

## Supporting Information

### **High rate and long cycling life lithium metal anode with a self-repairing alloy coating**

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**Keywords:** Li metal batteries; Dendrite free anode; Artificial SEI; Self-repairing alloy.

## **Experimental Section**

### **Preparation of self-repairing alloy protected Li metal.**

The gallium (Ga) nanoparticles dispersion was obtained by a simple liquid-based magnetic stirring and sonication process. The dispersing solvent is 1,3-dioxolane. dropping the dispersed liquid onto the surface of Li foil, then an in-situ formed alloy layer is produced.

### **Characterization.**

For the ex-situ SEM (Hitachi S4800, Japan) characterizations, different stages of Li plating/stripping process on alloy protected Li anode and Li anode were conducted. The cells were taken apart in the Ar filled glove box and the electrodes were rinsed with DOL and dried. Electrodes were pasted onto sample stage and sealed in Ar-filled transfer vessels for immediate SEM observation. Unavoidable contact with air may contribute to some slight surface features on the Li metal seen in SEM images.

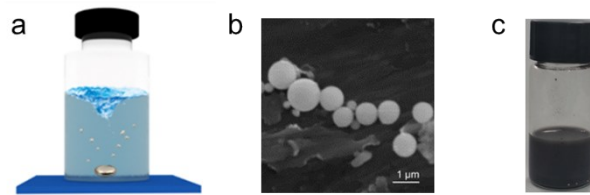
### **Electrochemistry.**

For galvanostatic cycling of symmetric cells, 2032-type coin cells were assembled with alloy protected Li or Li foil, 2325 PP separator, using 60  $\mu\text{l}$  electrolyte of 1 M LiTFSi in DOL/1 M LiPF<sub>6</sub> in EC/DEC/1 M LiTFSI in DOL/DME. The lithium foil used in this experiment is a commercial product (China Energy Lithium Co., Ltd.) with a thickness of about  $\sim 500$   $\mu\text{m}$ . The electrode used in full cell is self-made electrode by rolling and punching Li foil directly. EIS was measured in the frequency range of 0.01 Hz to 100 kHz with potentiostatic signal amplitude of 5 mV using the Princeton VersaSTAT 3F method. To test the practical performance in a full cell, LiFePO<sub>4</sub> (MTI, Corp) with an areal capacity of 4 mAh cm<sup>-2</sup> was used as cathode material. The LiFePO<sub>4</sub> electrode was prepared by mixing LiFePO<sub>4</sub>, Super P and PVDF in the weight ratio of 8:1:1 in NMP solvent. Then the slurry was coated on Al foil by a doctor blade coater and dried in a vacuum drying oven at 60 °C for 12 h. Then compact the electrode with a grinding apparatus. The obtained cathode had a typical loading of  $\sim 25$  mg active material.

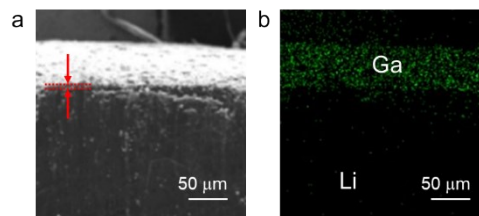
### **DFT Calculation.**

The first-principles calculations were conducted in castep module in Materials Studio

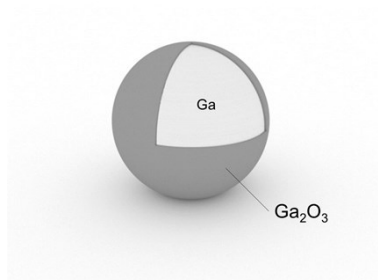
(version 7.0) of Accelrys Inc. with general gradient approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. An all-electron double numerical basis set with polarization functions (DNP basis set) was used during calculating. The convergence tolerance quality of geometry optimization was set to fine:  $1.0 \times 10^{-5}$  au for energy,  $2.0 \times 10^{-3}$  au  $\text{\AA}^{-1}$  for maximum force and  $5.0 \times 10^{-3}$   $\text{\AA}$  for maximum displacement. The k-points for Brillouin zone were selected by Monkhorst-Pack method and set to  $3 \times 3 \times 1$  for  $\text{Li}_2\text{Ga}(100)$ . Besides, the self-consistent field (SCF) tolerance was set to  $1.0 \times 10^{-6}$  au. The adsorption energies ( $E_a$ ) for Li on the metal oxide surfaces are defined as  $E_a = E_{\text{total}} - E_{\text{ads}} - E_{\text{surf}}$ , where  $E_{\text{total}}$  is the total energy of the adsorbed system,  $E_{\text{ads}}$  is the energy of the adsorbate in vacuum and  $E_{\text{surf}}$  is the energy of the optimized clean surface slab.



