Supporting Information

Reactivation of air-passivated lithium metal anode through halogen regulation

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Experimental section

Materials. 1,2-dimethoxyethane (DME, 99.9%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.9%), and 1,3-dioxolane (DOL, 99.9%) were procured from Dodo chem. Lithium nitrate ($LiNO_3$, 99.99%) was obtained from Sigma. Li foils (φ 14 mm, 400 µm or 50 µm) were sourced from China Energy Lithium Co., Ltd. Iodine (I_2, 99.99%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Polyvinylidene fluoride (PVDF) was purchased from Aladdin Technology Co., Ltd. The superconducting carbon black conductive agent (Super P) and $LiFePO_4$ (LFP) were acquired from the Kelude website. Carbon-coated Al foil (8 + 2 μm) was procured from Shenzhen Kejing Star Technology Co., Ltd.

Treatment of Li foils. A series of Li foils were subjected to different treatment protocols in this study. The first group, denoted as "exposed Li," remained untreated and was exposed to air for various durations. The second group, referred to as "treated Li," involved exposing Li foils to air for 10 min followed by immersion in the 0.3 M I_2 in DME treatment solution for 1 min, 3 min, and 10 min, respectively. After each immersion step, the foils were removed from the treatment solution and subjected to a drying process to eliminate surface solvents. All exposure procedures were conducted under controlled environmental conditions of 25 °C and 40% relative humidity to maintain consistency and enable meaningful comparisons.

Characterizations. The Li foils were exposed to air for 10 min, both the original untreated ones (exposed Li) and the treated ones (treated Li), were rinsed and dried in a solution of 1,2-dimethoxyethane (DME). The scanning electron microscope (SEM) and Energy dispersive X-ray spectroscopy (EDX) were carried out with field-emission NANO SEM430. And the X-ray photoelectron spectroscopy (XPS) system with the model Thermo Fisher Scientific K-Alpha. These instruments were used to obtain information about the surface morphology and surface composition of the Li foils. The exposed Li and the treated Li were characterized using the X-ray diffraction (XRD) instrument with the model MiniFlex600-C. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is used to detect the surface of the treated Li. The instrument model used is ION-TOF TOF.SIMS5 and the sputtering time is 800 seconds.

Electrochemical Tests. Testing in this study, the electrochemical performance testing includes Li-Li symmetric cell testing, Li-LFP cell testing, Tafel curve testing, and electrochemical impedance spectroscopy (EIS) testing. For the Tafel curve test, we select 0.1 V to 0.15 V (or -0.1 V to -0.15 V) as the tangent of the Tafel region, and the current density corresponding to the intersection of the zero overpotential line is the exchange current density. All CR2032 coin cells were assembled inside a glovebox (H_2O< 0.1 ppm, O_2< 0.1 ppm) using 1 M LiTFSI in DOL: DME (1: 1, v/v) with 1 wt % $LiNO_3$ as the electrolytes. For Li-LFP cells, a 40 µL volume of electrolyte was used, and constant current tests were performed within the voltage range of 3 V to 4.3 V. To prepare the $LiFePO_4$ cathode, a mixture of $LiFePO_4$ powder, Super P, and PVDF was made with a weight ratio of 8:1:1, and then this slurry was coated onto a carbon-coated Al foil. After drying overnight at 60 °C under vacuum, the final loading of the $LiFePO_4$ cathode was approximately 1.3 mg cm^{-2}. For Li-Li cells, a 50 µL volume of electrolyte was used, and the cells were charged and discharged at at different current densities and capacities. The Tafel curve testing and electrochemical impedance spectroscopy (EIS) testing of Li-Li cells were carried out using the CHI660E electrochemical workstation. The Tafel curve was measured using a scan rate of 1 mV s^{-1}, and the EIS was measured within a frequency range of 0.1 Hz to 100 kHz with a voltage amplitude of 5 mV.

