SUPPORTING INFORMATION

3D Lithium Metal Anodes Hosted in Asymmetric Garnet Frameworks toward High Energy Density Batteries

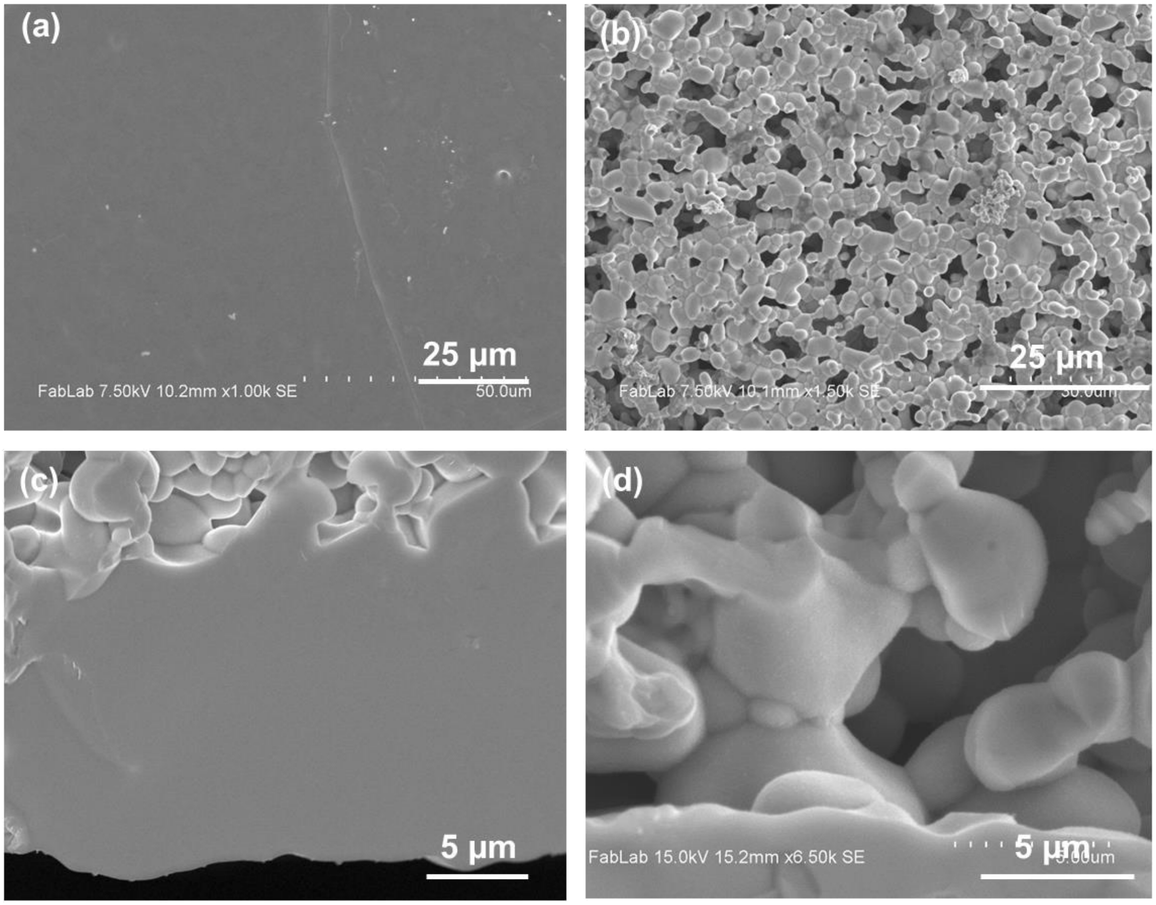

Figure S1. Additional scanning electron microscope (SEM) images of the bilayer framework. (a) Top view of the dense side with high densification for preventing short-circuits and high flatness for integrating with the cathode. (b) Top view of the porous side with open holes enabling Li metal infusion. (c) Cross-sectional view of the dense layer with high densification. (d) Interface between the porous layer and the dense layer, indicating the seamless connection between the two layers by co-sintering.

