Supporting Information

Continuous Plating/Stripping Behavior of Solid-State Lithium Metal Anode in a 3D Ion-Conductive Framework

Chunpeng Yang,‡ Lei Zhang,‡ Boyang Liu, Shaomao Xu, Tanner Hamann, Dennis McOwen, Jiaqi Dai, Wei Luo, Yunhui Gong, Eric D. Wachsman*, and Liangbing Hu*

Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA

* Email: L. Hu, binghu@umd.edu; E. D. Wachsman, ewach@umd.edu

‡ These authors contributed equally to this work.

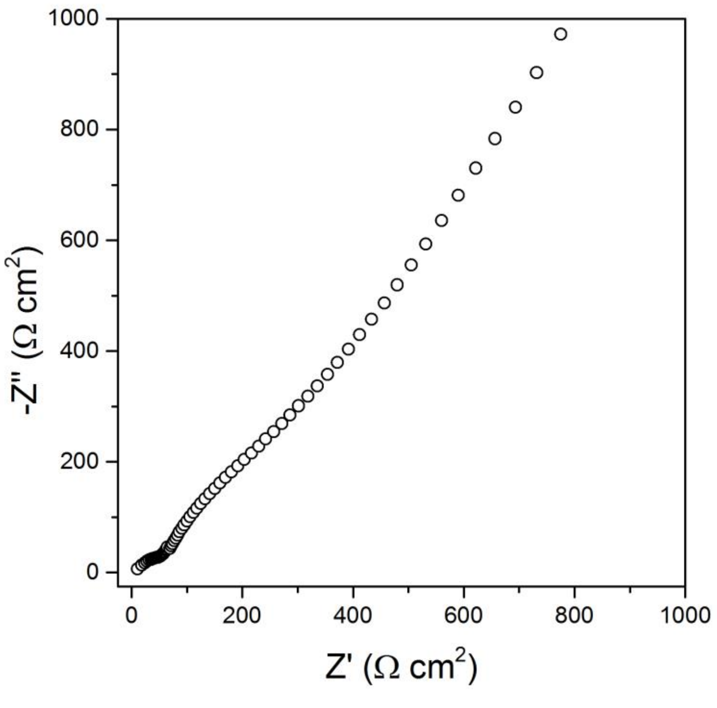

Figure S1. Nyquist plot of dense garnet pellet for calculating the ionic conductivity of garnet. The dense garnet pellet is 230 μm thick and 0.56 cm^2 in area. The impedance of the garnet pellet is 131 Ω by fitting the EIS data. Thus, the ionic conductivity of the dense garnet pellet is 3×10^{-4} S cm^{-1}.

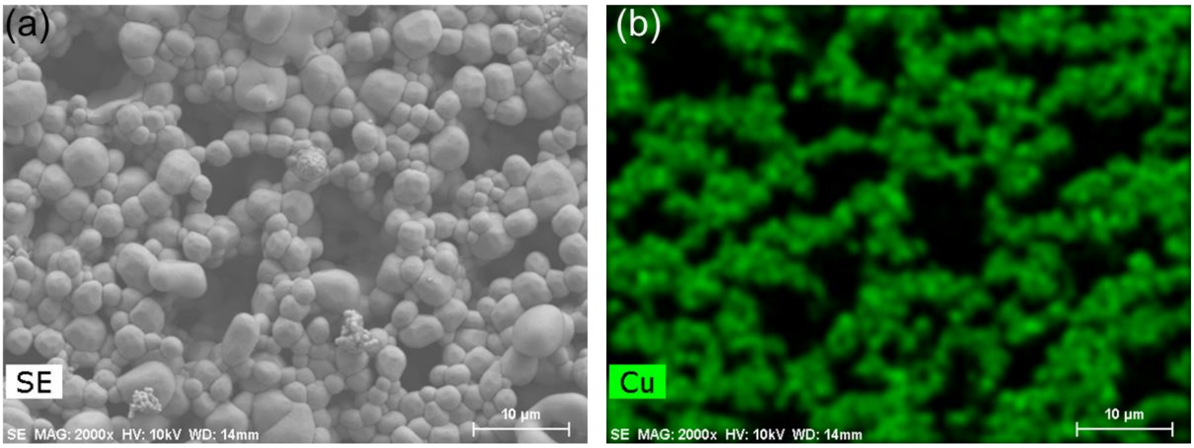

Figure S2. (a) Plain-view SEM image and (b) corresponding elemental mapping of Cu on the bottom of garnet framework coated with Cu by an e-beam evaporation method. The Cu shows conformal coating on the bottom of the garnet framework.

