Three-Dimensional Bilayer Garnet Solid Electrolyte Based High Energy Density Li Metal-Sulfur Batteries

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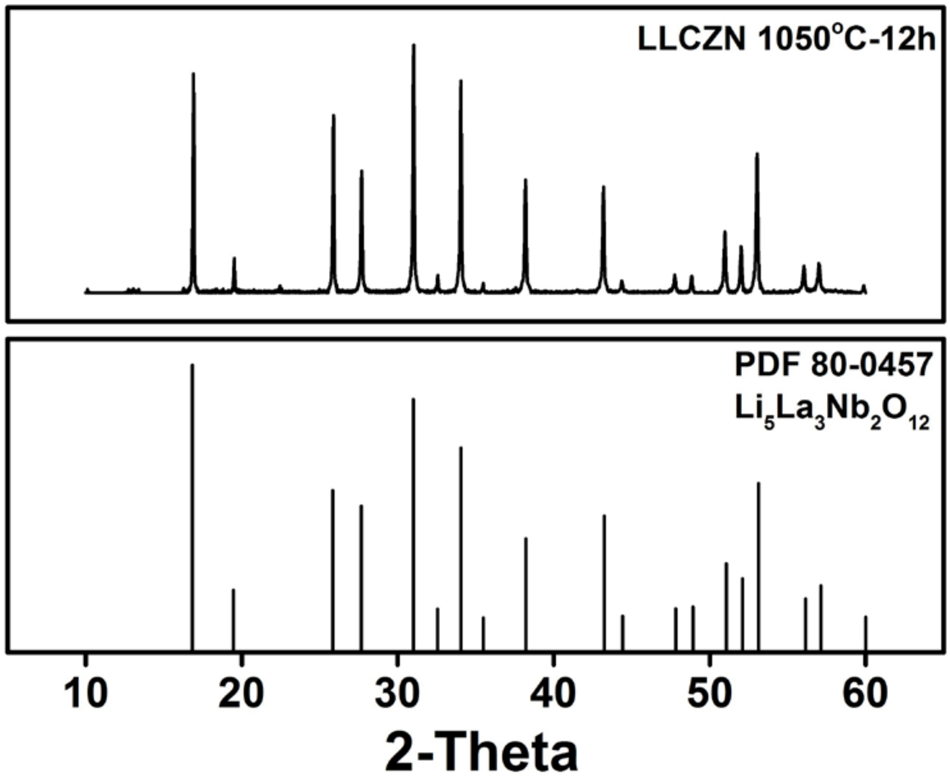

Figure S1. XRD pattern of sintered garnet (LLCZNO). Cubic garnet-type $Li_5La_3Nb_2O_{12}$ (PDF 80-0457) is used as the standard XRD pattern to confirm the phase structure of the as-synthesized materials.

