Supporting Information for

Stereolithography 3D Printing Solid Polymer Electrolytes for All-Solid-State Lithium-Metal Batteries

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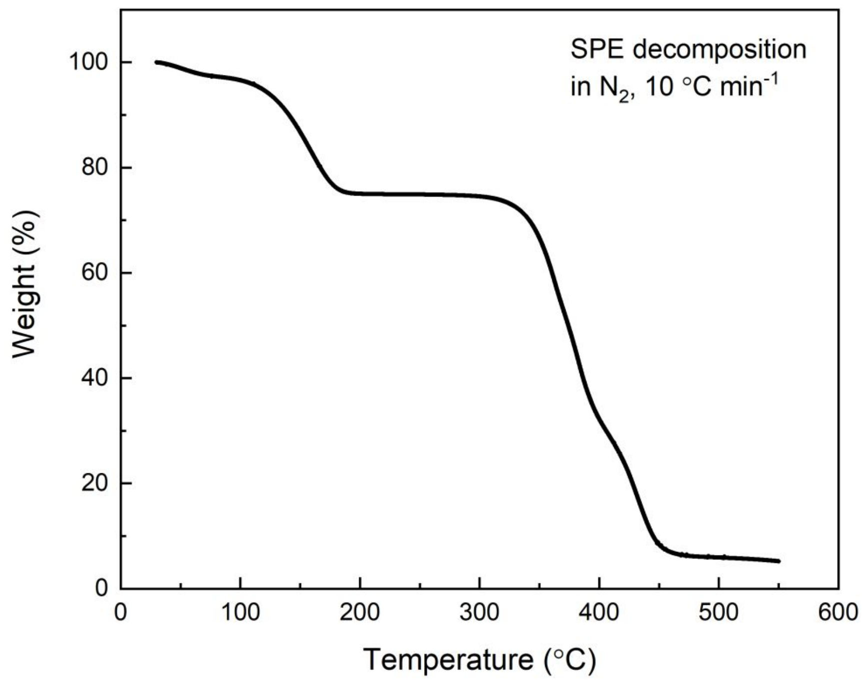

Figure S1. Thermogravimetric analysis (TGA) showing the weight loss of SPE when heat up in the nitrogen to 550 °C with a scanning speed of 10 °C min^{-1}. The weight of SPE shows a platform below 350 °C, indicating its thermal stability.

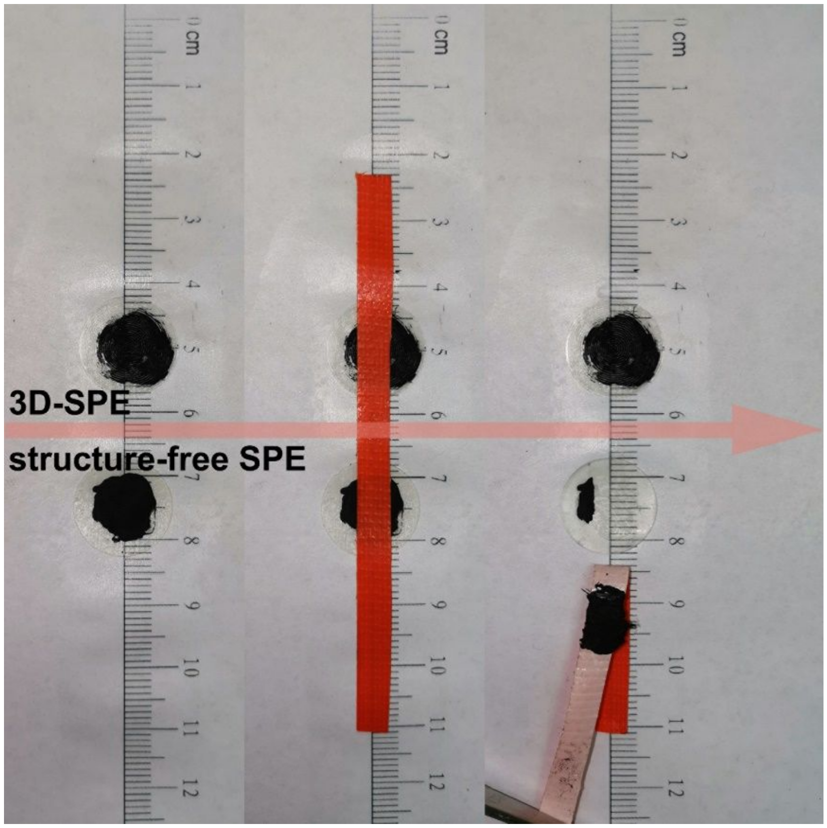

Figure S2. Tape test of 3D-SPE and structure-free SPE supported cathode.

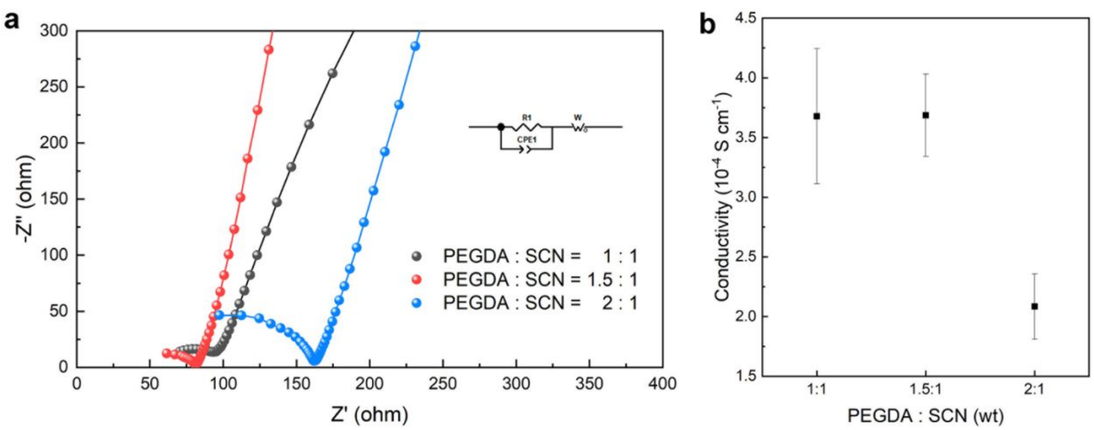

Figure S3. Electrochemical performance of the photopolymerized SPE with different weight ratios at 25 °C. (**a**) Nyquist plots and (**b**) conductivity.