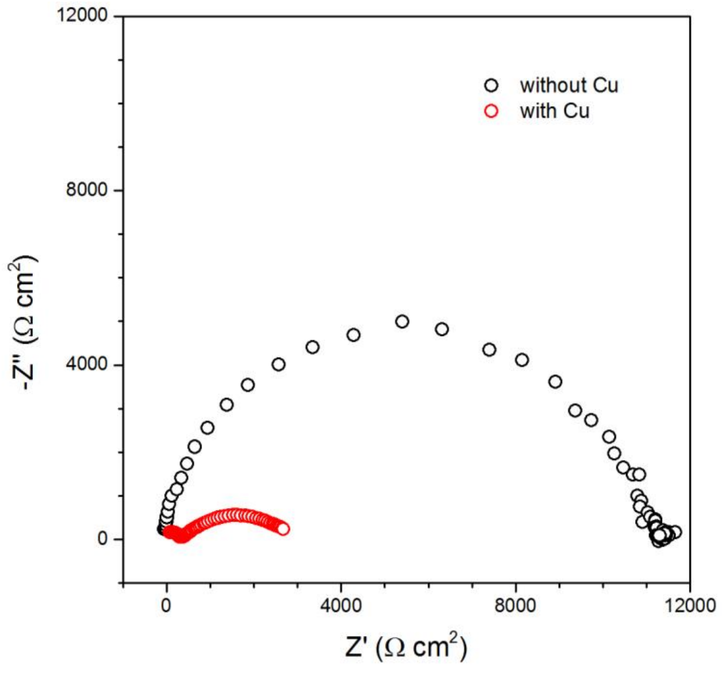

Figure S3. EIS of Li-garnet cell with and without Cu coating at the bottom of the garnet framework. Cu coating layer on the garnet framework greatly reduces the contact resistance at the garnet interface in the cell.