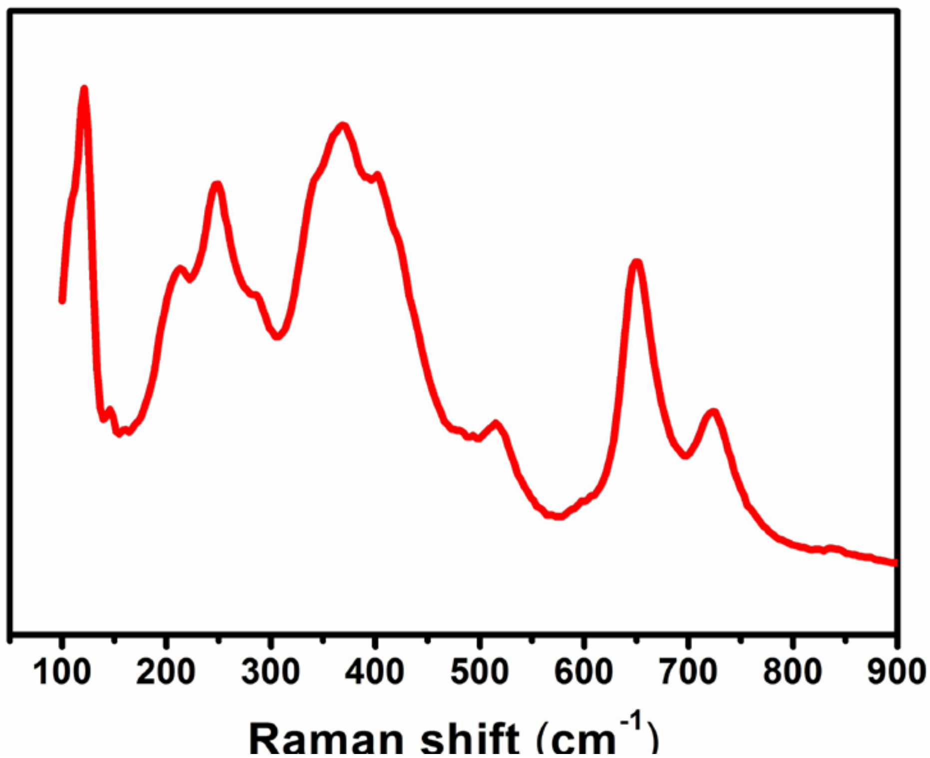

Figure S2. Raman spectrum of LLCZNO to confirm the cubic garnet phase.

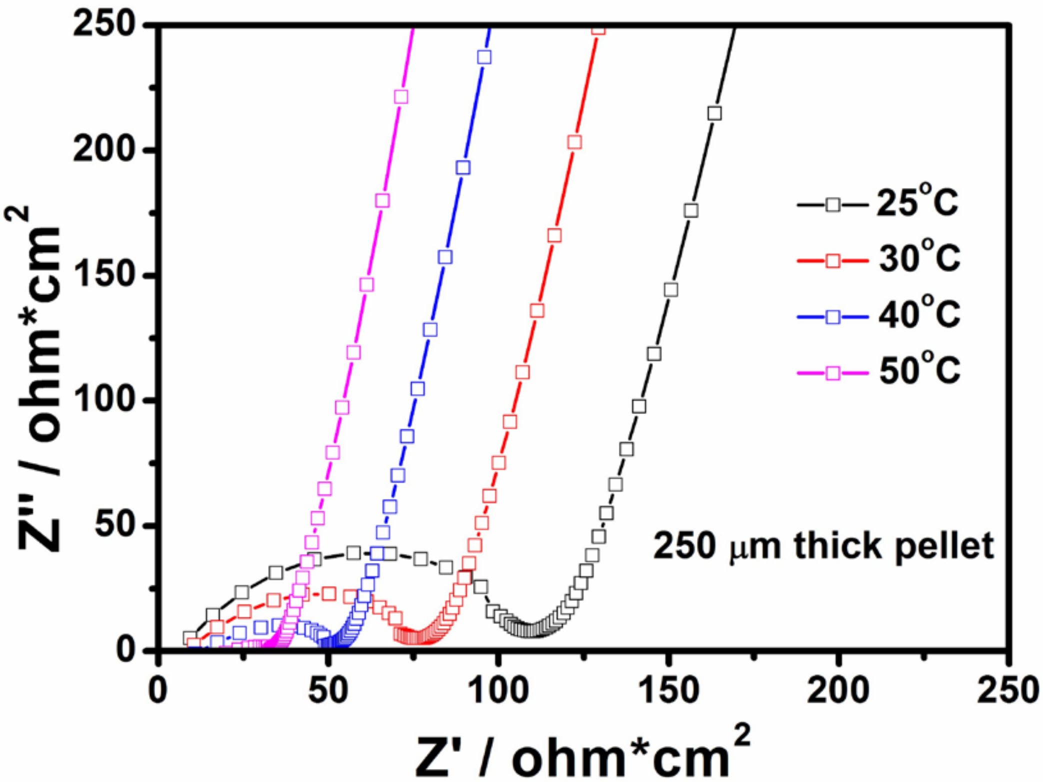

Figure S3. Nyquist plots of the dense garnet solid-state electrolyte pellet at different temperatures (25, 30, 40, and 50^{o}C). The dense garnet pellet had a thickness of ~250 µm.

