

Promoting a highly stable lithium metal anode by superficial alloying with an ultrathin indium sheet

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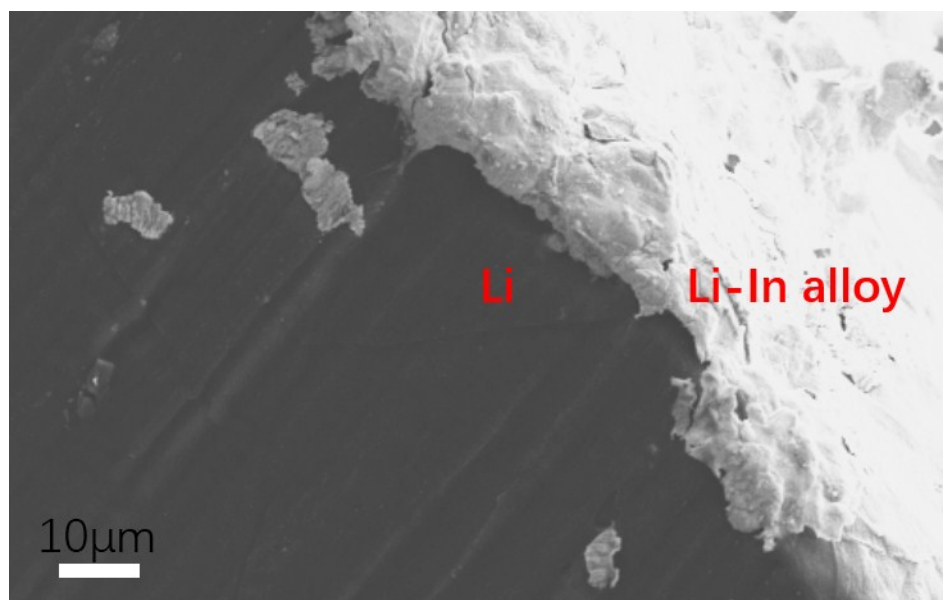


Figure S1. The cross-section of the lithium rich lithium-indium hybrid anode.

Experimental section

Indium sheet and hybrid anode preparing: ultrathin indium sheet was prepared by a rolling method depending on the essential ductility. Metallic indium foil (0.2mm in thickness, Shenzhen) was used and sandwiched between two ultra-cleaned aluminum foil (0.5mm in thickness, Shenzhen), rolled and calendared by a rolling machine. This process was repeated nearly ten times. Subsequently, to obtain the indium sheet, the

rolled aluminum-indium metal foil was placed in 0.1 M hydroxide sodium for one hour with the aluminum dissolution. The indium ultrathin sheet was extracted with the aid of plastic slice and washed several times with deionized water till the pH approaching neutral and dried in an oven at 60 °C, 5h before using. The preparation procedure of Li-In alloy covered anode was facile and conducted in an Ar filled glovebox. During the covering of lithium foil by ultrathin indium sheet, 10 kN/cm² pressure was introduced to make a good connection between the indium sheet and lithium foil on a flat stage. Only after a few seconds, the lithium-rich Li-In hybrid anode was obtained with the color turning into dark grey. What needs to be emphasized is that the obtained alloy layer is integral in this work, which maybe attribute to the certain pressure used. The thickness of the alloy interphase was examined to be ~2 μm (supporting information, Figure S1).

Structural characterization: X-ray diffraction (XRD) measurements were carried out on a Bruker D8-Advance powder X-ray diffractometer operating at 40 kV and 30 mA, using Cu K α radiation ($\lambda=0.15405$ nm). Scanning electron microscopy (SEM) studies were carried out on a Zeiss. Lithium, indium sheet and lithium-rich Li-In alloy anode were flat and sealed with Kapton (polyimide) tape for XRD test. To avoid the reaction with moisture in SEM test, the samples with metallic lithium was sealed in an Ar-filled container before being quickly transferring to the ultrahigh vacuum chamber of Zeiss.