Supplementary Figures

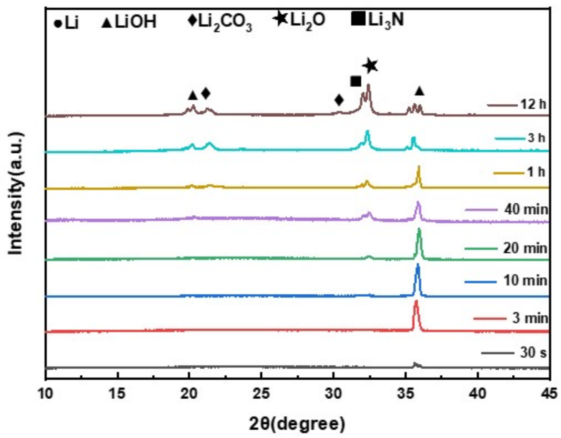

Fig. S1 XRD patterns of metallic Li exposed to air for different times.

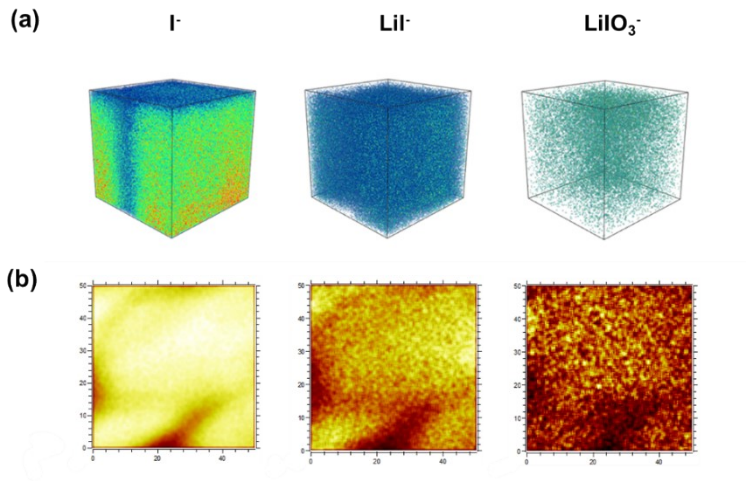

Fig. S2 (a) TOF-SIMS three-dimensional composition distribution of the treated Li. (b) Cross-profile images of TOF-SIMS depth sputtering on the surface of the treated Li.

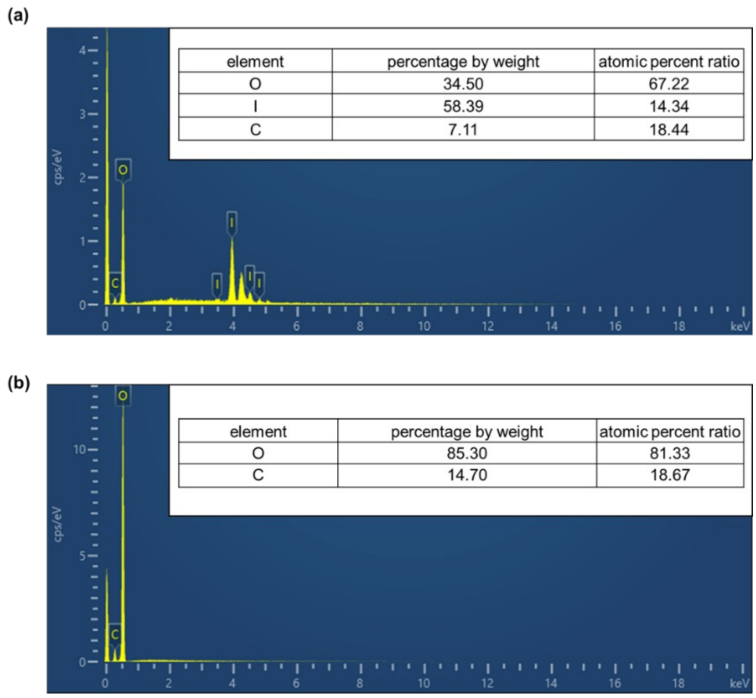

Fig. S3 The corresponding EDX element distribution of (a)treated Li and (b)exposed Li.

