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Solid Electrolyte Bimodal Grain Structures for

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Improved Cycling Performance

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19

20 Abstract

21 The application of solid-state electrolytes in Li batteries has been hampered by the
22 occurrence of Li-dendrite-caused short circuits. To avoid cell failure, the electrolytes
23 can only be stressed with rather low current densities, severely restricting their
24 performance. Since grain size and pore distributions significantly affect dendrite
25 growth in ceramic electrolytes like $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and its variants, here we have
26 proposed a “detour and buffer” strategy to bring the superiority of both coarse and fine
27 grains into play. To validate the mechanism, a coarse/fine bimodal grain
28 microstructure was obtained by seeding unpulverized large particles in the green body.
29 The rearrangement of coarse grains and fine pores was fine-tuned through changing
30 the ratio of pulverized and unpulverized powders. The optimized bimodal
31 microstructure, obtained when the two powders are equally mixed, allowed, without
32 extra interface decoration, cycling for over 2000 h as the current density was increased
33 from $1.0 \text{ mA}\cdot\text{cm}^{-2}$ gradually up to $2.0 \text{ mA}\cdot\text{cm}^{-2}$. The “detour and buffer” effects was
34 confirmed from postmortem analysis. The complex grain boundaries formed by fine
35 grains discourage the direct infiltration of Li. Simultaneously, the coarse grains further
36 increase the tortuosity of the Li path. Our study sheds light on the microstructure
37 optimization for the polycrystalline solid-state electrolytes.

38

39 Keywords:

40 LLZO solid-state electrolyte; bimodal microstructure; Li dendrite suppression; cycling
41 performance; detour and buffer effects

42 Introduction

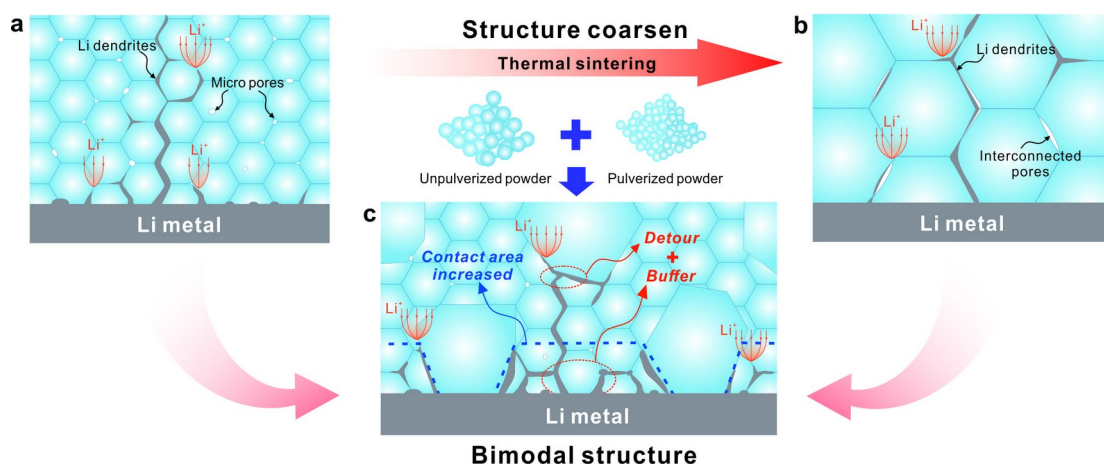
43 The deployment of solid-state electrolytes (SSEs) in all-solid-state Li batteries
44 presents a compelling opportunity due to their nonflammability and compatibility with
45 Li metal, and thus can potentially meet increasing demands for higher energy density
46 and better safety^{1, 2}. Among the various SSEs, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), which is doped
47 with Al, Ga, Ta and so on to stabilize the cubic structure, exhibits high ionic
48 conductivities (10^{-4} to 10^{-3} S·cm⁻¹), a wide operating voltage window, and excellent
49 elastic and shear moduli³. These make LLZO attractive for use in batteries, but a
50 formidable obstacle still exists: Li dendrites (filaments) form easily and eventually
51 cause short-circuit failure to the cells during electrochemical cycling when a certain
52 critical current density (CCD) is exceeded. The CCD values of SSEs are on the order
53 of hundreds μA at room temperature and much lower than those of liquid electrolytes⁴
54 ⁶, leading all-solid-state Li batteries to operate at low rates. Therefore, circumventing
55 Li dendrites at increased current densities is essential to obtain satisfactory
56 performance on commercially applicable all-solid-state Li batteries.

57 The exact mechanism of dendrite growth in SSEs remains elusive^{7, 8}, prompting
58 various strategies to enhance all-solid-state Li battery performance, such as improving
59 Li wettability on the interface⁹⁻¹², boosting the Coble creep of Li^{13, 14}, and adjusting the
60 ratio of ionic and electrical conductivity in SSEs^{15, 16}. Besides interface and transport
61 modification, the intrinsic polycrystalline ceramic nature of LLZO SSEs suggests that
62 microstructures such as grain size, grain boundaries, and pores are closely relevant to
63 Li dendrite growth and CCD¹⁷⁻²⁴. Consequently, designing and optimizing these
64 microstructures are crucial to improving the cycling properties of SSEs.

65 Recent studies have shown that fine-grained solid electrolytes, featuring higher
66 grain boundary densities and isolated pores²⁵, effectively disperse currents and
67 enhance interfacial contacts, allowing higher current densities^{26, 27}. However, such
68 almost straight grain boundary microstructures offer insufficient barriers to Li dendrite
69 growth^{28, 29} (Figure 1a), limiting the CCD of fine-grained SSEs to below $1 \text{ mA}\cdot\text{cm}^{-2}$ ^{20,}
70 ³⁰⁻³². Additionally, the processing window for SSEs with normally distributed fine
71 grains is narrow^{33, 34}. The low energy barrier for sintering fine powders means that
72 grains grow easily. Randomly distributed abnormal grain growth and loose grain
73 boundaries are often observed due to the different mass diffusion rate between grains

74 (In general the larger the grains, the faster they grow). A highly densified structure
 75 with Ostwald ripening and grain coarsening can occur when the sintering time is
 76 prolonged. Even though coarse grains can provide higher ionic conductivity, the loss
 77 of grain boundary complexity, usually accompanied with large interconnected pores
 78 encourage Li-dendrite growth^{22, 35} (Figure 1b). Consequently, neither fine nor coarse
 79 grains solely can effectively promote the electrochemical cycling performance of
 80 LLZO SSEs, since both have pros and cons.

