Supplementary Information

Solubility-dependent protective effects of binary alloys for lithium anode

Yan Xu,[‡] Shuyang Zhao,[♯] Guangmin Zhou,[⊥] Wei Chen,[⊥] Fei Zhou,[Φ] Ze Rong,[Φ] Yang Wu,[⌡] Jia Li,[♯] Jinghua Guo,*[∥] Yuegang Zhang*[‡,§]

‡ i-Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou, Jiangsu, 215123, China;

♯ Laboratory for Computation Materials Engineering, Division of Energy and Environment, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, China;

⊥ Department of Materials Science and Engineering, Stanford University, Stanford, CA 94305, USA;

Φ Monta Vista Energy Technologies Corporation, Hefei, 230601, China;

∥ Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, United States;

⌡ Department of Mechanical Engineering, Tsinghua University, Beijing, 100084, China;

§ Department of Physics, Tsinghua University, Beijing, 100084, China

Corresponding authors: J. Guo (E-mail: jguo@lbl.gov); Y. Zhang (E-mail: yuegang.zhang@tsinghua.edu.cn)

METHODS

Preparation of the protected lithium electrode. Electrode preparation was carried out in an argon-filled glove box (O_2 level <10 ppm and H_2O level < 0.5 ppm). Lithium metal foil (99.9%, Aldrich) was polished to get a shiny surface. After polishing, 50 μL carbonate-based electrolyte (1M $LiPF_6$ in 1:1 EC/DEC, BASF) with 50 mM different additives was dropped onto the lithium foil.

Electrochemical testing. To investigate the electrochemical performances of protected and unprotected Li metal, symmetric type-2032 coin cells were assembled with two identical electrodes. The impedance spectra were recorded over the frequency from 100 kHz to 100 mHz using a Bio-Logic VMP3 system. For the fabrication of LCO cathode, LCO slurry containing LCO: Super P: PVDF =70:20:10 was coated onto an Al foil with a total mass loading of ~3 mg/cm^2 and dried at 80 °C under vacuum for 2 days. Coin cells were assembled using a Li metal foil as counter/reference electrode. Galvanostatic cycling of symmetric Li metal cells and Li-LCO cells were carried out on a LAND battery testing system with the potential range of 3.0-4.2 V (*vs.* Li/Li$^+$).

Characterizations. The pristine and cycled Li metal electrodes were mounted onto SEM stages and sealed in Ar-filled transfer vessels for immediate SEM (FEI Quanta 200) observation. Powder X-ray diffraction was performed on a PANalytical X'Pert with Ni-filtered Cu Kα radiation. The XRD samples were sealed with Kapton tape (DuPont). XPS analysis was performed on PHI Versa Probe 5000, Physical Electronics, USA. For sputter depth profiling, Ar$^+$ ions of 2 keV energy at a scan size

of 1 mm×1 mm was utilized.

Simulation method: Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP)[1]. Projector augmented wave (PAW) potentials and generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) functional were adopted to describe electron–ion interactions and electron exchange-correlation, respectively[2,3]. The cutoff energy was set as 400 eV for planewave basis set and all atoms were fully relaxed by conjugated gradient algorithm with a criterion of convergence of 0.01 eV/Å. The binding energy E_b is defined as $E_b = E_{Li\text{-}M} - E_{Li} - E_M$, where $E_{Li\text{-}M}$, E_{Li} and E_M are the total energies of the Li-M alloy, the bulk metal Li, and the bulk metal M, respectively.

Table S1 | Six kinds of selected metals and corresponding mutual solubility with Li.

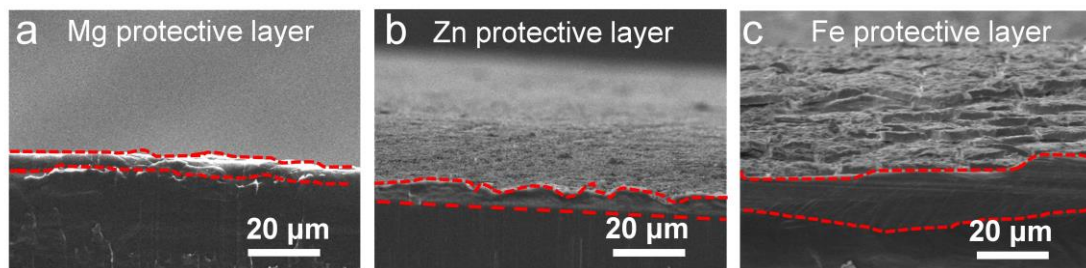| Metal	The maximal Li ratio in M	The maximal M ratio in Li
Mg	16%	68%
Au	17%	<0.1%
Zn	1.5%	<0.1%
Al	1.0%	<0.1%
Fe	unknown	0%
Cu	9.7%	0%

