Electronic Supplementary Information for

# Direct Imaging of Dynamic Heterogeneous Lithium–Gold Interaction at the Electrochemical Interface during the Charging/Discharging Processes

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#### Supplementary experimental procedures

#### Experimental electrochemical cell system preparation

Cover glass substrates were ultrasonically cleaned in deionized water (Shanghai Titan Technology) and isopropanol (99.7%, Dongjiang) to remove surface attachments. Metallic thin films including 10 nm-thick Cu, 14 nm-thick Au, 2 nm-thick Cr, and 20 nm-thick Ag were deposited on the cover glass substrates by electron-beam evaporation (HHV, TF500) for *operando* optical observation.

Cu wire ( $\Phi$  0.5 mm, Lige Science) was inserted into the lateral perforated area of a polymethyl methacrylate lid using silicone sealant (121, Wacker Chemie AG) and preserved for 12 h. Then, grease (Type H, Apiezon) was applied to the edge and pore of the lid to prevent air entry. The operations described henceforth were all performed in an Ar-filled glove box (O<sub>2</sub> and H<sub>2</sub>O < 1.0 ppm, Mikrouna). Li foil (99.9%, CEL) was folded, and the Cu wire was clipped. The thin films were covered with a perforated 100-µm-thick polydimethylsiloxane (PDMS) membrane (pore diameter, 3 mm) to define the area of electrode. 1M LiPF<sub>6</sub> electrolyte in a 1 : 1 vol% mixture of EC and DEC with 5% FEC (Capchem) with a volume of 7 µL was used to fill the pores in the PDMS layer.

#### **Opto-electrochemical analysis**

The *operando* optical investigation was performed using an optical microscope (ECLIPSE Ti2-E, Nikon) with an oil immersion objective (CFI Apochromat TIRF 60XC, 1.49 numerical aperture [NA]), an sCMOS camera (Zyla 4.2, Andor), a light-emitting diode for trans-illumination, and a xenon lamp for epi-illumination. The exposure time is 50ms with an Andor Zyla sCMOS Camera in 16-bit recording mode. For the recording of rapidly evolving processes (fast charging/discharging), the frame rate could be 20 Hz. However, for a slower process, e.g. a recording lasting 6min or 30 min, the frame rate was set as 1 Hz with an exposure time of 50 ms. The size of ROI is usually 512 pixel x 512 pixel or 55.47 µm x 55.47 µm. Electrochemical curves were acquired by galvanostatic charge–discharge cycling using an electrochemical workstation (V46840, Ivium). The metallic films deposited onto the cover glass substrates were used as counter and reference electrodes, and Li foil (99.9%, CEL) was used as both working electrodes.

#### **Image analysis**

Normalized absorbance: The determination of normalized absorbance involves defining the transmitted intensity of the initial frame as  $I_0$ . Transmittance (T) is subsequently normalized by establishing the ratio between the transmitted intensity ( $I_{trans}$ ) and  $I_0$  (formula SI). The absorbance of the sample is then calculated in accordance with Lambert-Beer's law (formula SII).

$$T = \frac{I_{trans}}{I_0}$$
(SI)

$$A = \log\left(\frac{1}{T}\right) \tag{SII}$$

Temporal-color code: In the context of temporal color-coded alloying paths, the recorded data underwent a process of intensity inversion and differentiation. This process entailed subtracting earlier frames from later frames, followed by conversion into temporal color-coded images using ImageJ. The identification of Li nucleation sites merging with temporal color-coded images was achieved through analysis of selected intensity-inverted frames that depicted distinct and recognizable disk-shaped Li metal particles. Thunderstorm plugin and Create Selection functions in ImageJ facilitated this analysis.

Colocalization: Pearson's r values for alloyed or unalloyed regions during the initial and intermediate stages of alloying, as well as Li nucleation sites, were computed using the JACoP plugin in ImageJ. The selected frame underwent intensity inversion and conversion to an 8-bit type. Subsequently, it was subtracted from an identical frame that had undergone the same operations and had been filtered by Gaussian Blur (sigma: 50.00 radius) in ImageJ to eliminate background. Notably, in the case of the Li–Au system, intensity reversion was omitted for regions brighter than the background during the analysis of unalloyed regions in the intermediate stages of the first step and alloyed regions in the intermediate stages of the first step and alloyed regions in the intermediate, or contiguous frames were aggregated to sum slices. Following these operations, the default Threshold value was typically employed to comprehensively encompass the region of interest for image processing using the JACoP plugin.