81 To solve this dilemma, we adopted a “bimodal” strategy to the fabrication of
 82 dense LLZO samples. As shown in Figure 1c, by seeding unpulverized powders (mean
 83 diameter of approximately 20 – 30 μm) into the green body with submicron-sized
 84 pulverized powders, we achieved inhomogeneous grain growth during the sintering
 85 process. The result was a microstructure with bimodally distributed grain sizes. Fine
 86 grains filled in the gaps between coarse ones, so that large interconnected pores are
 87 effectively avoided. The microstructure with a bimodal grain size distribution, together
 88 with finely dispersed pores, increased the tortuosity of Li dendrite paths resulting in a
 89 “buffer and detour” effect. As a result, without any additional interface modifications,
 90 the LLZO electrolytes with the bimodal microstructure operated stably at current
 91 densities higher than 1 $\text{mA}\cdot\text{cm}^{-2}$ for more than 2000 hours, and successfully cycled
 92 more than 100 hours at a current density of 2 $\text{mA}\cdot\text{cm}^{-2}$. Our results shed light on the
 93 rational design of the SSE microstructures and advancement of cycling performance of
 94 the all-solid-state Li batteries.



95

96 **Figure 1. Illustration of polycrystalline SSE with different grain size distributions.**

97 (a) Li dendrites propagate along relatively straight pathways inside the fine-grained SSE.

98 (b) Interconnected pores encourage Li dendrite growth in the SSEs with coarse grains. (c)

99 Expected “detour and buffer” effects to suppress Li dendrite growth in SSE with the

100 bimodal grain microstructure.

101

102 **Experimental**

103 **Synthesis of LLZO powder**

104 The Al-doped LLZO powders were synthesized using a sol-gel method,
105 employing LiNO_3 (AR, 99%; Aladdin), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, 99.0%; Aladdin),
106 $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (AR, 99.0%; Aladdin), and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99%; Sigma-Aldrich) as
107 precursors. An extra 14wt% LiNO_3 was added to offset any Li loss during the sintering
108 process. These constituents were dissolved in a mixture of deionized water and citric
109 acid. The resultant solution was boiled at 150 °C and then heated to 400 °C to form a
110 uniform brown foam. This foam was crushed in an agate mortar and calcined at 750
111 °C for 2 h in an Al crucible to produce Al-doped LLZO powder with the cubic
112 structure.

113

114 **Fabrication of bimodal LLZO pellets**

115 The synthesized LLZO was sieved into two aliquots of fine and coarse powders.
116 The fine powder was ball-milled at 400 rpm for 30 min and then air-dried. The
117 particle size was measured using an Omic laser particle analyzer for unpulverized
118 coarse powders and a Malvern Zetasizer Nano ZSE particle analyzer for pulverized
119 fine powders. The size distributions of both powders are shown in Figure S1, having
120 median diameters of 0.95 μm and 26.8 μm , respectively. Subsequently, the pulverized
121 and unpulverized powders were mixed in specific weight ratios and pressed into pellets
122 of 13 mm diameter. The weight percent of the unpulverized coarse powder in the
123 green bodies were adjusted to 0%, 25%, 50%, 75%, and 100% for comparative
124 analysis. These green bodies were sintered at 1180 °C for 6 h in Ar atmosphere to
125 achieve densification. The densified pellets, denoted CP0, CP25, CP50, CP75, and
126 CP100, respectively, were polished with sandpaper to clean the surface and eliminate
127 potential surface impurities. The final LLZO pellets had a thickness of 850 μm and a
128 diameter of approximately 10 mm.

129

130 **Microstructure characterizations**

131 The phase purity of the LLZO was ascertained using a Shimadzu XRD-6100

132 diffractometer equipped with Cu K α radiation. The synthesized LLZO powders and
133 densified pellets were examined using scanning electron microscope (SEM) equipped
134 with X-ray energy dispersive spectroscopy (EDS). A lab-based X-ray computed
135 tomography (CT, Zeiss Xradia 610 Versa) was employed to analyze the pores in the
136 densified LLZO pellets. The X-ray energy was set to 140 keV to ensure sample
137 penetration. The voxel dimension, based on the setup, was 1.4-1.5 μm . More than 990
138 slices were collected for each sample, and tomographic reconstruction was performed
139 using Avizo software from FEI.

140 Synchrotron X-ray nano-Laue-diffraction (nano-Laue) experiments were
141 conducted on Beamline 21A at Taiwan Photon Source (TPS). A polychromatic X-ray
142 beam (5 - 30 keV) was focused to $100 \times 100 \text{ nm}^2$. The LLZO samples were mounted
143 on a scan stage 45° oblique to the incident X-ray. The built-in SEM was utilized to
144 locate the areas of interest. An area of $900 \times 900 \mu\text{m}^2$ was scanned with a step size of
145 $5 \mu\text{m}$ on each sample. At each scanning position, a Laue diffraction pattern was
146 recorded in reflection mode with a 2D detector situated 90° to the X-ray beam, and the
147 fluorescence signals of Zr, Al and La were collected using a Si-drift detector
148 concurrently. The Laue patterns were analyzed using a custom-developed algorithm³⁶,
149 ³⁷ to map the crystal grain distribution on the sintered LLZO.

150

151 **Electrochemical tests**

152 Ionic conductivity was measured via electrochemical impedance spectroscopy
153 (EIS) tests. 10 mV AC voltage (0.1 Hz to 1 MHz) was applied at room temperature
154 using a PARSTAT MC multichannel workstation. The top and bottom surfaces of the
155 LLZO pellets were sputter coated with Pt as blocking electrodes.

156 Li symmetric cells were fabricated by affixing a Li foil on both sides of the
157 LLZO pellets and assembling 2032-type coin cells in a glovebox. The Li foils were 8
158 mm in diameter and $600 \mu\text{m}$ thick. To secure the contact with Li metal, the assembled
159 coin cells were annealed at 150°C for 10 min. Galvanostatic and CCD tests were
160 conducted using a Neware BTS 4000 at room temperature.

