Supporting information

Figure S1. The structure crumbled after sintering in air (the yellow powder in the right bottle), and the XRD shows that a large amount of lithium was lost, resulting in the formation of $La_2Zr_2O_7$.

Figure S2. The water-processed freeze casting sample. (a) and (b) shows the overall looking of the fracture surface for the sample with 25 wt% LLZO. The oriented texture in the cracked freeze casting sample, as shown in (a), is obvious. (c) is the comparison with different LLZO mass loading which ranges from 15 wt% to 30 wt%. And (d) is the NMC infiltration for the 25 wt% sample. (e) used Polyaniline as an additive in the NMC slurry preparation. Both (d) and (e) are using the scaffold after sintering. The water-processed sample is prepared by first mixing 25 wt%, 1wt% Darvan, 1 wt% Poly(vinyl alcohol) (PVA) and 73 wt% deionized water, then ball milling overnight and freezing under a cooling rate about ~20 ^{o}C/min by using the same machine adopted in the TBA-processed LLZO scaffold.

Figure S3. Water-processed sample with Gelation as additive rather than PVA, which shows the lamellar stacked structure along the dendrites growing direction.

Figure S4. SEM photo for the top view of the scaffold slice. The left one is the original SEM photo, and the right one is the same photo after binarization.

Figure S5. Partially infiltrated LLZO scaffold with small NMC particles.

Figure S6. (a) and (b) are the cross-section illustrations showing shrinking of the two layers, and (b) is the situation for the local uneven shrinking after the formation of connections during sintering. The arrows are the shrink direction, and the length indicates the shrink rate. (c) shows massive pinholes in dense layer due to extremely uneven shrinkage.

Figure S7. The OCV curve for the all-solid-state battery.

Figure S8. After infiltration test for bilayer structure, the small carbon particles are observed going through the pinhole in the dense film.

Figure S1

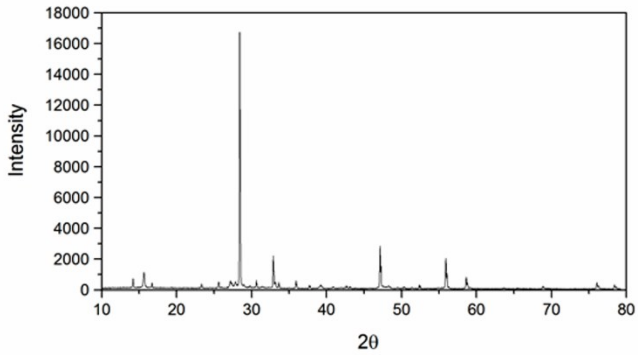
Intensity
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
70
80
2θ