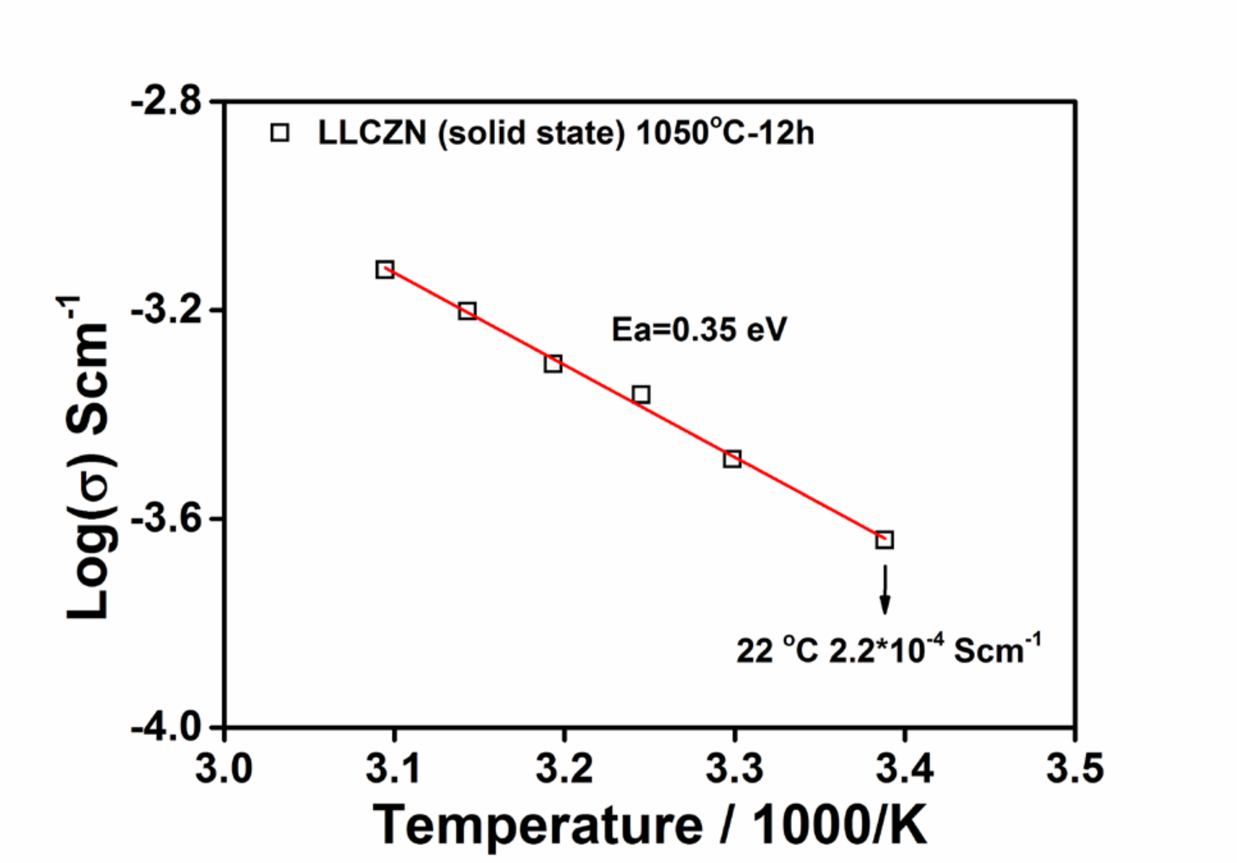

Figure S4. Arrhenius plot of garnet solid-state electrolyte conductivity. The activation energy is 0.35 eV.

Table S1. The calculations of the specific energy density of the tested garnet bilayer Li-S battery.