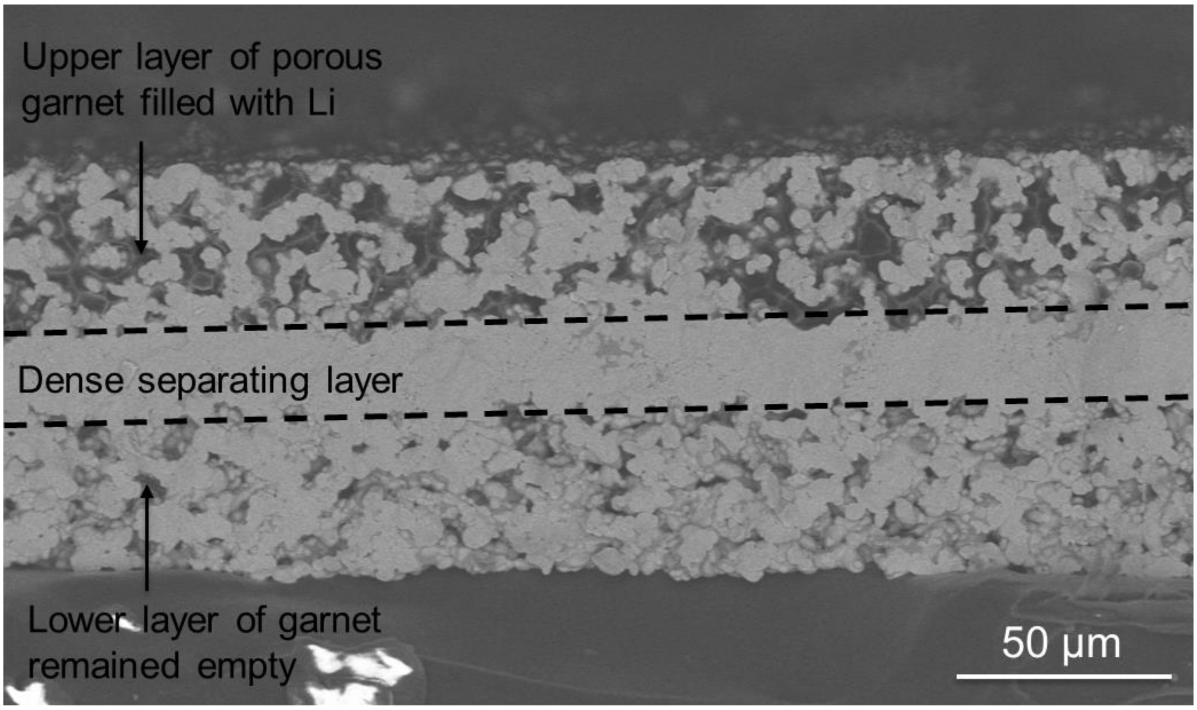

Figure S4. Low magnification cross-sectional SEM image of the garnet framework with Li infiltrated in the upper layer. The dense separating layer effectively blocks the Li metal from penetrating to the other side.

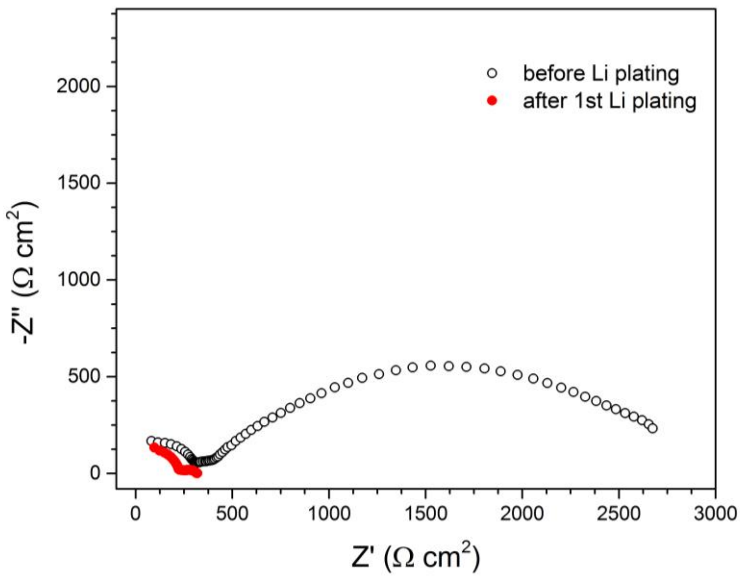

Figure S5. EIS of Li-garnet cell before and after initial Li plating. The interface impedance was significantly reduced after first Li plating into the empty bottom layer of the garnet host.

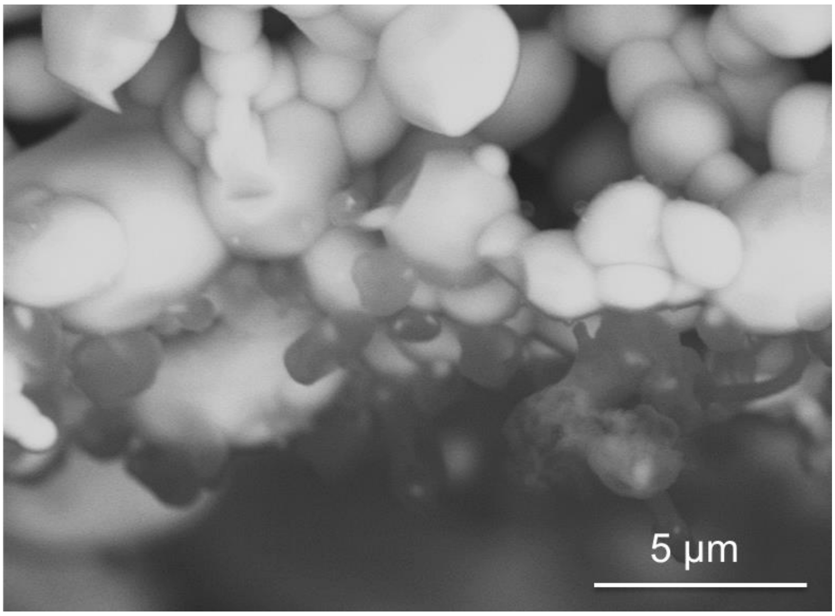

Figure S6. Deposition of Li into the garnet framework without a Cu coating layer and instead a carbon paper current collector. Li plated outside of the garnet framework because of the poor electrical contact between the current collector and garnet framework.