Figure S2

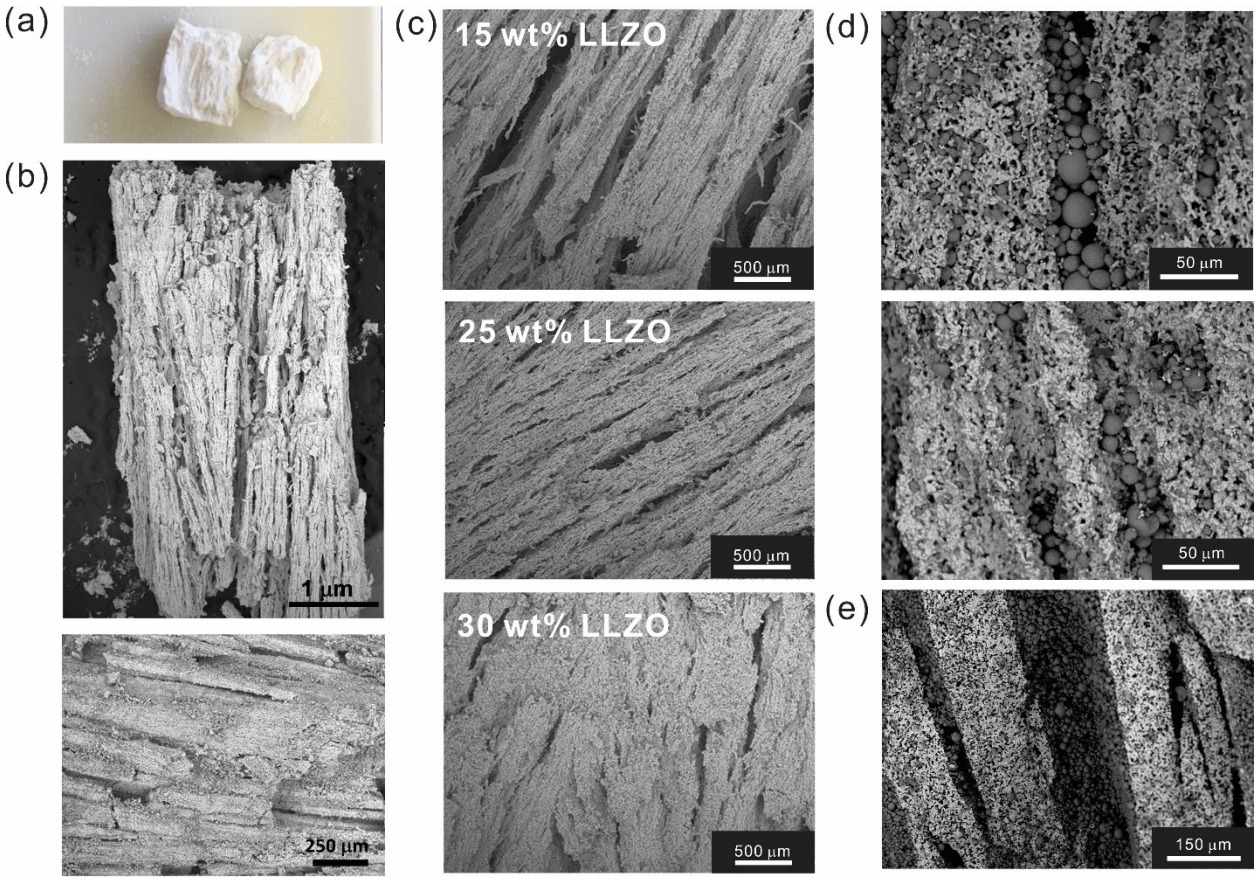
(a)
(b)
1 µm
250 µm
(c)
15 wt% LLZO
500 µm
25 wt% LLZO
500 µm
30 wt% LLZO
500 µm
(d)
50 µm
50 µm
(e)
150 µm

Figure S3

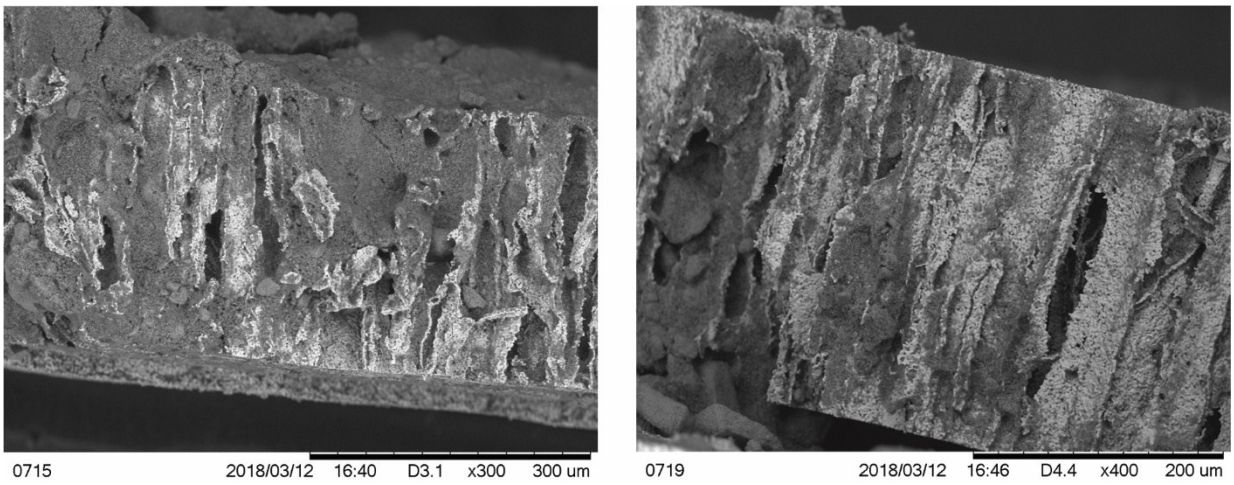
0715 2018/03/12 16:40 D3.1 x300 300 um
0719 2018/03/12 16:46 D4.4 x400 200 um