161

162 **Results**

163 X-ray diffraction analyses of the synthesized LLZO powder are consistent with a

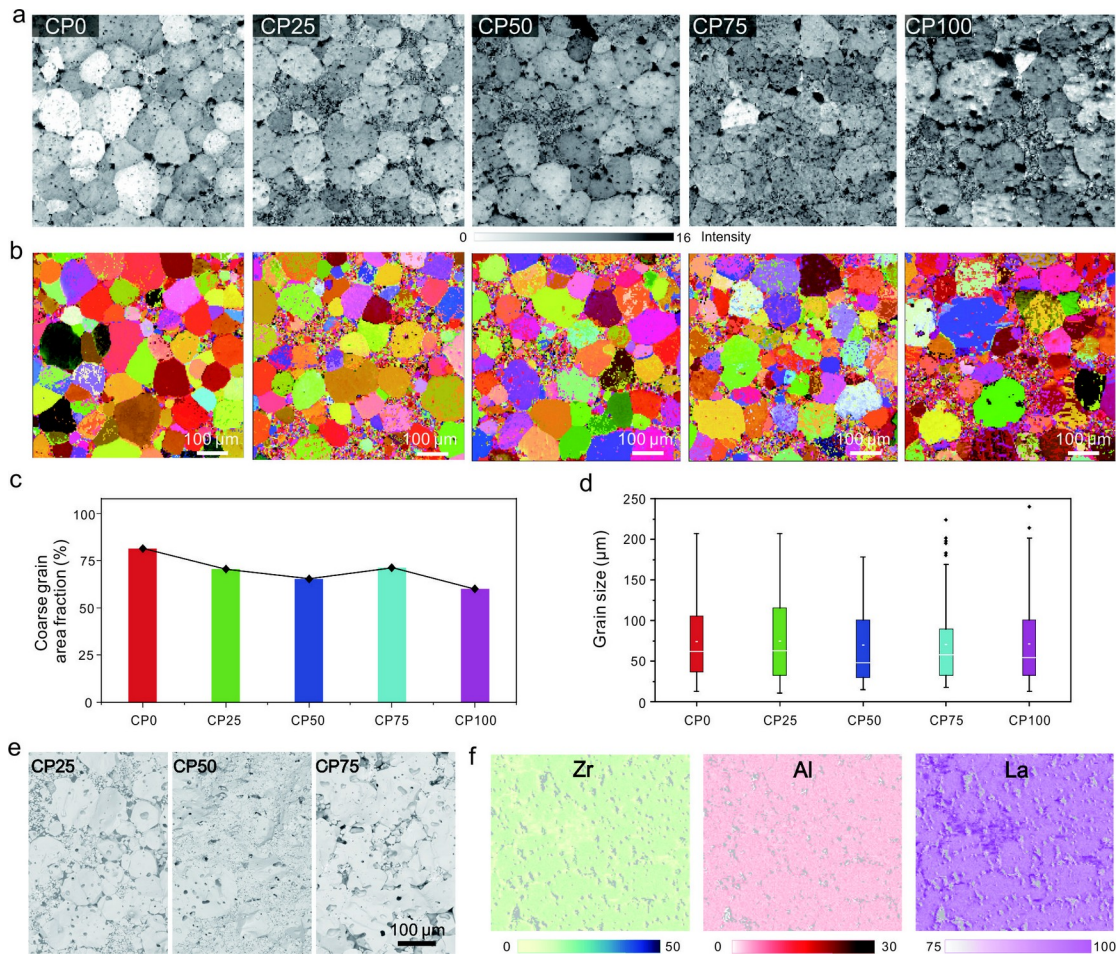
164 cubic phase in the space group Ia-3d (Figure S2a). Minor impurities, primarily LiAlO_2
165 and LaAlO_3 , were detected in the LLZO powder, mainly due to the locally
166 inhomogeneous chemical reaction. These impurities, as shown in Figure S3, will be
167 eliminated during the sintering process, and thus their effects are ignored in this study.
168 The morphology and chemical distributions of both types of powders are displayed in
169 Figure S2b to S2f.

170 After sintering, all the samples, CP0 to CP100, are well-densified and retain the
171 cubic structure (Figure S3). Their relative densities are listed in Table S1. The
172 microstructural characteristics of the post-sintered samples, from CP0 to CP100, were
173 investigated using nano-Laue. Combining the diffraction peak intensity and grain
174 maps plotted in Figure 2a and b, which depict the microscopic defect density and
175 crystal orientation distributions^{38, 39}, CP0 exhibits a normally distributed grain size
176 across the scanned area and does not have a bimodal microstructure, with limited
177 number of pores among the grains. CP25, CP50, and CP75 display increasing area of
178 fine grains (indicated by the mosaic regions) adjacent to the large ones. Considering
179 that each pixel in the map represents an area of $5 \times 5 \mu\text{m}^2$, most of the fine grains
180 within the mosaic regions are less than $10 \mu\text{m}$. CP100 exhibits the largest grains and
181 pores.

182 Subsequently, the sizes of coarse grains were measured quantitatively after
183 filtering fine grains and pores. Pixels within an individual coarse grain were counted to
184 calculate the area and equivalent diameter. As illustrated in Figure 2c, the area fraction
185 of coarse grains initially decreased when the ratio of unpulverized powders in the
186 green body rose to 50%. However, it increased in CP75 and dropped again in CP100.
187 In the statistical analysis (Figure 2d, with total number of measured coarse grains
188 exceeding 100 for each sample), the grain size of all tested samples was predominantly
189 below $120 \mu\text{m}$. Specifically, in CP50, grain growth appears inhibited, resulting in the
190 lowest median grain size among the five samples. The number of grains sized larger
191 than $120 \mu\text{m}$ and smaller than $200 \mu\text{m}$ reduced as the ratio of unpulverized powder
192 increased from 0 to 50%; however, in CP75 and CP100, there was more abnormal
193 grain growth with sizes exceeding $200 \mu\text{m}$.

194 The SEM images of the fracture surfaces of CP25, CP50, and CP75 (Figure 2e)
195 indicate that the coarse grains are surrounded by fine ones, with CP50 displaying the

196 densest structure. As shown in Figure 2f, slight element segregation was observed
 197 between grains. The grey color in the maps are the pores. Areas enriched with La have
 198 less Zr, an effect attributed to Li excess⁴⁰.