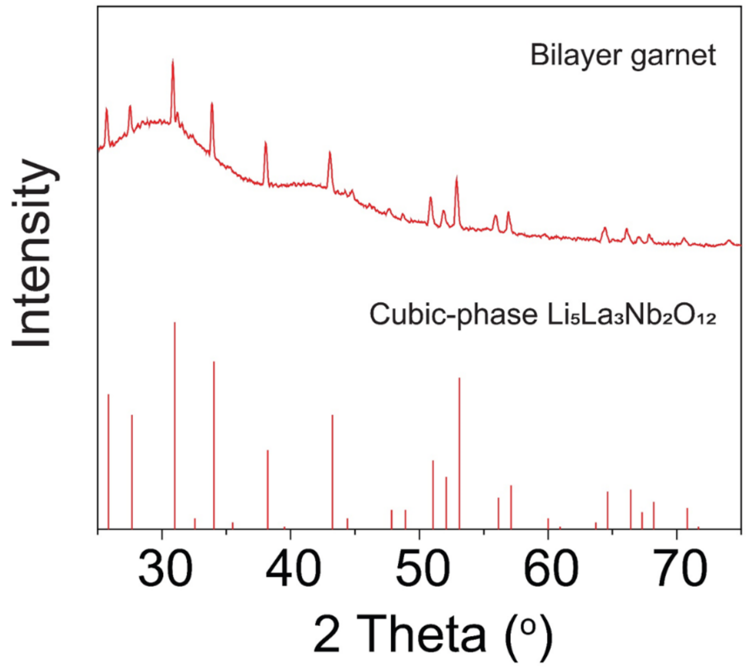

Figure S2. X-ray diffraction plot of bilayer garnet $Li_7La_3Zr_2O_{12}$, compared with the standard cubic-phase garnet $Li_5La_3Nb_2O_{12}$ (JCPDS 80-0457). The coincidence demonstrates cubic garnet phase of the bilayer framework.

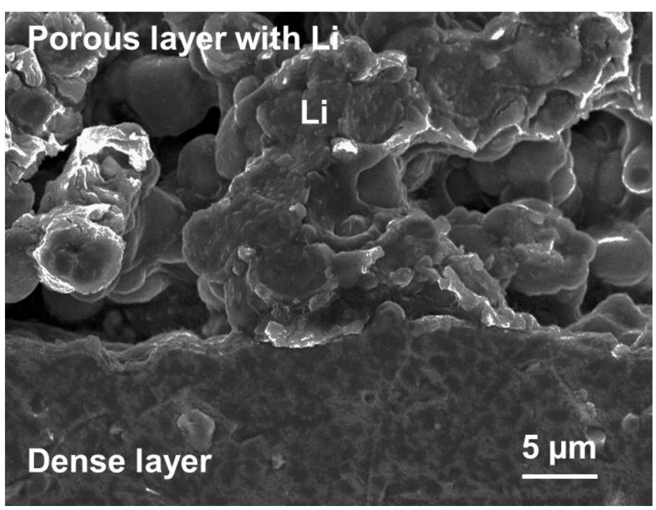

Figure S3. The corresponding secondary electrons SEM image of Figure 2f, showing the Li metal distribution at the porous/dense interface after Li infiltration.

