Supplementary Information

**Volumetric variation confinement: Surface protective structure towards high cyclic stability of lithium metal electrode**

*Zhe Peng, Shuwei Wang, Jingjing Zhou, Yan Jin, Yang Liu, Yinping Qin, Cai Shen*,

*Weiqiang Han*, Deyu Wang*

**Corresponding Author**

E-mail: (C. S.) shencai@nimte.ac.cn; (W. H.) hanweiqiang@nimte.ac.cn; (D. W.) wangdy@nimte.ac.cn

**Experimental section**

*Al₂O₃ porous layer preparations and skin-layer formation*

Al₂O₃ nano-powder (particle size ~10 nm, Aladdin Industrial Inc.), Super-P and Polyimide, PI were mixed at a weight ratio of 79:1:20 in N-Methyl-2-pyrrolidone, NMP (Aladdin Industrial Inc.) till fully homogeneous slurry was obtained. The Al₂O₃ slurry was cast onto Li or Cu foils. After Ar atmosphere drying at 80°C for Li foil and vacuum drying at 120°C for Cu foil during 12h, the Al₂O₃ porous layer coated electrodes were obtained and transferred in argon-filled glove box (MBRAUN, H₂O ≤ 0.1 ppm, O₂ ≤ 0.1 ppm) for further cell assembly. The 1% of SP used in the Al₂O₃ porous layer was to reduce the over-potential since the Al₂O₃ and PI are both inert to electron or ion
conduction. Once the Al\(_2\)O\(_3\) porous layer coated electrode was assembled in cell, the skin-layer was formed during the first Li deposition process.

We have compared our porous layer (Al\(_2\)O\(_3\):SP:PI = 79:1:20) to a layer only constituted of SP:PI = 80:20, in the Cu | LiFePO\(_4\) system, as shown in the Fig. S5. As we can see, the layer of SP:PI = 80:20 consume large amount of Li in the 1\(^{st}\) cycle to form SEI layer due to its high specific area, the capacity dropped from \(~150\) to 26 mAh g\(^{-1}\), with a Coulombic efficiency of only 17\%. Furthermore, after the 1\(^{st}\) cycle, the charge-discharge profiles of the layer of SP:PI = 80:20 simply behave as a graphitic anode, i.e. intercalation of Li ions in the SP material, without flat plateaus corresponding to Li metal plating/stripping as observed in case of the Al\(_2\)O\(_3\) porous layer (Al\(_2\)O\(_3\):SP:PI = 79:1:20). Thus, we think that the layer of SP:PI = 80:20 acts more likely as a graphitic anode, but not a protecting layer of Li metal.

**Electrochemistry**

Cycling tests were performed using a battery testing system (LandCT2001 from LAND electronics Co., Ltd.). Cu electrodes were used as working electrodes. Li foils and LiFePO\(_4\) cathodes were used as counter electrodes. For LiFePO\(_4\) cathodes, LiFePO\(_4\) slurry was prepared by mixing LiFePO\(_4\) (STL Energy Technology Co., Ltd.), super-P and Poly(Vinylidene Fluoride), PVdF at a weight ratio of 8:1:1 in NMP. The obtained homogeneous slurry was cast onto Al foils and dried under vacuum at 120\(^{\circ}\)C for 12h. The area capacity loading of LiFePO\(_4\) was 0.5 mAh cm\(^{-2}\). Coin cells CR2032 were used for cell assembly, with Celgard separator film (diameter: 18 mm; thickness: 20 \(\mu\)m) in which an electrolyte amount of 70 \(\mu\)L was deposed. The electrolytes consisted of a commercial
electrolyte (1M LiPF$_6$ in 1:1 ethylene carbonate, EC and dimethyl carbonate, DMC, Guotai-Huarong New Chemical Materials Co., Ltd.) with/without additives.

The voltage profiles and Electrochemical Impedance Spectra, EIS of the Li$\mid$Li symmetrical cells were measured using a potentiostat/galvanostat 1470E equipped with a frequency response analyzer, FRA 1455A from Solartron. For each symmetrical cell, an alternative current density of 2.125 mA cm$^{-2}$ was applied between the two electrodes with a period of 2h (i.e. 1h for one way, which corresponds to a Li deposition of 2.125 mAh cm$^{-2}$), then followed by an in situ EIS measurement under open-circuit condition. This routine was repeated to ensure a continuous Li deposition/stripping cycles at each Li surface. The EIS measurements were performed on the frequency range of $0.1-10^5$ Hz with a voltage perturbation of 5 mV.