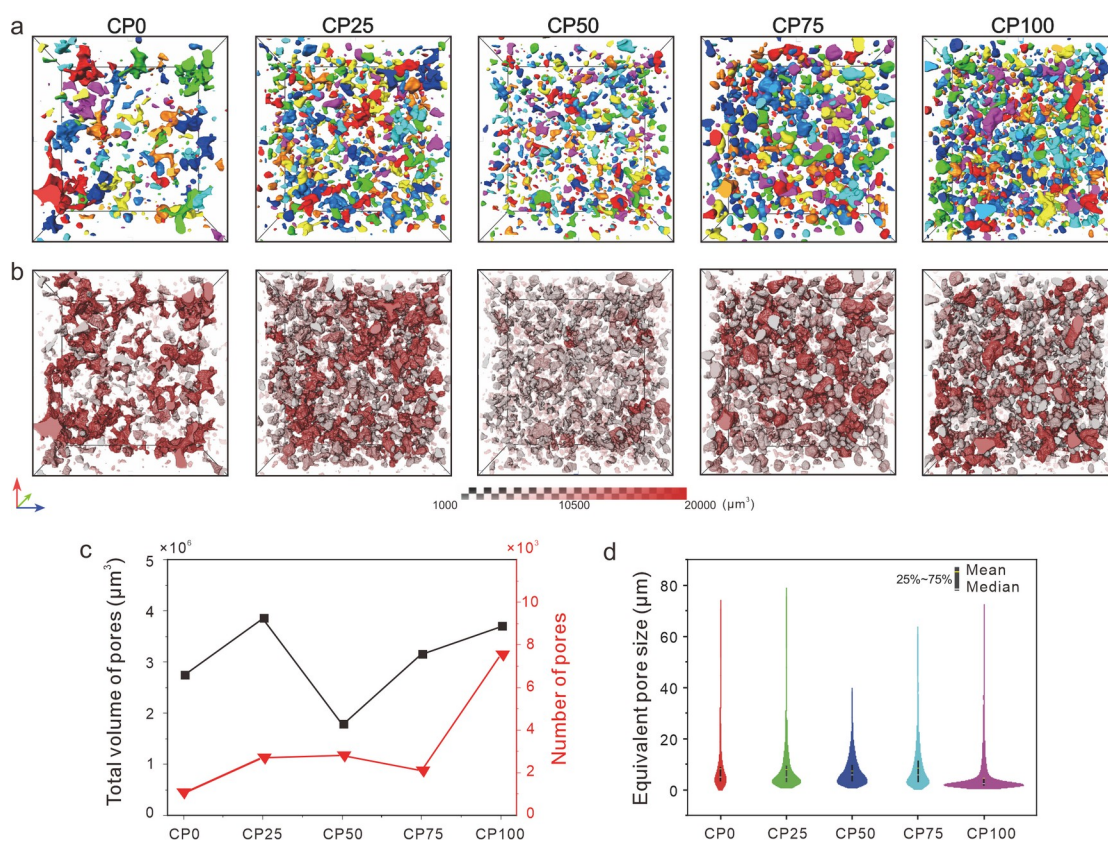


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200 **Figure 2. Grain study of LLZO with bimodal arrangement.** Nano-Laue analyzed grain
 201 distribution as shown in (a) intensity map and (b) color-labeled orientation map. (c) Area
 202 fraction of coarse grains in all five samples. (d) Box chart of coarse grain size
 203 distribution, red line and black dots inside the boxes indicate the mean and median,
 204 respectively. (e) SEM-BSE images of the cross-sectional morphology. (f) X-ray
 205 fluorescence maps on the same nano-Laue scanned area of CP50.
 206

207 The influence of the bimodal microstructure on pore morphology and
 208 distribution within the densified LLZO was investigated using CT. A $431 \times 453 \times 293$
 209 μm^3 volume was selected from a similar position in each fabricated sample for
 210 comparison. In Figure 3a, by labelling adjacent pores with distinct colors, it is clear
 211 that CP0 features large and interconnected pores, while the pores are mostly isolated
 212 in the samples from CP25 to CP100. In Figure 3b, where the translucent-scarlet shades
 213 are employed to represent pore volume distribution, the scarlet color is hardly

214 observed in CP50, proving that pore growth and coalescence was suppressed.
 215 Furthermore, CP50 possesses the smallest total pore volume ($1.78 \times 10^6 \mu\text{m}^3$) among
 216 all five samples, whereas the total number of pores in CP25, CP50 and CP75 are
 217 similar (Figure 3c). Although CP0 has the least number of pores, CP50 is the densest
 218 structure (95.1% density, Table S1). In the violin plot (Figure 3d), pore size
 219 distribution is better visualized. CP50 demonstrates the narrowest pore size
 220 distribution, averaging at $7.2 \mu\text{m}$. Even though CP100 has the lowest average pore size
 221 ($4.3 \mu\text{m}$), a number of large pores ($> 40 \mu\text{m}$) still exist, resulting in the lowest density
 222 among all five samples.



223

224 **Figure 3. Pore rearrangement and morphology study of LLZO samples with bimodal**
 225 **structures.** (a) Morphology and distribution density of the pores are observed using lab-
 226 lab-based CT in sequence, with sampling volume of $431 \times 453 \times 293 \mu\text{m}^3$. (b) Translucent-
 227 scarlet shades are employed to show pore volume distribution and connectivity in each
 228 sample. The evolution of (c) total volume, population and (d) equivalent size are
 229 statistically studied in each sample.
 230