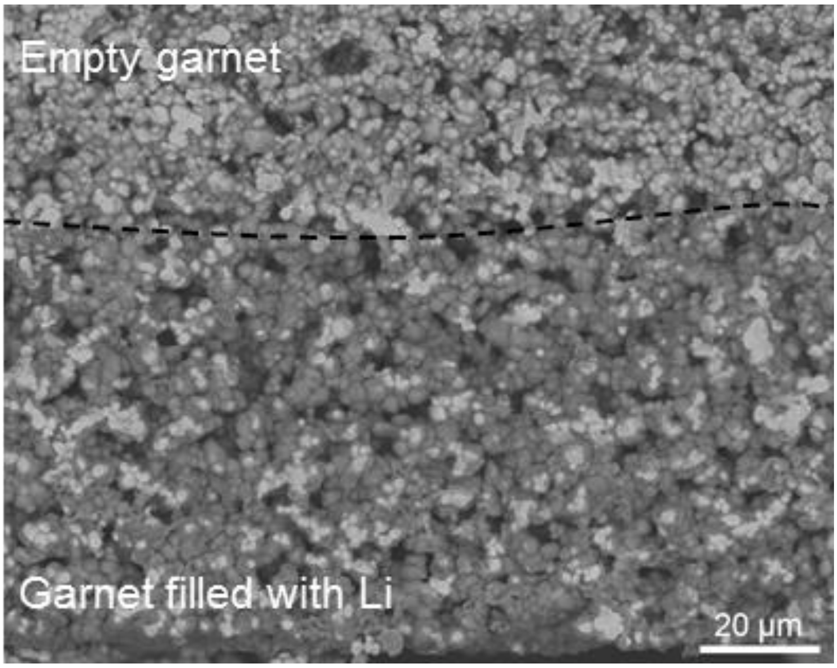

Figure S7. Cross-sectional SEM image of 3 mA h cm^{-2} of Li deposited in the lower layer of the garnet host. The thickness of deposited Li is ~70 µm and the region near the separating layer remains empty without Li penetration.

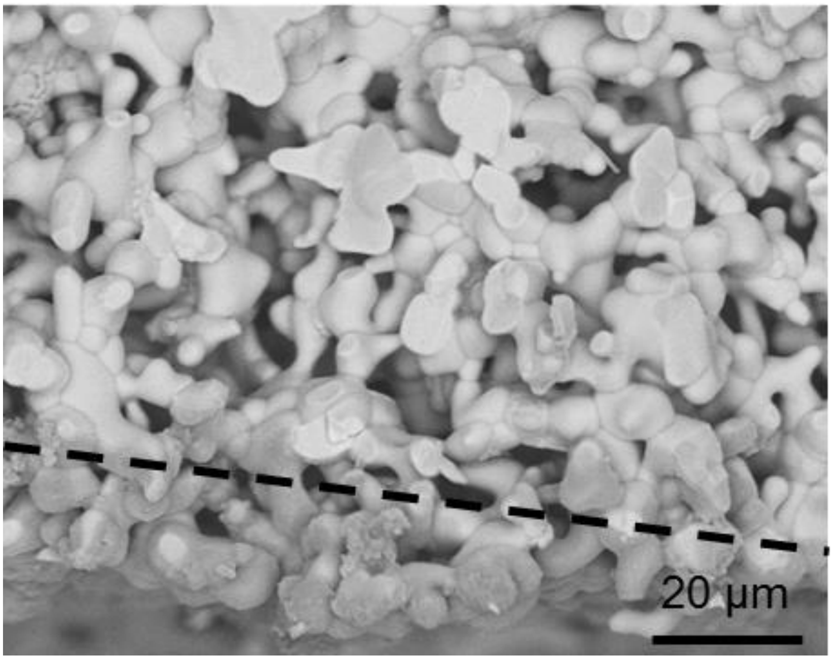

Figure S8. Cross-sectional SEM image of Li metal anode in the garnet host after stripping. Only residual Li remains on Cu current collector at the bottom of the garnet host after Li stripping.