Electrode characterizations

After being cycled, the cells with Cu electrodes were carefully disassembled in glove box. The Cu electrodes were rinsed with pure DMC in order to eliminate residual trace of solvents and salts, and then stored in glove box for further characterization. The microscopy analysis of the surface morphology was performed using Scanning Electron Microscopy (SEM, FEI, QUANTA 250 FEG). Magnetic Properties Measurement System (MPMS) combining Superconducting quantum interference device, SQUID - Vibrating Sample Magnetometer, VSM (Quantum Design MPMS 3 EverCool) was used to probe the magnetization of cycled Cu electrodes. All the measurements were performed at 300 K.

AFM characterizations
*In situ* Atomic Force Microscopy (AFM, Bruker Icon) experiments were conducted in an argon-filled glovebox (MBRAUN, H_2O ≤ 0.1 ppm, O_2 ≤ 0.1 ppm) at room temperature. Highly ordered pyrolytic graphite, HOPG (Bruker Corporation, ZYB Grade, 12×12×2 mm) was cleaved with adhesive tape to obtain a flat basal plane. The Li-HOPG cell was composed of HOPG substrate as working electrode and Li wire as counter and reference electrodes. Electrolyte solution used was 1 M LiPF_6 dissolved in EC/DMC or FEC/DMC or VC/DMC or HDI/DMC, with volume ratio of 1:1 (Shanshan Corporation). In order to form SEI layer on HOPG, the Li-HOPG cells were cycled under Cyclic Voltammetry (CV) mode at a scanning rate of 0.5 mV s\(^{-1}\) between 3 and 0 V. AFM topography was collected in ScanAsyst mode using nitride coated silicon probes (tip model: SCANNASYST-FLUID with k = 0.7 N m\(^{-1}\), Bruker Corporation). Contact mode was applied to scratch the surface using the same probe.

**Supplementary Figures**

![SEM images of the Cu electrode only containing the porous layer after the 50\(^{th}\) cycle.](image-url)
Fig. S2 Coulombic efficiencies of Cu│Li cells, for the Cu electrodes containing porous layers with different additives. (a) Voltage profiles of the 2$^{\text{nd}}$ cycle. (b) Coulombic efficiencies with current density of 0.5 mA cm$^2$. The amount of Li plated in each cycle is 1 mAh cm$^2$. 
**Fig. S3** Isothermal curves of magnetic moment $M(H)$ of the protected Cu electrodes (with porous and skin-layers) at different states (discharged, charged at 1, 2, 3 and 4 mAh), and the Li foil of 10 mAh.
Fig. S4 Galvanostatic charge-discharge profiles of Cu│LiFePO₄ cells for (a) Bare system and (b) Protected system coupling the porous layer and FEC in electrolyte. (c) The Coulombic efficiency from the 1ˢᵗ to 5₀ˢᵗ cycles.
Fig. S5 Galvanostatic charge-discharge profiles of Cu | LiFePO₄ cells for the comparison of the porous layer (Al₂O₃:SP:PI = 79:1:20) and a layer only constituted of SP:PI = 80:20.

Supplementary Tables

<table>
<thead>
<tr>
<th>Chemical components</th>
<th>Li</th>
<th>Li₂CO₃</th>
<th>LiOH</th>
<th>LiF</th>
<th>Cu</th>
<th>Al₂O₃</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic susceptibility (10⁻⁶ cm³ mol⁻¹)</td>
<td>+14.2</td>
<td>-27</td>
<td>-12.3</td>
<td>-10.1</td>
<td>-5.46</td>
<td>-37</td>
<td>-5.9</td>
</tr>
</tbody>
</table>

Tab. S1 Magnetic susceptibility of the present chemical components in the protected Cu electrodes.¹,²
Physical principle of the MPMS measurements

The detection of Li metal is technically and physically difficult with the optical analysis such as XPS, Raman or Infrared. Thus, inspired by the different magnetic properties of ionic and metal states of Li, we have proposed for the first time the use of Magnetic Properties Measurement System, MPMS to probe the magnetization of Li metal in the porous space of the protected electrodes. As shown with the Fig. S3, the linearity of the obtained M(H) curves first indicates the absence of ferromagnetic material in our sample, and the derivation of each curvy is directly related to the effective magnetic moment $\mu_{eff}$ of the sample which is equal to the sum of all the present elementary magnetic moments $\mu_i$ with their atomic concentration $\alpha_i$:

$$\mu_{eff} = \sum_i \alpha_i \mu_i$$

As given in the Tab. S1, only the Li metal is paramagnetic among the present materials in the electrodes. Thus, the higher the Li metal quantity is, the more the slope of the M(H) is increased. This kind of measurements can be considered as a useful method to quantify the Li metal quantity confined in an isolated space.