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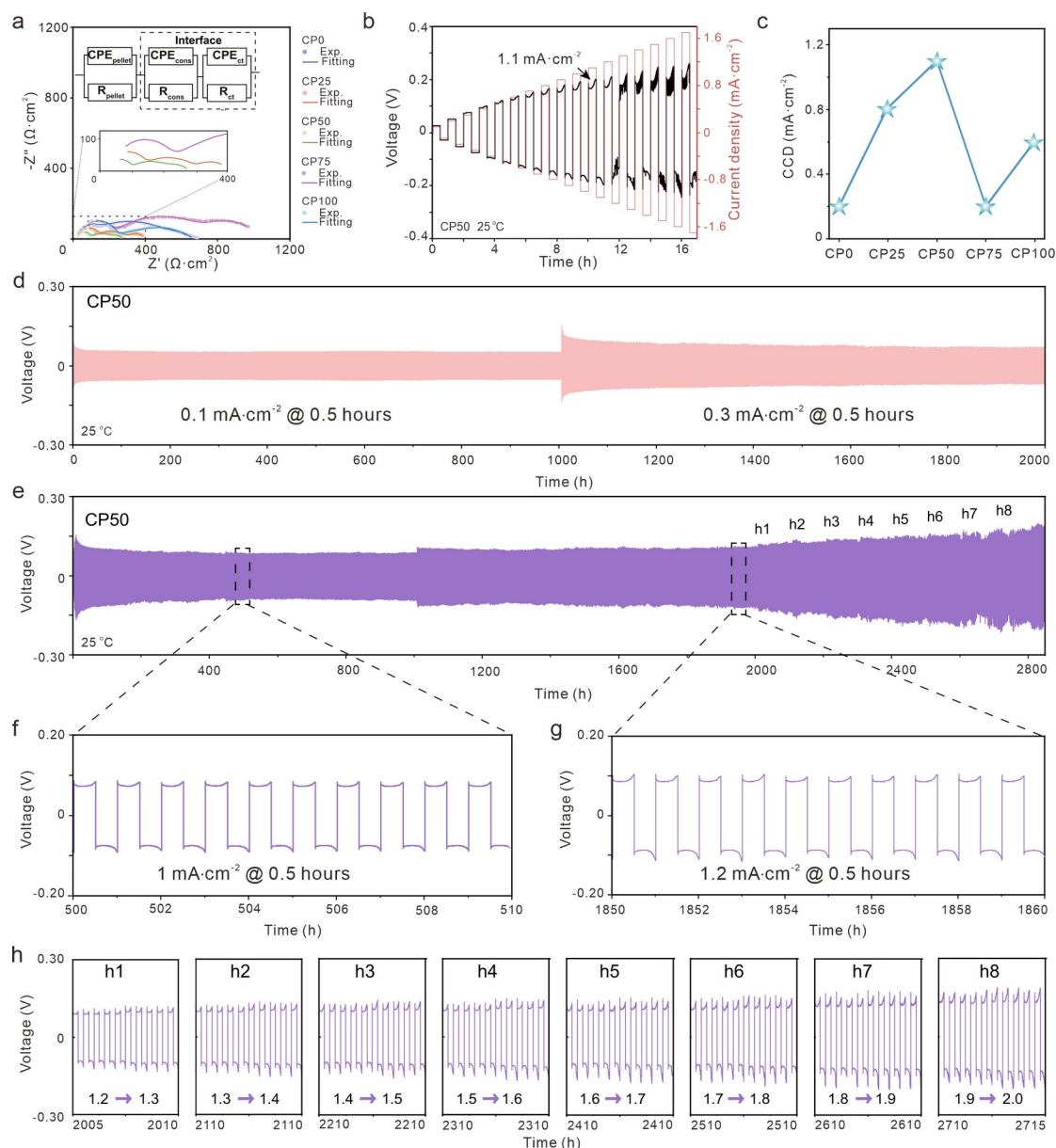
For room-temperature electrochemical tests, all LLZO pellets underwent similar
 polishing processes to minimize artificial effects. The pellets were then sandwiched
 between Li electrodes under consistent pressure and heated at $150 \text{ }^\circ\text{C}$ for 10 min to

234 fabricate symmetric cells. As revealed in the Nyquist plot (Figure 4a), the curves
235 consist of one partial semicircle in the high-frequency range and flattened semicircles
236 at lower frequencies. The high-frequency semicircles represent the total resistance of
237 the LLZO pellets, while the lower-frequency impedances are attributed to the
238 resistances at the Li/LLZO interfaces^{41,42}, which is mainly due to the interface
239 morphology caused constriction resistance and charge transfer resistance^{43,44}. The
240 measured total conductivities of all samples are about the same order of magnitude,
241 ranging from 2 to 4×10^{-4} S·cm⁻¹ (see Table S1). The impedance data are fitted and
242 presented as continuous curves, and the fitted resistances are listed in Table S2.
243 Generally, from CP0 to CP50, the interface resistance drops from 603 to 203 $\Omega\cdot\text{cm}^2$.
244 In CP50, the combined effects of more fine grains, fewer pores, and smaller pore size
245 contribute to the decrease of both constriction resistance and charge transfer
246 resistance. The decreased coarse grain fraction promotes charge transfer properties,
247 which has been corroborated by previous reports²⁶. In contrast, in CP75, the presence
248 of abnormally-grown grains and increased volume fraction of pores leads to increased
249 constriction and charge transfer resistance. As a result, the interface impedance of
250 CP75 is several times higher than that of the CP50. CP100 exhibits a relatively low
251 constriction resistance but high charge transfer resistance, probably because most
252 pores in it are small (Figure 3d), while the abnormal growth of grains is not
253 prohibited. Additionally, the bulk resistances of CP25, CP75 and CP100 are high,
254 because of their increased pore volume fractions that increase the tortuosity of Li
255 transfer path⁴⁵. Apart from decreasing interfacial resistance, the optimal bimodal
256 microstructure plays a significant role in enhancing the cycling behavior. Figure 4b
257 shows DC stepped current cycling of the symmetrical cells containing CP50. The
258 current density was raised to as much as 1.1 mA·cm⁻² at 25 °C, without causing any
259 detectable hard short. When the CP50 sample was thinned to 500 μm , the critical
260 current density was further elevated to 1.6 mA·cm⁻² (see Figure S4, SEM, impedance
261 and cycling test results of this sample are also presented). The voltage drops are not
262 proportional to current densities (Figure S5), indicating the drop of cell resistance,
263 probably because Li infiltrates into LLZO and fulfills the pores on/near the interfaces
264 during the stripping and plating processes⁴⁶⁻⁴⁸. This is equivalent to the reduction of the
265 LLZO thickness and the improvement of interface contact. Another possible

266 explanation to the lowered resistance might be the modification of solid electrolyte
267 interphase via passage of current, making it less resistive⁴⁹.