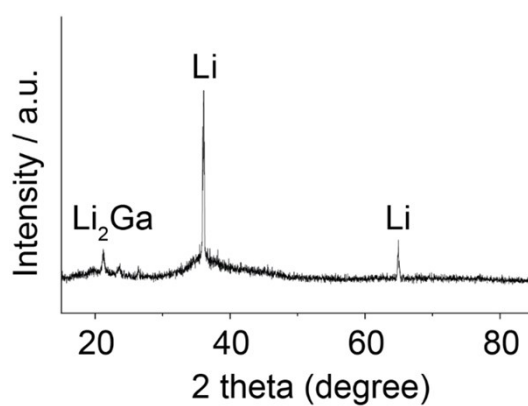
**Figure S1.** a) Schematic diagram of preparation of gallium nanoparticles. First, magnetic stirring for 6 hours, and then ultrasonic for 1 hour. b) SEM image of gallium nanoparticles after sonication in 1,3-dioxolane, the base is copper foil. c) The gallium (Ga) nanoparticles dispersion.



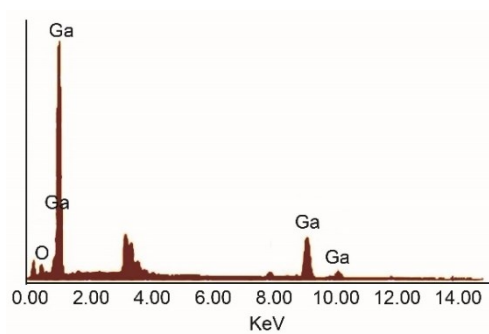
**Figure S2.** a) Cross-sectional SEM images of  $\text{Li}_x\text{Ga}$  alloy protected Li and the b) corresponding EDS mapping.



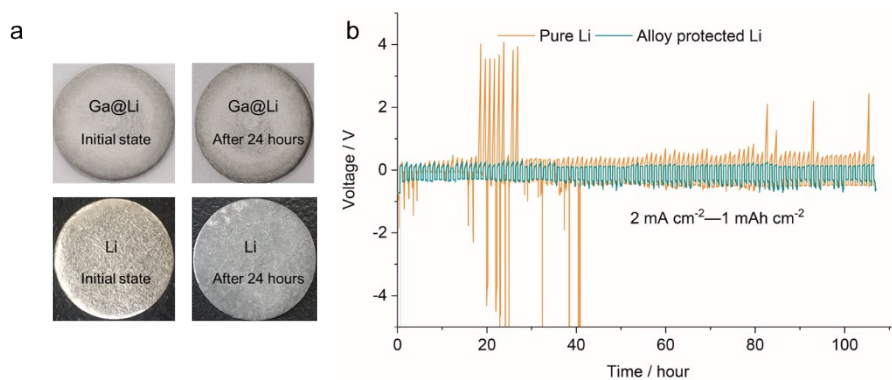
**Figure S3.** Schematic illustration of gallium nanoparticle coated with oxide layer<sup>[1]</sup>.



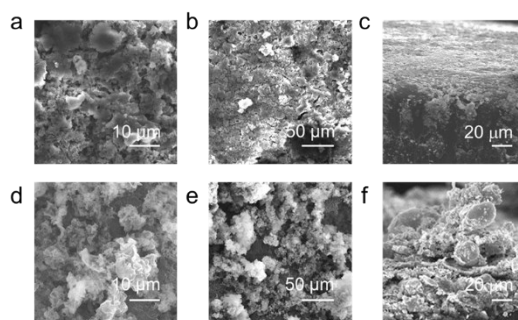
**Figure S4.** X-ray diffraction pattern of Li<sub>x</sub>Ga alloy protected Li metal (JCPDS files: 36-0934, Li<sub>2</sub>Ga).