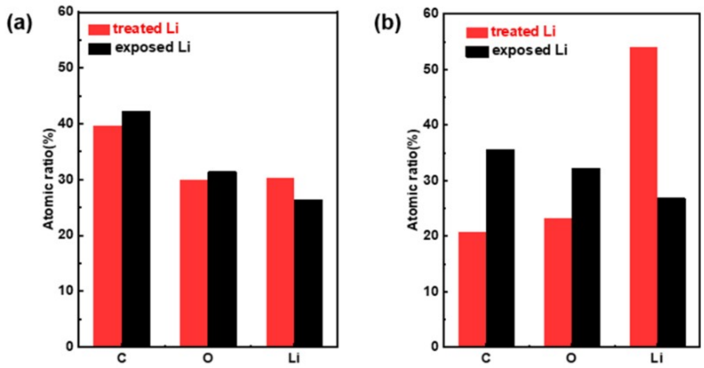

Fig. S4 XPS atomic ratio comparison in the surface of the (a) pristine treated Li and (b) cycled treated Li.

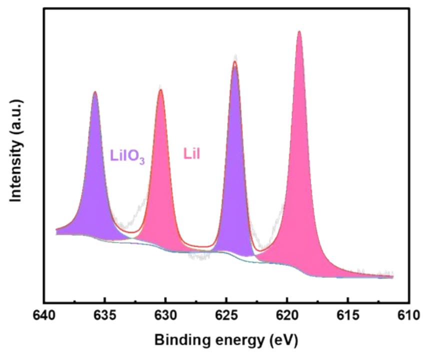

Fig. S5 XPS I 3*d* spectra of cycled treated Li.

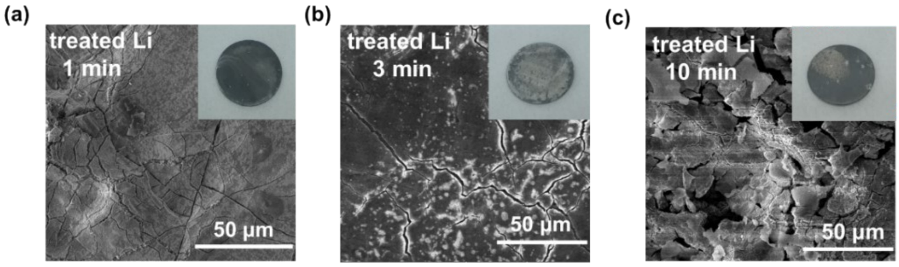

Fig. S6 Surface SEM images of the treated Li in treatment solution for (a) 1 min, (b) 3 min, and (c) 10 min.

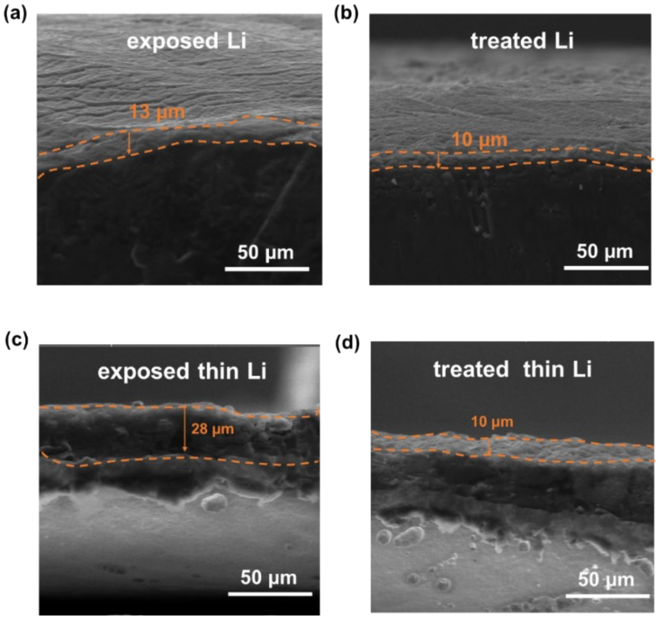

Fig. S7 Cross-sectional images of the (a) exposed Li (400 μm), (b) treated Li (400 μm), (c) exposed thin Li (50 μm) and (d) treated thin Li (50 μm).

