
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Figure 5



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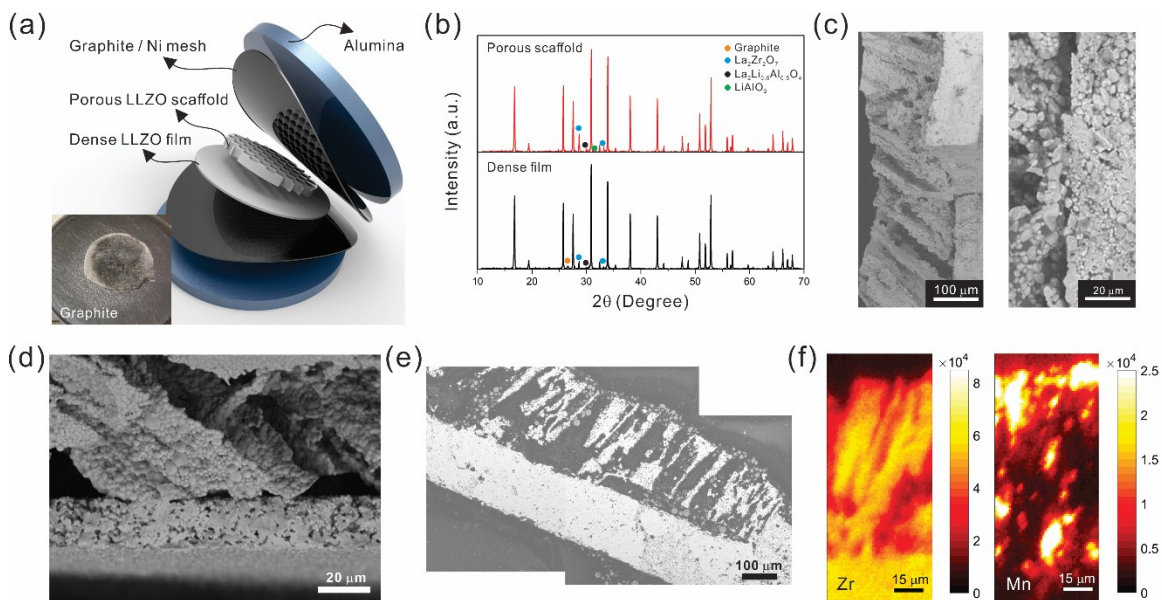
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**Figure 6**



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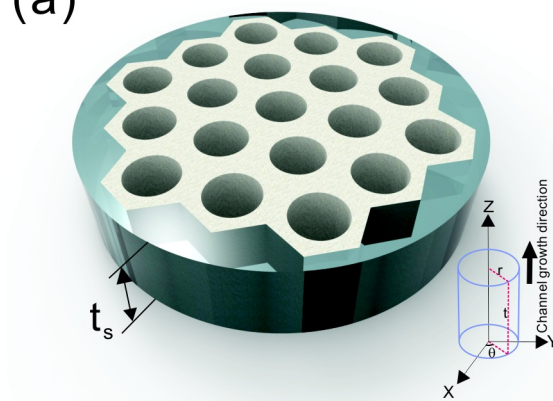
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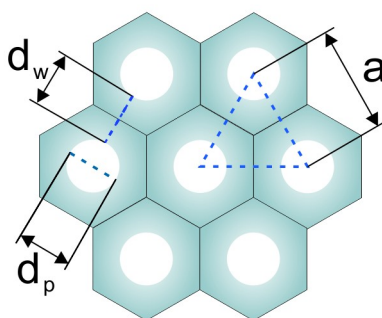
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**Figure 7**

(a)



(b)



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