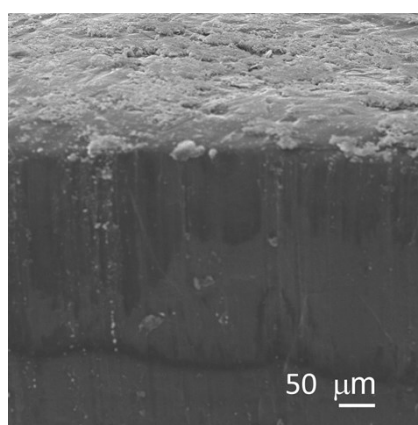
**Figure S5.** Typical EDS spectra of Li<sub>x</sub>Ga alloy-protected Li metal.



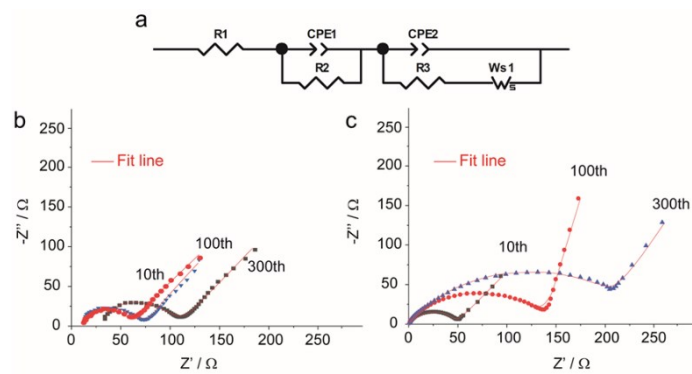
**Figure S6.** a) Optical photographs of pristine Li anode compared to the alloy protected Li anode. b) Symmetric cycling of two anodes after placed in air for 24 hours.



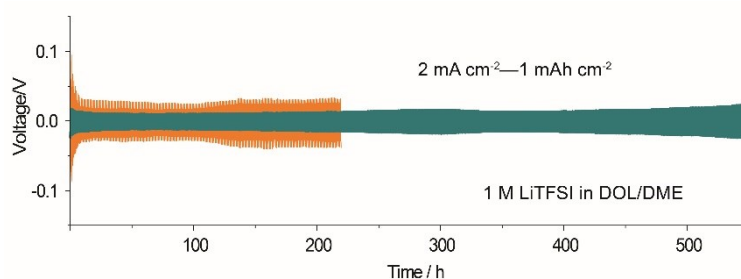
**Figure S7.** SEM images of a-c) alloy-protected Li metal and d-f) pure Li after 200<sup>th</sup> cycling. The electrolyte is 1 M LiTFSI in DOL electrolyte.



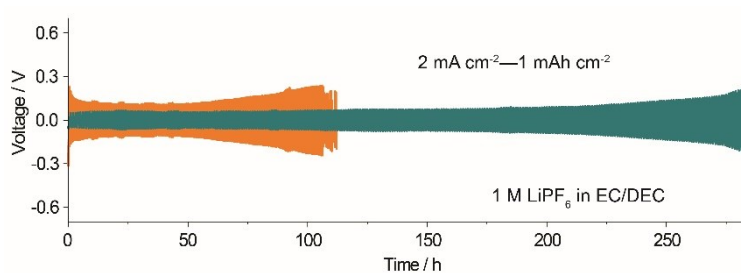
**Figure S8.** Cross-sectional SEM images of the alloy-protected Li anode after deposition of 15 mAh cm<sup>-2</sup> Li.