Li metal nuclei count and size: The selected frame underwent intensity inversion and background subtraction using an appropriate rolling ball radius. Subsequent to a threshold operation with a suitable value, Li metal nuclei were quantified utilizing the "Analyze Particles" function in ImageJ. The diameter of these nuclei was determined through multiple manual measurements.

#### Ex situ characterization

All *ex situ* characterization experiments were performed after disassembling the tested cells in an Ar-filled glove box and thoroughly washing the electrodes with dimethyl carbonate (Aldrich).

The morphologies of the Li–Au alloy and Li metal after charge/discharge cycling were examined by SEM (Nova NanoSem 450, FEI) and HIM (ORION NanoFab, Zeiss).

## Coin cell preparation and cycling performance tests

Coin cells (2025, Canrd) were assembled in an Ar-filled glovebox (O<sub>2</sub> and H<sub>2</sub>O < 0.01 ppm, Mikrouna). For the cycling performance tests, Cu foil (20  $\mu$ m, Lige) was soaked in HCl (1 M) to remove oxides and then used as a substrate to directly deposit 20 nm-thick Au thin films by electron-beam evaporation. A separator ( $\Phi$ : 19 mm, h: 12  $\mu$ m; Canrd) was inserted between the negative electrode (the Cu foil [ $\Phi$ : 14 mm] with the Au film) and the positive electrode (Li foil [ $\Phi$ : 14 mm]). Elastomeric and flap-type metal gaskets near to the negative electrode were integrated with the electrodes and separator inside the coin-type cells. The cells were filled with LiPF<sub>6</sub> electrolyte (1.0 M in 1:1 vol% EC:DEC with 5.0% FEC, 100  $\mu$ L; Capchem). The cells were tested by galvanostatic charge–discharge cycling at 0.5 mA cm<sup>-2</sup> using an NEWARE system. The cycling program involved discharging to 0.5 mAh·cm<sup>-2</sup> (1 h) and charging to 0.5 V versus Li/Li+, with a resting period of 5 min.

### **Supplementary figures**



Fig. S1 Cycling performance of lithium metal cells with different electrodes. The different colors represent distinct

electrodes: Cu foil (red), a 20 nm-thick Au film plated on the Cu foil by electron-beam evaporation (denoted as Au/Cu, blue), a 20 nm-thick Au film plated on the Ni foil (denoted as Au/Ni, yellow), a 20 nm-thick Au and a 20 nm-thick Ni film plated on the Cu foil (denoted as Au/Ni/Cu, green). The electrolyte is LiPF6 (1.0 M) in a 1 : 1 vol% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 5% fluoroethylene carbonate (FEC). The enlarged version of the black boxed region shows the significant improvement in the CE of the cell with the Au film over the first few cycles and the subsequent decay.



Fig. S2 In situ UV-vis spectrum of gold film in epi mode by Xe lamp. The different colors represent distinct stages during electrochemical deposition (gray, pristine; black, SEI formation; blue, the first alloying step; magenta, the second alloying step; and green, Li metal deposition).



Fig. S3 Li electrochemical deposition on Cu film. A 100-s-long montage (20-s interval) of images obtained via transmode recording of lithium electrodeposition on a 20 nm-thick Cu film at a current density of 0.5 mA cm-2. Scale bar, 5 μm.



Fig. S4 Alloying sites in the first step under different charging rates. Images (A) acquired via trans-mode of alloying sites in the first step under different charging rates and count-rate curve (B). Scale bar, 5 μm.



Fig. S5 Li–Au alloying and lithium deposition processes. Corresponding intensity versus deposition time curve of different regions (blue, background; red, Li particle) during Li metal electrochemical deposition at a current density of 0.5 mA cm<sup>-2</sup>. Scale bar, 5 μm.