Figure S4

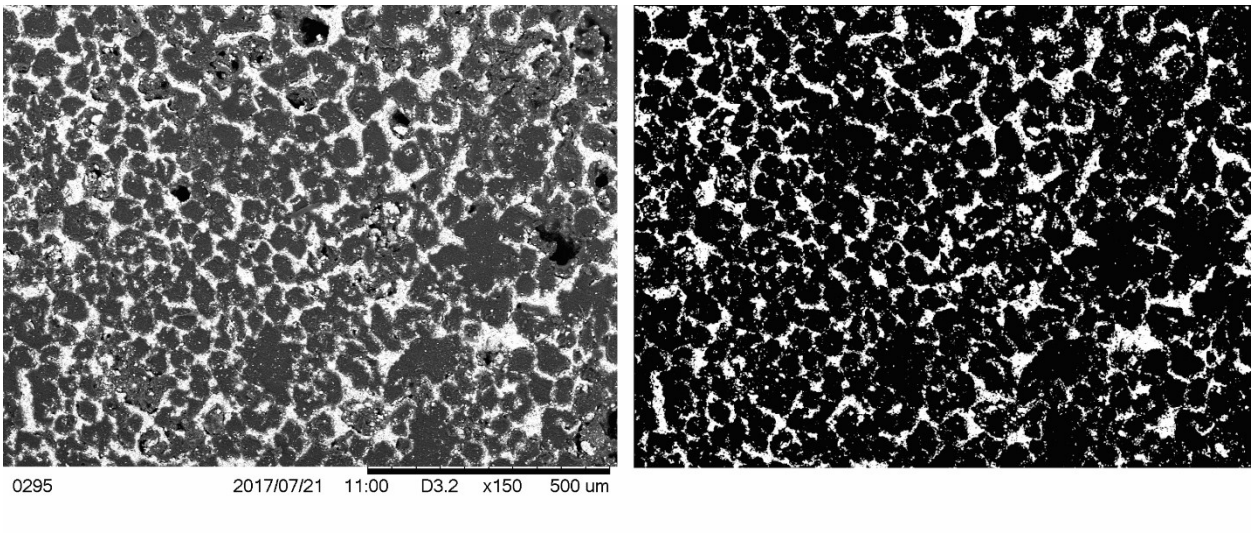

Figure S5

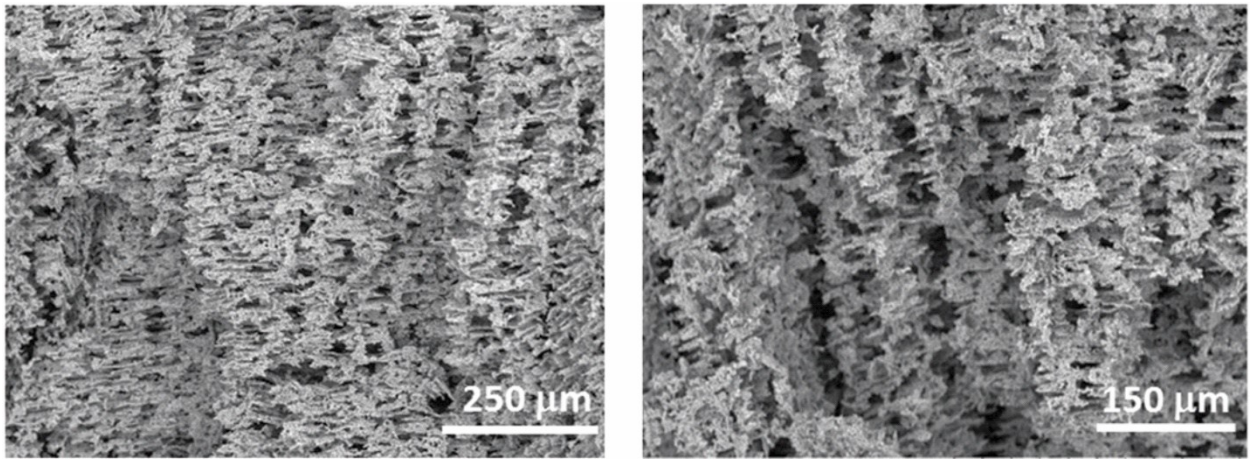