Figure S1. Cross-sectional SEM images of lithium with (a) Mg protective layer, (b) Zn protective layer and (c) Fe protective layer.
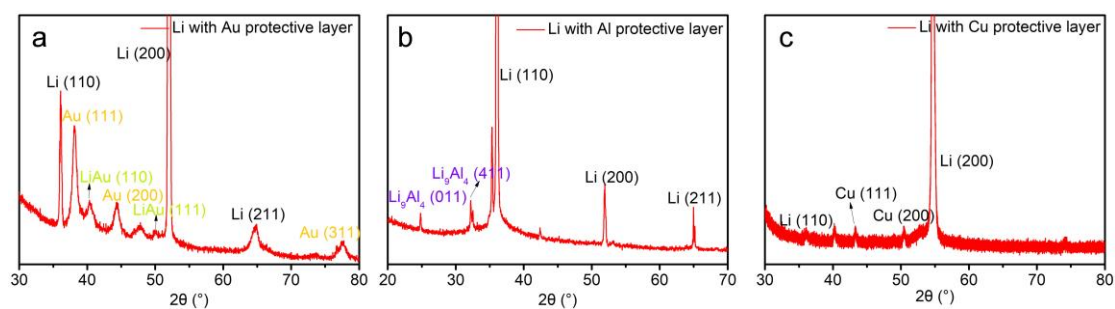