268 To assess the stability of the interfaces, cells were subjected to galvanostatic
269 charging and discharging at a consistent temperature of 25 °C. Each half-cycle lasted
270 30 min. For a holistic comparison, all symmetric cells from CP0 to CP100 were tested
271 and exhibited significant differences in cycling stability under a low current density of
272 $\pm 0.1 \text{ mA}\cdot\text{cm}^{-2}$ (Figure S6). As depicted in Figure 4d, the galvanostatic profile of the
273 Li/CP50/Li symmetric cell displayed an initial potential of approximately $\pm 90 \text{ mV}$,
274 which subsequently dropped to around $\pm 50 \text{ mV}$, cycling steadily over 1000h,
275 outperforming all others. The decrease in potential indicates that Li penetrates into
276 LLZO, forming a stable interface post activation cycles⁴⁶. When further cycling the Li/
277 CP50/Li symmetric cell at a current density of $\pm 0.3 \text{ mA}\cdot\text{cm}^{-2}$, the cell voltage
278 remained at $\sim 70 \text{ mV}$ for an extended cycling period of up to 1000 h. Another sample
279 experienced a quick increase in current density. Remarkably, stable cycling was
280 successfully achieved on it at high current densities of $1 \text{ mA}\cdot\text{cm}^{-2}$ and $1.2 \text{ mA}\cdot\text{cm}^{-2}$
281 (Figure 4e) for approximately 2000 h. In a previously reported system that showed a
282 similar voltage profile to those in Figure 4f and 4g, Li filaments were observed inside
283 LLZO, but their growth was reversible and cyclable⁵⁰. Subsequently, as the current
284 density was increased stepwise in units of $\pm 0.1 \text{ mA}\cdot\text{cm}^{-2}$ from $\pm 1.2 \text{ mA}\cdot\text{cm}^{-2}$ to ± 2.0
285 $\text{mA}\cdot\text{cm}^{-2}$ with each increment lasting 100 h (Figure 4h1-h8), the voltage profile
286 remained similar to that observed at lower current densities. As the current density
287 increased, the deviation of the voltage profile from the expected square shape became
288 more severe, suggesting that Li was stripped faster at the interface than it could diffuse
289 from the bulk to compensate the stripped Li. The cycling started to lose stability with
290 an obvious voltage drop (Figure 4e, see voltage profile between h7 and h8) when the
291 current density was approximately $1.8 \text{ mA}\cdot\text{cm}^{-2}$, due to soft shorting; however, the
292 symmetric cell did not fail even at $2.0 \text{ mA}\cdot\text{cm}^{-2}$. This suggests that the bimodal
293 structure of CP50 prevented the propagation of Li filaments/dendrites or healed them,

294 ensuring robust cycling. With another CP50 symmetrical cell, the evolution of the
295 impedances as a function of cycles was investigated. As displayed in Figure S7, the
296 cell (Cell #1) was cycled with the current densities ramping up in a stepwise manner
297 from 0.3 to 1 mA·cm⁻² (Figure S7a). At 0.3 mA·cm⁻², the interface resistance first
298 decreased and then stabilized in the following cycles, as shown in Figure S7b and c.
299 As the current density was increased from 0.3 to 0.8 mA·cm⁻², the impedance became
300 lower (Figure S7d), indicating that more Li had infiltrated into LLZO. The evolution
301 of solid electrolyte interphase might also play a role. Soft shorting was detected from
302 the impedance curve measured after 16 cycles at 1 mA·cm⁻². Afterwards, the
303 impedance became unstable and dropped down rapidly (Figure S7e). In another
304 symmetrical cell (Cell #2), the cycling current density was increased from 0 to 1.0
305 mA·cm⁻² in 10 cycles, kept constant at 1.0 mA·cm⁻² for 50 cycles, ramped up in a
306 stepwise manner to 1.8 mA·cm⁻² and finally kept at 1.8 mA·cm⁻² for 77 cycles (Figure
307 S8a). The evolution of impedance during the 50 cycles at 1.0 mA·cm⁻² and 77 cycles at
308 1.8 mA·cm⁻² was quite similar to that in Cell #1 under 0.3 mA·cm⁻². The impedance
309 dropped slightly at the beginning and then **reached** a stable state after about 40 cycles
310 (Figure S8b).
311



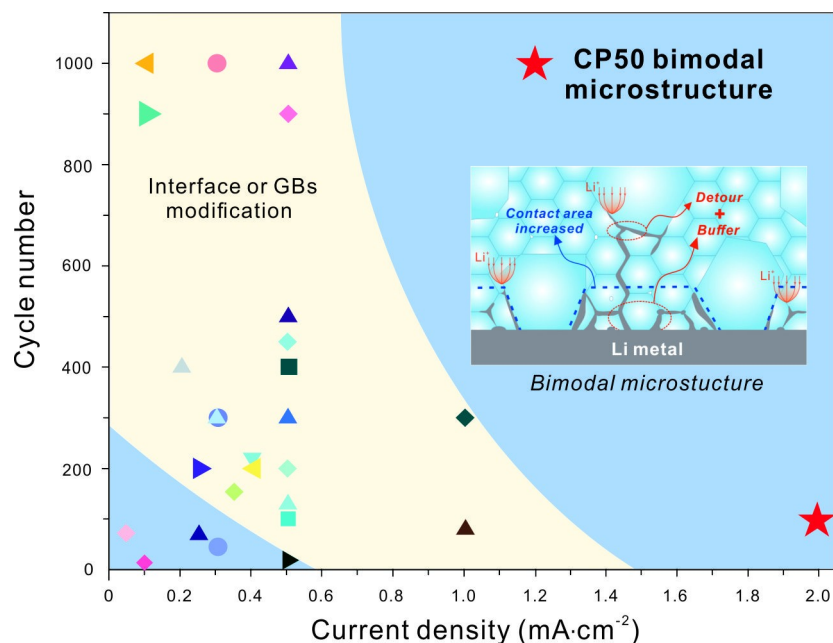
312

313 **Figure 4. Electrochemical performance of the symmetric cells containing bimodal**
 314 **microstructured LLZO. (a) The ionic conductivity of Li symmetric cells containing**
 315 **samples with various types of bimodal microstructures was studied using EIS. (b) The**
 316 **CCD of the symmetric cell containing CP50 was measured by increasing the current**
 317 **stepwise** and (c) a comparison of the CCD of cells containing the different samples. (d, e)
 318 Voltage profiles of the CP50 symmetric cells cycled under increased current densities,
 319 with zoom-in details shown in (f-h).