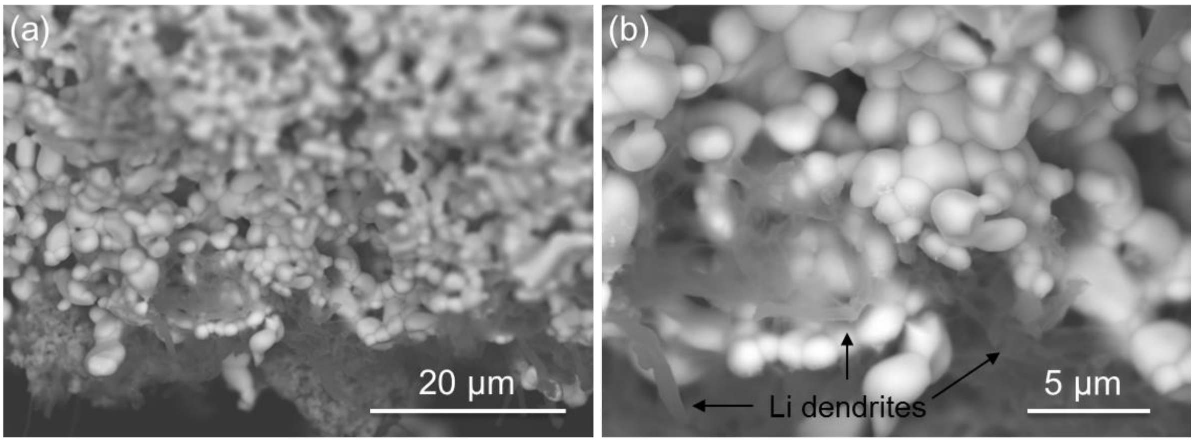

Figure S9. Cross-sectional SEM images of Li deposition at the bottom layer of the garnet framework (coated with copper) with the addition of 10 μL of organic electrolyte (1 M LiTFSI in 1,3-dioxolane/1,2-dimethoxyethane, 1:1 by volume). Li was mainly deposited outside of the garnet host and formed a dendritic morphology (indicated by arrows) after plating 1 mA h cm^{-2} of Li at 0.5 mA cm^{-2}, which is commonly observed in liquid Li metal batteries and is inferior to the Li anode with solid-state garnet framework.

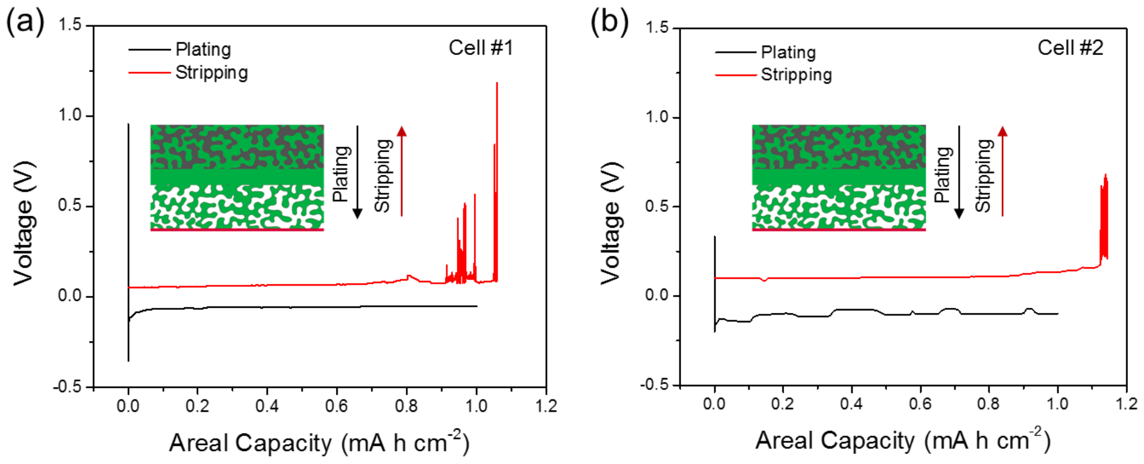

Figure S10. Plating and stripping voltage profiles at 0.5 mA/cm^2 in Coulombic efficiency (CE) tests: (a) CE = 106%, (b) CE = 113%.