Figure S2. XRD characterizations of Li surface with (a) Au, (b) Al and (c) Cu protective layers, respectively.
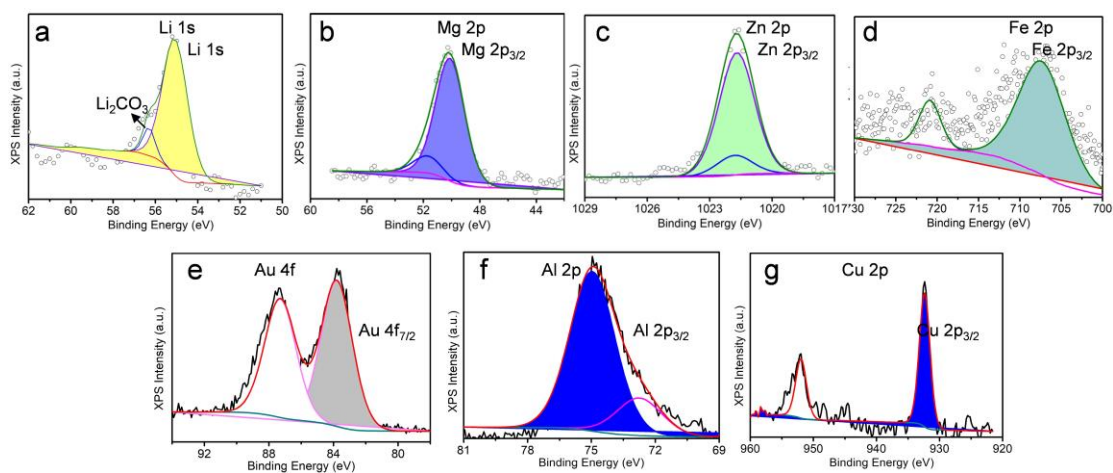
Figure S3. XPS spectra of pristine Li anode with respective protective layer. (a) Li 1s (b) Mg 2p (c) Zn 2p (d) Fe 2p (e) Au 4f (f) Al 2p (g) Cu 2p for Li foil, Mg protective layer, Zn protective layer, Fe protective layer, Au protective layer, Al protective layer, and Cu protective layer are presented. In XPS spectra, Mg 2p peak, Au 4f peak, Zn 2p peak, Al 2p peak, Cu 2p peak and Fe 2p peak are shown at 50.2 eV, 84.0 eV, 1021.8 eV, 72.6 eV, 932.5 eV and 711.0 eV, which can be ascribed to metallic Mg, metallic Au or associated Li_xAu alloy, metallic Zn or associated Li_xZn, Li_xAl alloy, metallic Cu and metallic Fe, respectively.
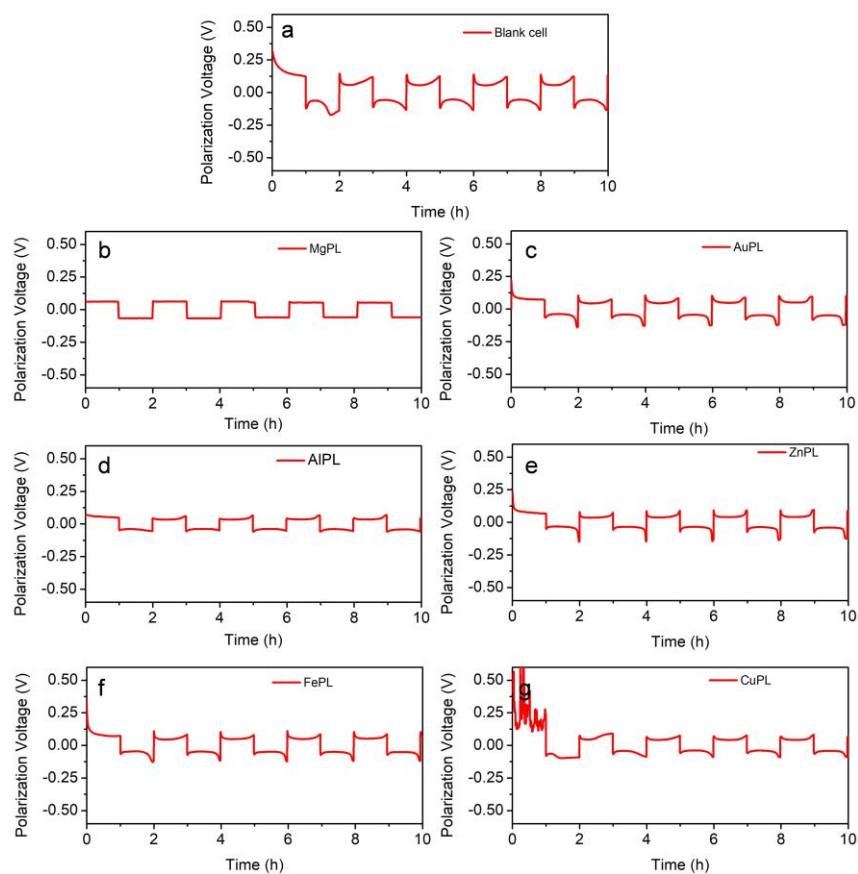
Figure S4. The typical voltage profiles of Li symmetric cells (a) without protective layer, with (b) Mg, (c) Au, (d) Al, (e) Zn, (f) Fe, (g) Cu protective layers for the first 5 cycles.
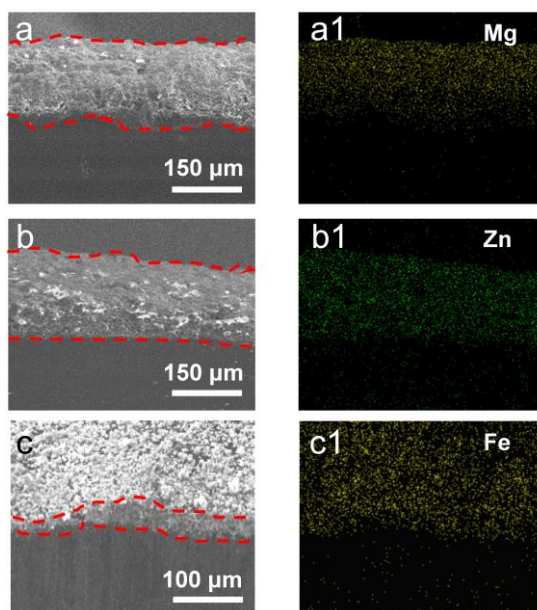
Figure S5. SEM images of Li metal with (a) Mg, (b) Zn and (c) Fe protective layers after 5 cycles and corresponding (a1-c1) EDS elemental mapping.
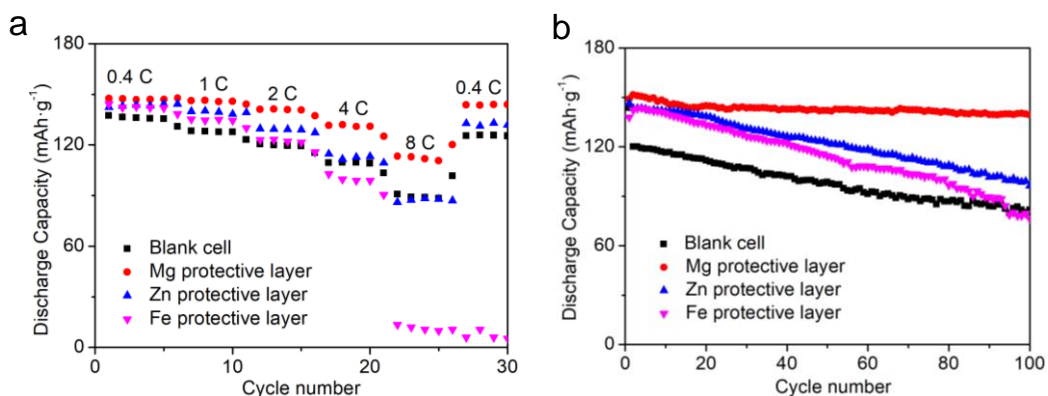

Figure S6. Electrochemical performance of LCO/Li cells. (a) Rate capability of LCO/Li cells without protective layer, with Mg protective layer, Zn protective layer and Fe protective layer at various rates from 0.4 to 8C. (b) Cycling stability of LCO/Li without protective layer, with Mg protective layer, Zn protective layer and Fe protective layer.

Reference

(1) Kresse, G.; & Furthmüller, J., Efficiency of ab-initio Total Energy Calculations for Metals and Semiconductors Using a Plane-wave Basis Set. *Com. Mater. Sci.* **1996**, *6*, 15-50.

(2) Kresse, G., & Joubert, D., From Ultra-soft Pseudopotentials to the Projector Augmented-wave Method. *Phys. Rev. B* **1999**, *59*, 1758.

(3) Perdew, J. P., Burke, K., & Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.