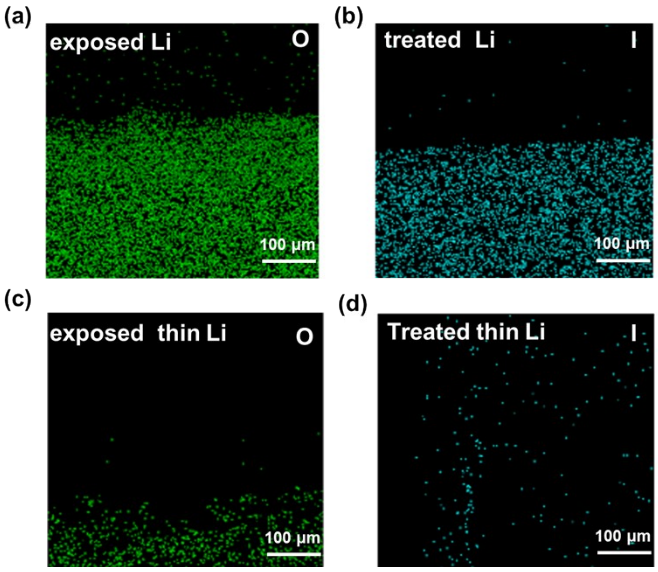

Fig. S8 The corresponding element mapping of the (a) exposed Li (400 μm), (b) treated Li (400 μm), (c) exposed thin Li (50 μm) and (d) treated thin Li (50 μm).

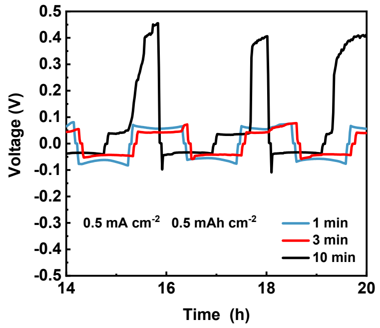

Fig. S9 Cycling performance of Li-Li cells under different soaking times.

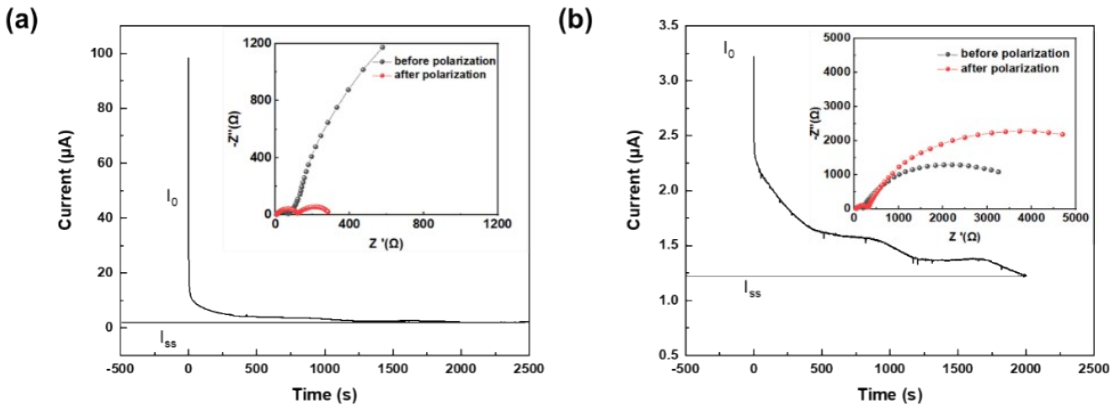

Fig. S10 The measurement of Li ions transfer number with (a)treated Li and (b)exposed Li

Note: Based on the changes in resistance and current before and after disturbance, the calculation formula is

$$t_+ = \frac{(\Delta V - R_0 I_0) I_{SS}}{(\Delta V - R_{ss} I_{ss}) I_0}$$

, with a deviation in voltage of 10 mV denoted as ΔV. In this context, R_0 and I_0 signify the initial resistance and current values prior to the perturbation, while Rss and Iss denote the resistance and current levels reached in a stable state under a 10 mV deviation in voltage (ΔV = 10 mV) [1,2].