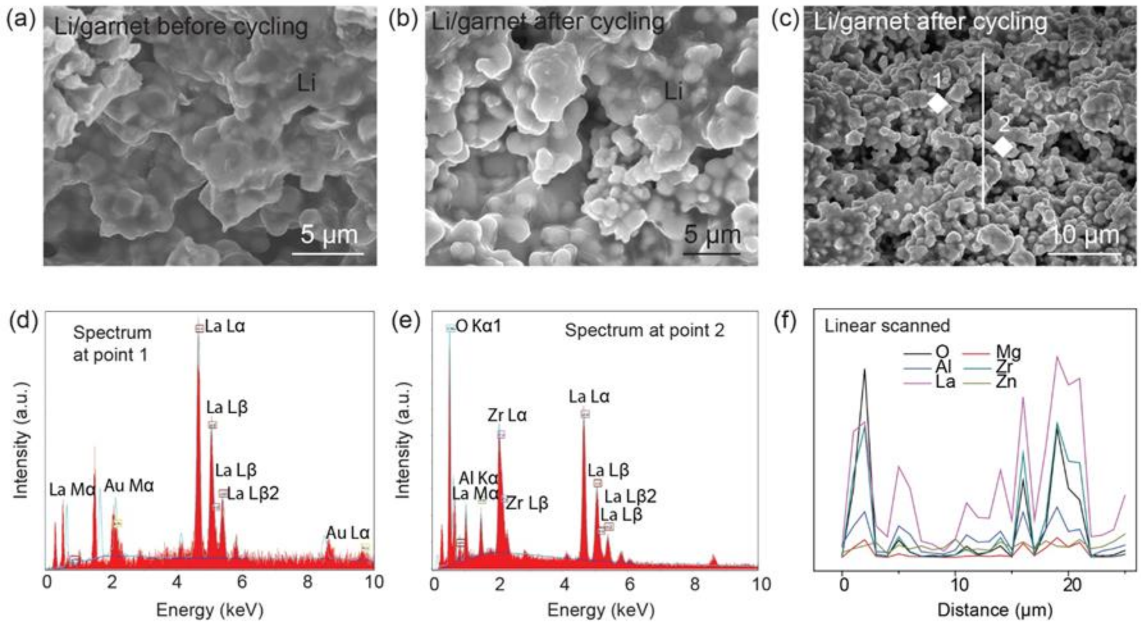

Figure S4. Characterizations of the bilayer garnet framework after Li/Li cell cycling at 0.5 mA/cm^2 for 150 hours. (a-b). Porous garnet framework with Li metal inside, before and after cycling, respectively. The morphology of Li in the framework kept stable. (c-f). Energy-dispersive X-ray (EDX) spectra of the framework after cycling. (c). The positions of EDX detections in the framework. Two spots and one line are scanned. (d). Spectrum at spot 1. (e). Spectrum at spot 2. (f). Spectrum of the line. The elements of gel electrolyte (P and F) are not detected in any scan. This confirms that no gel electrolyte penetrated into the porous framework after cycling.

Calculations of battery energy densities with the bilayer garnet framework and NMC cathodes (14 and 32 mg/cm^2).

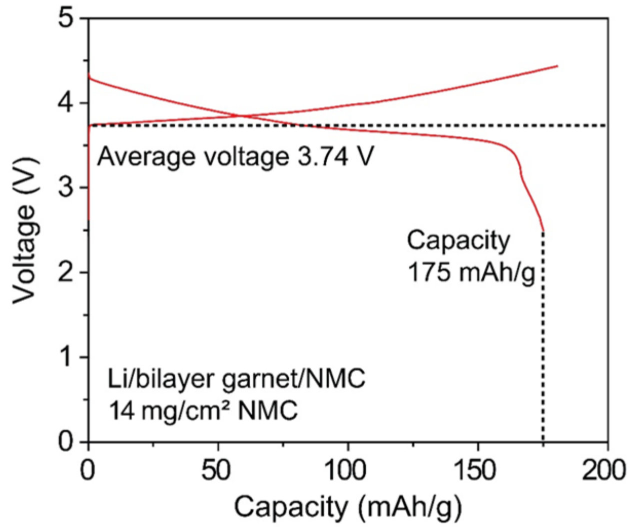

Figure S5. Voltage profile of the Li/bilayer garnet/NMC battery with 14 mg/cm^2 cathode mass loading, for energy density calculations.

Table S1. Energy density of Li/bilayer garnet/NMC battery with the commercial cathode.

Component	Thickness (μm)	Material	Density (g/cm^3)	Mass (mg/cm^2)	Specific Capacity (mAh/g)	Capacity (mAh/cm^2)
Cathode	45	NMC 94%	N/A	14.0	175	2.45
		PVDF 3%		0.45	N/A	N/A
		Carbon 3%		0.45		
		Additional electrolyte 2 μL/cm^2	1.26	2.5		
Electrolyte	10	Gel	1.64	1.6		
	20	Garnet	4.97	9.9		
Anode	50	Garnet 30%	4.97	7.5		
		Li 60%	0.54	1.6		
Total	125	N/A	N/A	38.0		
Average voltage 3.74 V					Energy Density	241 Wh/kg
						733 Wh/L

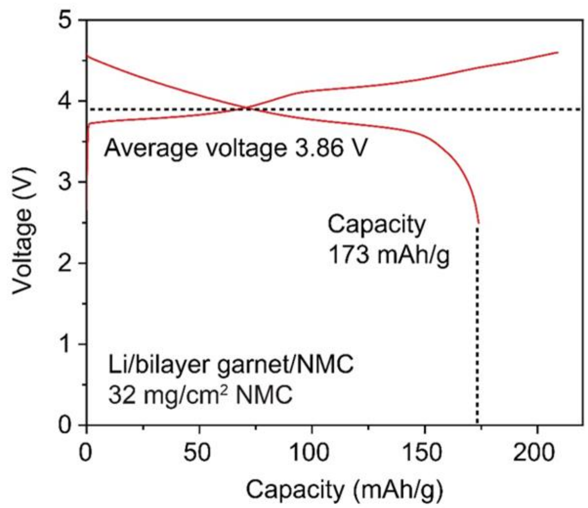

Figure S6. Voltage profile of the Li/bilayer garnet/NMC battery with 32 mg/cm^2 cathode mass loading, for energy density calculations.