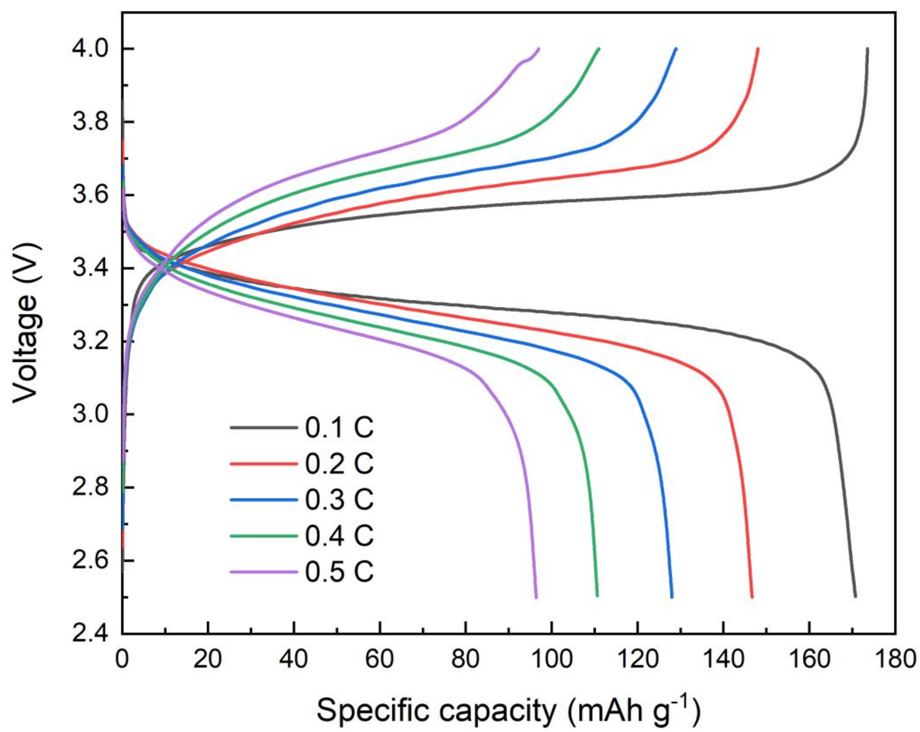

Figure S4. Voltage profiles of the Li|3D-SPE|LFP cell at various C-rates at 50 °C.

Note S1. Calculation the increased specific area between the cathode and 3D-SPE.

In this work, the Archimedes' Spiral is used as the 3D structure, and the polar equation is as follows:

$$\rho = a\theta \#(1)$$

the arc length is calculated by:

$$l = \frac{a}{2}\left[\theta\sqrt{1+\theta^2} + \ln\left(\theta + \sqrt{1+\theta^2}\right)\right] \#(2)$$

The increase in contact area is the ratio between the vertical contact area A_{cv} and the horizontal contact area A_{ch}:

$$\frac{A_{cv}}{A_{ch}} = \frac{2lh_s}{\pi r^2} = \frac{2lh_s}{\pi\rho^2} = \frac{h_s a\left[\theta\sqrt{1+\theta^2} + \ln\left(\theta + \sqrt{1+\theta^2}\right)\right]}{\pi(a\theta)^2} = \frac{h_s}{\pi a} \times \frac{\theta\sqrt{1+\theta^2} + \ln\left(\theta + \sqrt{1+\theta^2}\right)}{\theta^2} \#(3)$$

where h_s is the 3D structure height. When θ is infinity, $\frac{\theta\sqrt{1+\theta^2} + \ln\left(\theta + \sqrt{1+\theta^2}\right)}{\theta^2}$ approaches 1, which indicated that there are two ways to increase the ratio. However, increasing the 3D structure height(h_s) or reducing the spiral spacing (a) will weaken the 3D structure and trouble the filling of cathode slurry. To balance these factors, they're set as (a=0.05 mm, θ=45π, and h_s=0.15 mm), so the increase in contact area is calculated as 95%.

Table S1. Summary of fitting values for Nyquist plots

Cell type	Temp. [^oC]	R[Ω]	CPE1-T	CPE1-P	R_{int}[Ω]	CPE2-T	CPE2-P	R_{ct}[Ω]	CPE3-T	CPE3-P	W1-R	W1-T	W1-P
Li|structure-free SPE|LFP	25	148	3.84E-8	0.68	3409	6.46E-7	0.90	518	3.04E-6	0.77	308	0.25	0.20
	50	81.1	1.89E-6	0.47	372	8.85E-7	0.94	308	3.12E-6	0.68	265	0.24	0.35
Li|3D-SPE|LFP	25	128	2.07E-7	0.59	1199	8.63E-7	0.91	506	4.20E-6	0.73	1399	9.85	0.34
	50	78.6	6.64E-5	0.26	88.8	1.69E-6	1.08	305	2.74E-6	0.81	95.6	0.33	0.44