Cells fabrication and electrochemical performance test: Electrochemical studies were performed in 2032 coin cells. For the impedance, cyclic voltammetry and lithium

plating/stripping studies, symmetric (fresh lithium on each side or lithium-rich Li-In on each side) and asymmetric (lithium/copper foil, lithium/indium sheet) cells were assembled with 40 μL of 1M LiPF_6 in EC/DMC (1:1 vol) electrolyte without any additive and a Celgard three-layer PP/PE/PP separator. Li-In hybrid anodes and $\text{LiNi}_5\text{Co}_3\text{Mn}_2\text{O}_2$ (NCM-532) cathodes were used in the full cells. The cathode electrodes were prepared by casting a slurry containing $\text{LiNi}_5\text{Co}_3\text{Mn}_2\text{O}_2$ (Sigma), Super P and poly(vinylidene difluoride) (PVDF) in a ratio of 8:1:1 by weight onto aluminum foil with dimethylformamide (DMF) solvent. The cathodes were cut into disks with a diameter of 11 mm and dried at 60 $^\circ\text{C}$ prior to use. The areal loading of $\text{LiCo}_5\text{Ni}_3\text{Mn}_2\text{O}_2$ was about 3 mg cm^{-2} . Approximately 40 μL of 1 M LiPF_6 in EC/DMC (1:1 vol) electrolyte was used. Electrochemical impedance measurements were conducted at room temperature using electrochemical workstation (CH660E, Chenhua) with a frequency range of 0.1 Hz to 1 MHz.

Stability test of Li-In hybrid anode

As shown in Figure S2, to make a comparison, the SEM images of both pure Li and Li-In hybrid electrodes after stripping with a capacity of 1 mAh/cm^2 at 1 mA/cm^2 are performed. Evidently, a mass of holes and much corrosive region can be found on the surface of pure Li electrode after Li stripping in Figure S2a b. While, for the Li-In electrode, the alloy protection layer can maintain an integral structure without obvious pores or fracture in Figure S2c d, which can be attributed to the Li-rich Li-In hybrid electrode. In other words, the charge can transmit through the alloy layer to realize the Li stripping in the Li-rich Li-In hybrid electrode with improved interface impedance and

diffusion barrier. As a result, the alloy layer endow the hybrid anode a long lifespan with dendrite suppression.

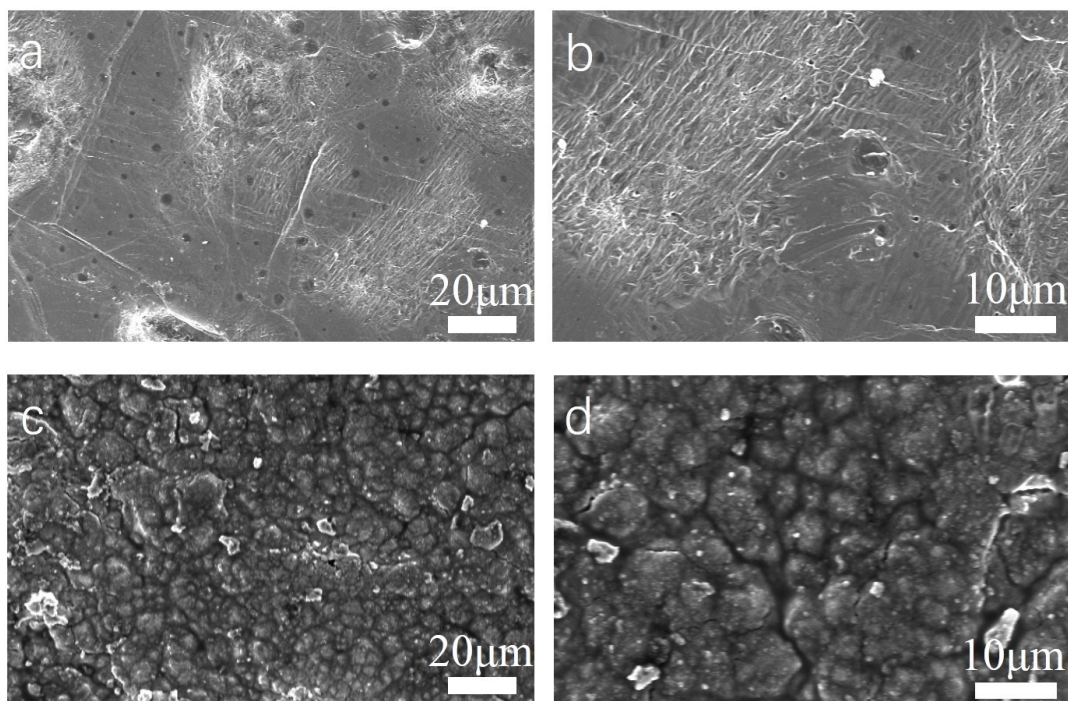


Figure S2. SEM images of Li and Li-In hybrid electrodes after stripping with capacity of 1.0 mAh cm⁻² at 1.0 mA cm⁻². (a) and (b) for pure Li electrode at different magnification; (c) and (d) for Li-In electrode at different magnification.