Table S2. Energy density of Li/bilayer garnet/NMC battery with the high loading cathode.

Component	Thickness (μm)	Material	Density (g/cm^3)	Mass (mg/cm^2)	Specific Capacity (mAh/g)	Capacity (mAh/cm^2)
Cathode	130	NMC 85%	N/A	32.0	173	5.54
		PVDF 5%		1.9	N/A	N/A
		Carbon 10%		3.8		
		Additional electrolyte 4 μL/cm^2	1.26	5.0		
Electrolyte	20	Gel	1.64	3.3		
	20	Garnet	4.97	9.9		
Anode	50	Garnet 30%	4.97	7.5		
		Li 60%	0.54	1.6		
Total	220	N/A	N/A	65.0		
Average voltage 3.86 V					Energy Density	329 Wh/kg
						972 Wh/L

Estimated calculation of the energy densities of batteries with dense garnet in Figure 4d. The thicknesses and electrode loadings are reported in publications or adopted from commonly used parameters.

Table S3. Energy density of battery with dense garnet in Ref. 1

Component	Thickness (μm)	Material	Density (g/cm^3)	Mass (mg/cm^2)	Specific Capacity (mAh/g)	Capacity (mAh/cm^2)
Cathode	20	$LiFePO_4$	N/A	0.6	140	0.084
Electrolyte	5	Gel	1.64	0.8	N/A	
	200	Garnet	4.97	99.4		
Anode	20	Li	0.54	1.1		
Total	245	N/A	N/A	101.9		
Average voltage 3.4 V					Energy density	3 Wh/kg
						12 Wh/L

Table S4. Energy density of battery with dense garnet in Ref. 2

Component	Thickness (μm)	Material	Density (g/cm^3)	Mass (mg/cm^2)	Specific Capacity (mAh/g)	Capacity (mAh/cm^2)
Cathode	45	$LiFePO_4$	N/A	5	140	0.7
Electrolyte	100	PEO	1.2	12	N/A	
	400	Garnet	4.97	198.8		
Anode	20	Li	0.54	1.1		
Total	565	N/A	N/A	216.9		
Average voltage 3.4 V					Energy density	11 Wh/kg
						42 Wh/L

Table S5. Energy density of battery with dense garnet in Ref. 3

Component	Thickness (μm)	Material	Density (g/cm^3)	Mass (mg/cm^2)	Specific Capacity (mAh/g)	Capacity (mAh/cm^2)
Cathode	40	$LiFeMnO_4$	N/A	2	105	0.21
Electrolyte	150	Garnet	4.97	75	N/A	
Anode	20	Li	0.54	1.1		
Total	210	N/A	N/A	78.1		
Average voltage 4.5 V					Energy density	12.1 Wh/kg
						45 Wh/L

Reference

(1) Luo, W.; Gong, Y.; Zhu, Y.; Li, Y.; Yao, Y.; Zhang, Y.; Fu, K. K.; Pastel, G.; Lin, C. F.; Mo, Y.; et al. Reducing Interfacial Resistance between Garnet-Structured Solid-State Electrolyte and Li-Metal Anode by a Germanium Layer. *Adv. Mater.* **2017**, *29*, 1-7.

(2) Li, Y.; Xu, B.; Xu, H.; Duan, H.; Lü, X.; Xin, S.; Zhou, W.; Xue, L.; Fu, G.; Manthiram, A.; et al. Hybrid Polymer/Garnet Electrolyte with a Small Interfacial Resistance for Lithium-Ion Batteries. *Angew. Chemie - Int. Ed.* **2017**, *56*, 753-756.

(3) Han, X.; Gong, Y.; Fu, K.; He, X.; Hitz, G. T.; Dai, J.; Pearse, A.; Liu, B.; Wang, H.; Rubloff, G.; et al. Negating Interfacial Impedance in Garnet-Based Solid-State Li Metal Batteries. *Nat. Mater.* **2017**, *16*, 572-579.