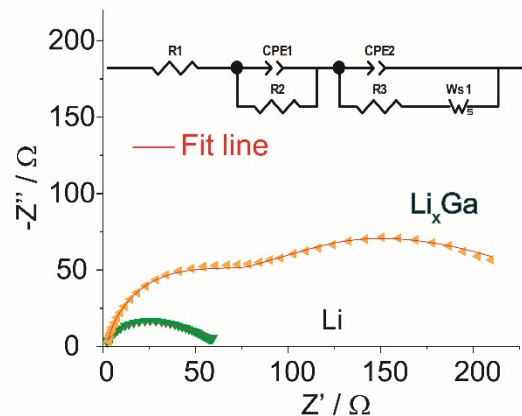
**Figure S9.** a) The equivalent circuit of Nyquist plot. b) Impedance spectra of  $\text{Li}_x\text{Ga@Li}|\text{Li}_x\text{Ga@Li}$  and c)  $\text{Li}|\text{Li}$  cells after various cycles.



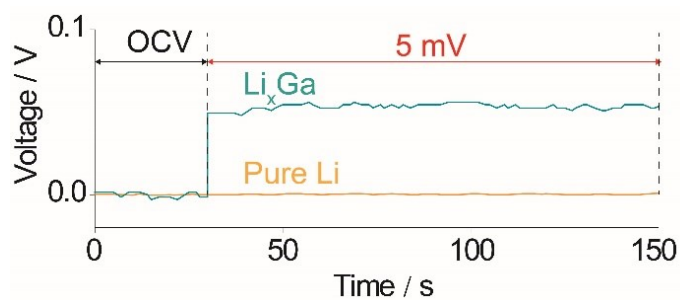
**Figure S10.** Lithium plating/stripping in symmetric cells at a current density of  $2 \text{ mA cm}^{-2}$  for 1 h in 1 M LiTFSI in DOL:DME (v:v = 1:1) electrolyte.



**Figure S11.** Lithium plating/stripping in symmetric cells at a current density of  $2 \text{ mA cm}^{-2}$  for 1 h in 1 M  $\text{LiPF}_6$  in EC:DEC (v:v = 1:1) electrolyte.



**Figure S12.** Impedance spectra of Li (green curve) and Li | Li<sub>x</sub>Ga (orange curve) electrodes recorded at 5 mV vs. OCV in 1 M LiTFSI in DOL electrolyte. Inset is the equivalent circuit of Nyquist plot.



**Figure S13.** Comparison of the voltage response to a current of 5 mA of the Li anode (orange curve) and alloy-protected anode (green curve). The voltage response indicates the resistivity of interface of alloy layer protected Li and pure Li foil [2].

**Table S1.** Compositions of symmetric-cell cycling with different approaches to protect Li metal based on the reported dates.

Work	Current density mA cm <sup>-2</sup>	Capacity mAh cm <sup>-2</sup>	Time hour	Electrolyte	Ref.
PVDF-HFP@Al	3	3	400	1.0 M LiTFSI in DOL/DME	J. Mater. Chem. A, 2020,8, 1247-1253
F3 composite separator	3	1	600	1.0 M LiTFSI in DOL/DME	
Sn-Li hybrid electrodes	3	1	500	1 M LiPF <sub>6</sub> +10% FEC+1% VC	Nat. Energy. 2018 3, 310–316.
MgCl <sub>2</sub> electrolyte additive	1	1	300	1 M LiPF <sub>6</sub> in EC/DMC/EMC+10 mM MgCl <sub>2</sub>	ACS Appl. Mater. Interfaces, 2019, 11, 11360-11368
Pyr1(12)F SI Ionic liquid Additive	0.5	2	800	1 M LiTFSI in DOL/DME+ Pyr1(12) FSI	Adv. Energy Mater., 2018, 8, 1702744.
Liquid-metal-coated Cu foil	0.5	0.5	350	1 M LiTFSI in DOL/DME+1 % LiNO <sub>3</sub>	J. Mater. Chem. A, 2019, 7, 18861-18870.
Li <sub>x</sub> Ga alloy-protected anode	2	1	1800	1 M LiTFSI in DOL	This Work
	5	2.5	1400		
	15	15	350		



## References

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- 2 X. Liang, Q. Pang, I. R. Kochetkov, M. S. Sempere, H. Huang, X. Sun, L. F. Nazar, *Nat. Energy*, 2017, 2, 17119.