To have an insight into the enhanced electrochemical behavior, the related electrode morphologies were detected after disassembled in figure S3a, b. It is notable that, relative to the flat hybrid anode surface in figure S3a, the chapped interface of pure Li anode can be found in figure S3b ascribing to the enrichment of Li dendritic structures. Particularly, when the capacity increased to 3 mAh cm⁻² at current density of 1 mA cm⁻², the huge difference of cycling stability between indium sheet modified and pure Li anode was made.. Figure S3c, d correspond to the related dissected SEM images of the hybrid and pure Li anodes cycled at 1 mA/cm² with three hours for each step. As predicted, an improved Li-In hybrid anode interface with dendrite suppression is

exhibited in figure S3c, which can attribute to the uniform Li electrodeposits. As opposed to the indium modified sample, which makes it a promising candidate for new types of Li battery since stable, long-term performing, pure Li anode subjected severe interface evolution resulting in much eroded holes in figure S3d. Moreover, Figure S3e, f report that such lithium rich Li-In anode can be operated in a prototype full cell configurations paired with intercalating NCM-532 cathodes. The 1st, 50th and 100th cycle all display a typical electrochemical behavior with smooth and monotonous voltage plateaus. There is beyond 90% capacity retention in 120 cycles at a rate of 0.3C with a high Coulombic efficiency ($>98.3\%$). We believe that such hybrid anode design can pave an attractive way to the practice implementation relying on the plating and alloying processes.

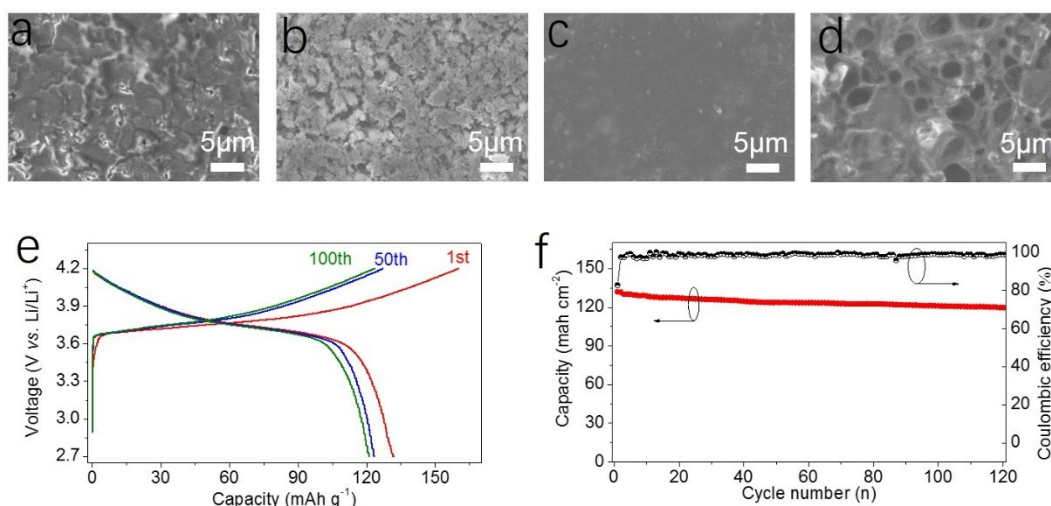


Figure S3. (a, b) SEM images of the hybrid electrodes and pure Li electrodes cycled at 0.5 mA/cm² with one hour for each step, respectively; (c, d) SEM images of the hybrid electrodes and pure Li electrodes cycled at 1 mA/cm² with three hours for each step, respectively; (e) Voltage-capacity curves and (f) cycling stability operated at 0.3C of the full cell.