Figure S6

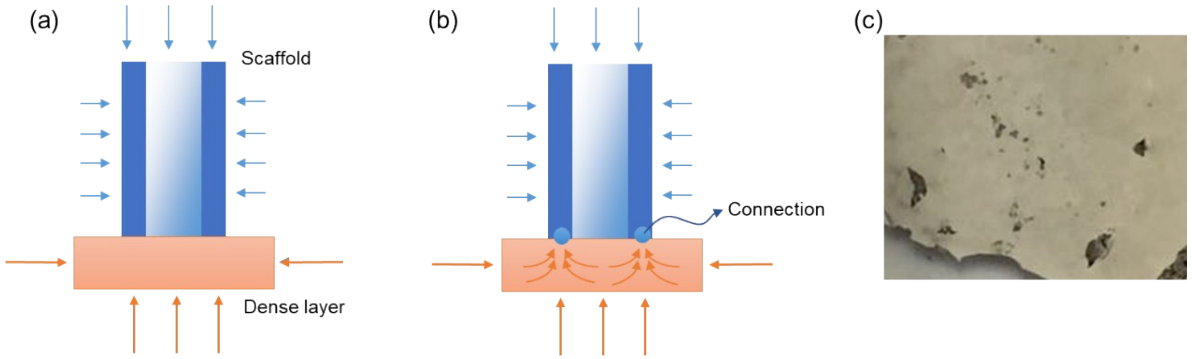

Figure S7

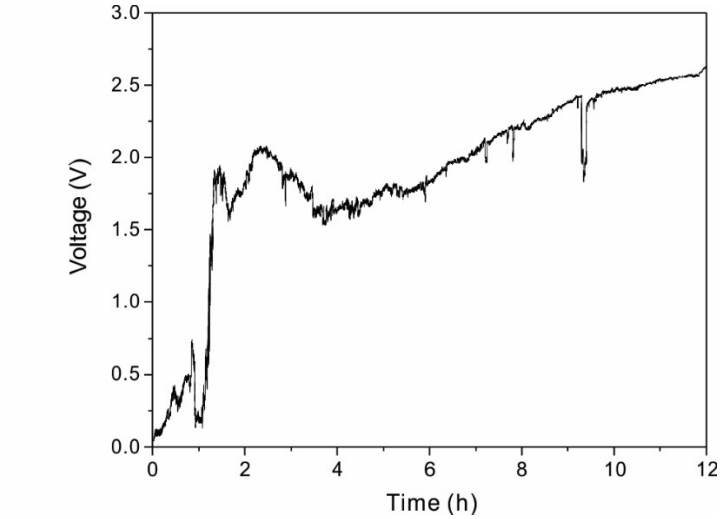

Figure S8