320

321 The cells containing CP50 outperform in every aspect, be it CCD (Figure 4c),
 322 overpotential, or cycling lifetime. For reference, the cycling stability and CCD test
 323 results for symmetric cells containing other bimodal microstructures are displayed in
 324 Figure S6 and Figure S9. Importantly, the interfaces in the tested cells are unadorned,
 325 i.e., free of any additional coatings. As demonstrated in Figure 5, the outcomes from

326 our CP50 specimens not only outperform the previously reported symmetric cells
 327 without interface and/or grain boundary decoration (in the blueish-grey area), but also
 328 surpass or at least run on a par with those incorporating interface modifications (in the
 329 yellow region).



330

331 **Figure 5. Galvanostatic cycling performance of Li symmetric cells with bulky**
 332 **garnet-type solid electrolytes (references are listed in Table S3).**

333

334 Discussion

335 The formation of bimodal microstructure

336 The bimodal microstructure was obtained by sintering a mixture of pulverized
 337 and unpulverized powders. In the mixed state, small particles fill the interstices
 338 between the large ones. During sintering, the inhomogeneous powder distribution
 339 results in non-uniform mass diffusion. The intra-agglomerate densification and grain
 340 growth occur in unpulverized powders more easily and rapidly, which consume the
 341 mass that is necessary for the pulverized fine powders to grow⁵¹. Moreover, sintering
 342 also influences the size, morphology, and spatial distributions of pores. As small
 343 particles coalesce, small pores are easily formed between them. On the other hand,
 344 when there are more large particles, more intragranular pores are trapped and cannot
 345 escape from the interior to the surface of the powder. According to experimental
 346 observations, grain growth takes place under the regular coarsening process in CP0,
 347 forming normally distributed coarse grains with large interconnected pores. CP25 has

348 more isolated pores but still suffers adverse effects from the interconnected ones. In
349 CP75 and CP100, the unpulverized coarse powders become the principal component
350 in green bodies, and the fast grain growth and fine grain consumption lead to more
351 abnormal large grains. In CP50, a synergy is achieved, as the competing grain growths
352 of unpulverized and pulverized powders are balanced. The coarse grains grow in a
353 constricted manner, sparing the fine grains opportunities to sinter well. Additionally,
354 the presence of excess Li can cause more pores to form^{40, 52}, because gas is entrapped
355 between particles during the rapid densification and volatilization of the Li-containing
356 compounds employed to replenish Li loss. It should be noticed that the adding of Li-
357 containing compounds which melt at low temperature, such as LiNO₃ and Li₂CO₃, can
358 boost densification due to liquid-phase sintering. In summary, the initial powder size,
359 grain growth rate, as well as Li excess affects the size and spatial distributions of
360 pores.

361 With these observations, we surmise that a balanced ratio of pulverized and
362 unpulverized powders, as in CP50, facilitates a bimodal microstructure of uniformly
363 distributed coarse grains encapsulated by fine grains. Small and isolated pores, as well
364 as a dense structure, are also obtained. Three guiding principles can be summarized
365 for microstructure control concerning particle size effects in the green body: (1)
366 adjacent large grains and rapid grain growth in polycrystalline SSE tend to create
367 interconnected pores and intragranular pores; (2) introducing a certain size of large
368 particles into the green body can significantly reduce interconnected pores via
369 differential densification; (3) by controlling the ratio of two different types of powders,
370 the size and population of pores can be adjusted, regardless of whether they are
371 between or inside grains.

372

373 **Buffer and detour effects in bimodal microstructure**

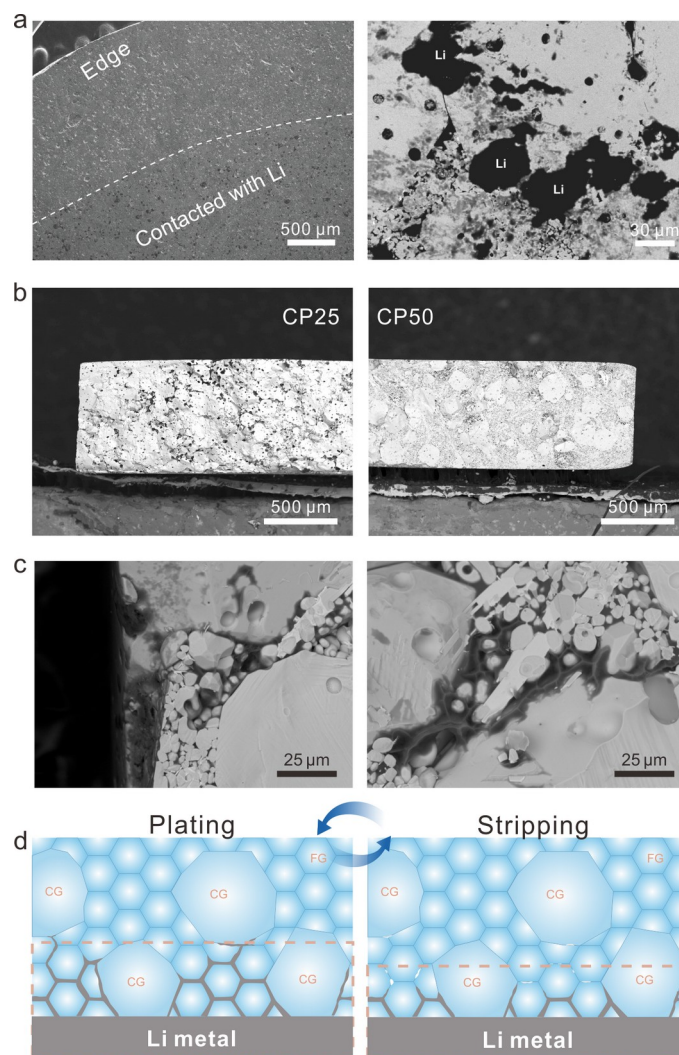
374 After cycling, the cells were disassembled to examine Li deposition behavior
375 within the bimodal microstructure. Figure 6a shows the interface that distinguishes
376 between areas with and without Li foil contact. As the Li foil diameter is 2 mm
377 smaller than LLZO, the periphery not in contact with Li is clean, while the dark spots
378 signify the existence of Li under back-scattered electron mode of the SEM image^{35, 53}.
379 Magnified images reveal prominent Li deposition within grain boundaries and pores.