Bilayer garnet (mg/cm^2)	20
Sulfur (mg/cm^2)	7.5
CNT (mg/cm^2)	1
Liquid electrolyte (mg/cm^2)	7.5
Li metal (mg/cm^2) (Estimated)	3
Total mass (mg/cm^2)	39
Energy (Wh/cm^2)	9.68
Specific energy density (Wh/kg)	248.2

This newly develop porous-dense bilayer framework represents a promising strategy to revolutionize Li-metal batteries. With further optimization of the thickness and mass-loading with Li metal and S cathodes, a cell energy density over 900 Wh/kg (Table S3) is achievable.

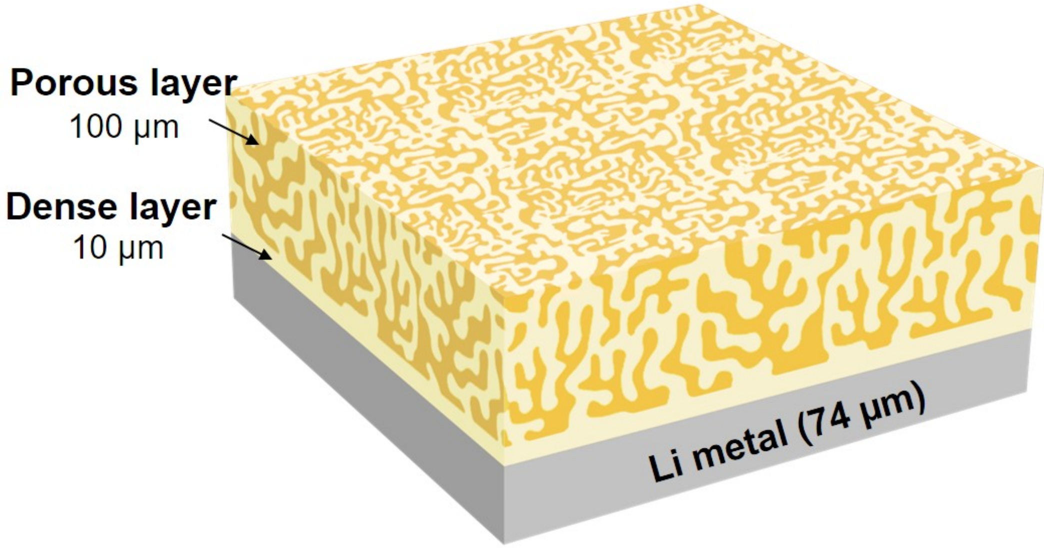

Figure S5. Schematic of a bilayer solid-state battery. The bilayer solid-state electrolyte framework has several unique advantages: (a) the thin dense layer is a mechanical barrier with high elastic modulus that can efficiently separate the electrodes from liquid electrolyte and prevent Li dendrite penetration; (2) the thick porous layer mechanically supports the thin dense layer; (3) the interface between dense and porous layers is well sintered with good mechanical integrity and continuous ion transport; (4) the solid-state framework can provide electronic and ionic conducting pathways for the encapsulated cathode materials; (5) the solid-state framework can physically confine the cathode materials locally and accommodate the volume change of the cathode materials, such as solid sulfur and polysulfide catholyte.

Table S2. Projected energy density of bilayer garnet solid-state Li-S batteries with optimized parameters.

	Material	Volume ratio	Volume (cm3)	Density (g/cm3)	Mass (mg/cm2)	Specific Capacity (mAh/g)	Capacity (mAh/cm2)	Loading (mg/cm2)
Cathode	Garnet	15%	0.15	4.97	7.450	0	0.0	
100 um	Sulfur	47%	0.47	1.96	9.210	1,675	15.4	9.2
	CNT	15%	0.15	1.7	2.550	0	0.0	
	Empty	23%	0.23	0	0.000	0	0.0	
Electrolyte	Garnet	100%	0.10	4.97	4.970	0	0.0	
10 um								
Anode	Lithium	100%	0.74	0.54	3.996	3,861	15.4	4.0
74 um								
		Totals:	1.940083		32.61345		15.4	
						Energy	993.6 Wh/kg	
						Density	1,670.2 Wh/L	