Fig. S6 Corresponding intensity versus deposition time curve of Li deposition on Au in epi mode. The current density is 0.5 mA cm<sup>-2</sup>. The curve in pink region corresponds stage of lithium metal deposition.



Fig. S7 Montages of images obtained via trans-mode recording of four Li deposition stages on Au with a thickness of 28 nm at a current density of 0.5 mA cm<sup>-2</sup>. The montages from top to bottom are SEI formation (t= 1-6s, 1-s interval, SEI for short), the first alloying step (t= 8-83s, 15-s interval, Step 1 for short), the second alloying step (t= 84-144s, 12-s interval, Step 2 for short), and Li metal deposition (t= 145-181s, 7-s interval, Li metal for short), respectively. The montages of each row were normalized according to their intensity range. The reading order of all montages is from left to right. Scale bar, 5 μm.



Fig. S8 Normalized absorbance versus time curve during the electrochemical alloying and deposition.



Fig. S9 Images (A) acquired via trans-mode at earlier (left) and later (right) stage and normalized absorbance versus time curves (B) of six selected regions in the first alloying step. The regions alloyed initially and finally were denoted as Label 1-3 and Label 4-6, respectively. Scale bar, 5 µm.



Fig. S10 Images (A) acquired via trans-mode at earlier (left) and later (right) stage and normalized absorbance versus time curves (B) of six selected regions in the second alloying step. The regions alloyed initially and finally were denoted as Label 1-3 and Label 4-6, respectively. Scale bar, 5 µm.



Fig. S11 Quantitative analysis of Li metal under different charging rates. Images (A) acquired via trans-mode under different charging rates of 0.2, 5, 20, 30, and 50C, respectively. Count (B) and diameter (C) of Li metal versus rate curve. Scale bar, 5 µm.



Fig. S12 Temporal color-coded image of alloying steps under different charging rates. These charging rates are 0.2, 5,
20, 30, and 50C, respectively. The complementarity of the two alloying steps was observed. Scale bar, 5 μm.



Fig. S13 Temporal color-coded images (top) of the first alloying step merged with Li nucleation sites and their intensity-inverted versions (bottom) on three samples with similar results. The corresponding alloying time of the three samples is 38s, 31s and 33s, respectively. Scale bar, 5 μm.



Fig. S14 Temporal color-coded images of the first alloying step merged with Li nucleation sites under different charging rates (Scale bar, 5 μm)



Fig. S15 Pearson's r values for the alloyed or unalloyed regions in two alloying steps and the Li nucleation sites under different charging rates. The different x-axis labels—(i) S1m&S2m, (ii) S1s&Li, (iii) S1m&Li, (iv) S2s&Li, and (v) S2m&Li—represent the following channels: (i) unalloyed regions in the middle stages of the first step, and alloyed regions in the middle stages of the second step; (ii) alloying sites in the first step and Li nucleation sites; (iii) alloyed regions in the middle stages of the first step and Li nucleation sites; (iv) alloying sites in the second step and Li nucleation sites; and (v) alloyed regions in the middle stages of the second step and Li nucleation sites; and (v) alloyed regions in the middle stages of the second step and Li nucleation sites; The different colors represent distinct rates (purple, 0.2C; blue, 1C; and orange, 5C). The values were calculated using a colocalization algorithm.



**Fig. S16** The montages (A) of images acquired via trans-mode recording of the selected five single dendrites during Li metal dissolution and the pores' size versus time curves (B), related to Fig. 3C. Scale bar, 1 µm.



Fig. S17 The distributions of the size of dendrites (A) related to Fig. 1B during initial stage of Li metal deposition and pores (B) related to Fig. 3A during final stage of Li metal dissolution.



Fig. S18 Galvanostatic curve of Ag film during alloying with Li at a current density of 0.5 mA/cm<sup>-2</sup>, related to Fig. 5B. The time values were converted into the Li content in the Li–Ag alloy.



Fig. S19 Epi-mode images of the Ag film surface exhibiting six states during three cycles, related to Fig. 5D. The electrochemical deposition and dissolution are denoted as De and Di, respectively. De1\*–De3\* and Di1\*–Di3\* represent the end of electrochemical deposition and dissolution of the three cycles, respectively. Scale bar, 5 μm.