The Coulombic efficiency (stripping/plating Li) of the solid-state Li metal anode with the garnet framework is greater than 100%, possibly because some Li-ions were extracted from $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN) electrolyte after completely stripping of Li metal during charging. The offset of Li might have contributed to the high CE and excellent cycling stability in Figure 5A. Of course, intentionally and continuously charging at high voltage would escalate side reactions and deteriorate the cell. Therefore, complete removal of Li from the anode should be avoided and a slight excess of Li anode (as we did in Figure 5) can greatly improve the cycling performance due to the high Coulombic efficiency.

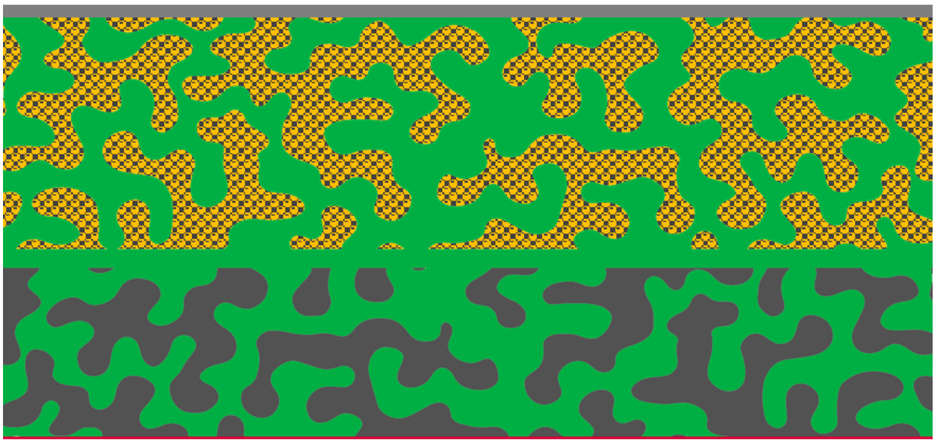

Figure S11. Schematic of projected solid-state Li-S battery with the garnet framework.

Table S1. Theoretical calculation for energy density of garnet-based solid-state Li-S battery.*

	Thickness (µm)	Material	Volume ratio	Volume (cm^3)	Density (g/cm^3)	Mass (g)	Specific Capacity (mAh/g)	Capacity (mAh)
Cathode	100	Garnet	30%	0.300	4.97	1.491	0	0
		Sulfur	33%	0.335	1.96	0.656	1675	1099.6
		Carbon	10%	0.100	1.7	0.171	0	0
		Empty	26%	0.265	0	0.000	0	0
Separator/Electrolyte	10	Garnet	100%	0.100	4.97	0.497	0	0
Anode	75.4	Garnet	30%	0.226	4.97	1.124	0	0
		Lithium	70%	0.528	0.54	0.285	3860	1099.6
		Empty	0%	0.000	0	0.000	0	0
Current collector	10	Titanium	100%	0.100	4.43	0.443	0	0
Total	195.4			1.954		4.67		1099.6
							Specific energy (Wh/kg)	518.4
							Energy density (Wh/L)	1210.1

* Calculations are based on a cell of 100 cm^2 dimensions (cell area has no effect on the specific capacity and energy density). As shown in Figure S11, the garnet framework has a 10 µm dense separating layer and two porous layers with 70% porosity. The cathode material is S/C with 80 wt% of S. The volume expansion (79%) of S cathode during fully lithiation is considered when calculating the energy density. The mass of the Cu deposited on the bottom of anode is negligible and was not counted.