380 In Figure 6b, widespread dark color is readily detected in CP25, indicating
381 conspicuous Li propagation due to the detour effect primarily caused by coarse grains.
382 In contrast, dark spots are barely seen in CP50 due to the considerable area fraction of
383 fine grains, leading to a finer and more complex Li propagation path. However, upon
384 closer examination (Figure 6c), it can be seen that Li propagation in the fine grain area
385 forms a net-like distribution. The fine grain areas, as well as fine pores, even those that
386 are submicron size, act as Li metal reservoirs, thereby enhancing cycling stability
387 under high current densities due to its buffering effect.

388 In recent studies, the presence of pores has been identified as one of the key
389 factors for Li dendrite initiation and propagation^{17, 54, 55}. The size and distance between
390 the pores and interfaces affect the current density that the SSE is able to withstand.
391 Reducing the size and quantity of pores at the subsurface, and preventing the build-up
392 stress caused by Li-filled pores from exceeding the local fracture toughness has been
393 shown to be beneficial. Our bimodal microstructure design is consistent with this
394 strategy. The introduction of coarse grains reduces subsurface pores and the chances
395 of Li dendrite contact. Coarse LLZO grains with lower defect densities provide higher
396 fracture toughness and thus can withstand higher current density. Furthermore, the
397 size of subsurface pores is effectively reduced by the bimodal microstructure in which
398 fine grains surround coarse ones, bringing the Li-pore-filling induced pressure to a
399 magnitude far below the fracture toughness. Additionally, the pores along LLZO grain
400 boundaries have the chance to form interconnected channels, which further lowers the
401 pressure during plating. The benefit of the microstructure is that crack initiation is
402 circumvented; even if cracking occurs, it consumes the energy for crack propagation
403 and prevents hard shorts.

404 Generally, the reasons for the enhanced cycling stability in bimodal SSE can be
405 divided into two aspects: (1) the fine grains surround the coarse ones, eliminating the
406 interconnected pores and providing a zigzagging propagation pathway to hamper the
407 direct and rapid infiltration of Li. In the meantime, the coarse grains lying on the
408 infiltration route of Li detours its migration and delays the failure of SSEs; (2) pores
409 filled with Li aid in moving the Li/LLZO interface forward, significantly increasing
410 the Li contact area, thereby dispersing the interfacial current and facilitating uniform
411 and reversible stripping and plating cycles (Figure 6d). This mitigates the void

412 formation and contact loss at the interface caused by high current density. Such
 413 improvements contribute to all-solid-state Li battery cycles without necessitating
 414 additional mechanical pressure for accelerating Li creep, which is deleterious to long-
 415 term cycling¹⁷.



416
 417 **Figure 6. Postmortem analysis of Li deposition after electrochemical cycling.** SEM-
 418 BSE images of (a) LLZO surface morphology and (b) cross-section after short circuit. (c)
 419 Li network propagation between the fine grains. (d) Schematic illustration of Li network
 420 infiltration between fine grains and in pores pushing the interface forward.
 421

422 On the LLZO surface, we also notice spallation cracks (Figure S10),
 423 predominantly around the pores in the coarse grain areas and along the grain
 424 boundaries where large wedges are not entirely filled with fine grains. These cracks
 425 are caused by stress buildup during the pre-filling procedure of viscoelastic Li metal⁵⁴.
 426 ⁵⁵. This suggests two aspects of future microstructure control. The intra-granular pores

427 should be minimized in both quantity and size, which can be achieved by reducing the
428 excess Li in the green body and curtailing the growth rate of coarse grains. Fine grains
429 should also be more tightly packed around the coarse grains.

430

431 **Conclusion**

432 In conclusion, our study focuses on the microstructure design and optimization of
433 polycrystalline LLZO SSEs to enhance cycling performance, incorporating both CCD
434 and long-term cycling stability. By mixing pulverized and unpulverized powders into
435 the green body, a bimodal microstructure was obtained. Tuning the ratio of these two
436 types of powders allows for the alteration of the distribution of grains and pores in the
437 sintered samples, and thus influences the electrochemical properties significantly.
438 When the pulverized and unpulverized powders are equally mixed, a microstructure in
439 which coarse grains are surrounded by fine-grains and isolated fine pores are obtained,
440 which results in efficient Li plating/stripping at a high current density. Long-term
441 cycling stability experiments underscore the exceptional stability of symmetric cells
442 containing the LLZO SSEs with the optimal bimodal microstructure, over 2000 h at
443 current densities of $1.0 \text{ mA}\cdot\text{cm}^{-2}$ and $1.2 \text{ mA}\cdot\text{cm}^{-2}$. It even exhibits the capacity to
444 endure over 100 h under a current density of $2 \text{ mA}\cdot\text{cm}^{-2}$.

445 Postmortem analysis reveals that intricate grain boundaries, formed by the fine
446 grains in the bimodal structure, make the Li penetration path more complex, thereby
447 reducing direct Li infiltration. Simultaneously, the coarse grains enhance the tortuosity
448 of the Li path. With the "buffer and detour" effects, the LLZO electrolyte gains the
449 potential to operate at elevated current densities. The propensity of Li to permeate
450 between fine grains indirectly propels the interface forward, promoting reversible Li
451 stripping and plating, and showcasing excellent cycling stability. Spallation cracks,
452 primarily surrounding the pores in coarse grains and the edges of coarse grains
453 without full contact with fine grains, are detected at the interface. These observations
454 hint at future opportunities for microstructure optimization. In the realm of battery

455 applications, it is also essential to investigate the compatibility of the solid-state
456 electrolytes with the cathode electrodes. This involves a thorough consideration of
457 cathode materials, additives, interfacial decorations, and cathodic composite structure
458 design. Our findings illuminate the path to rational and optimal design of bimodal
459 structures, offering new insights on mitigating dendrite growth-induced failure in
460 polycrystalline SSEs.

461

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