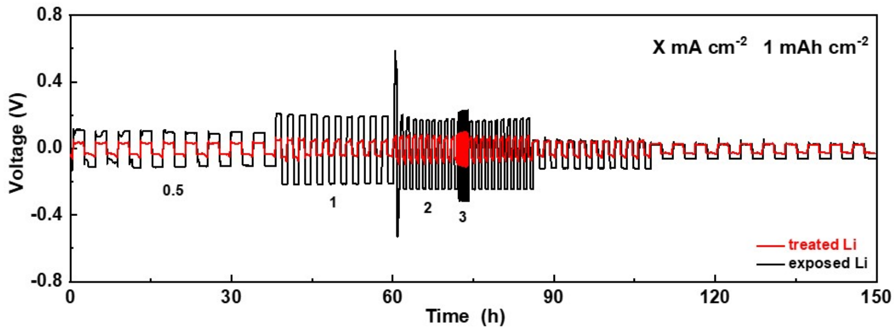

Fig. S11 Rate performance of Li-Li cells.

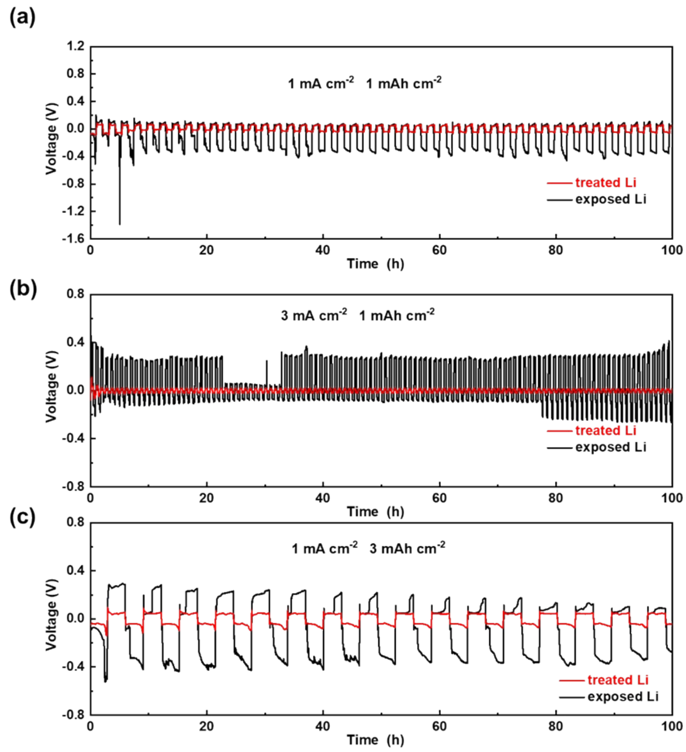

Fig. S12 Cycling performance of Li-Li cells with different test conditions. (a) 1 mA cm^{-2}, 1 mAh cm^{-2} (b) 3 mA cm^{-2}, 1 mAh cm^{-2} and (c) 1 mA cm^{-2}, 3 mAh cm^{-2}.

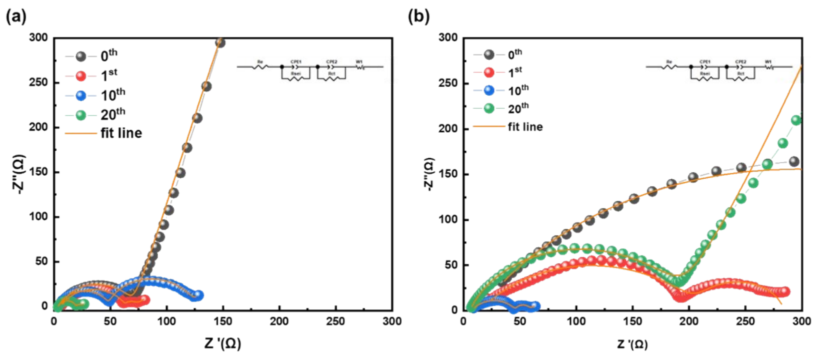

Fig. S13 EIS plots for the Li-Li symmetric cells during different cycles with the (a)treated Li and (b)exposed Li.

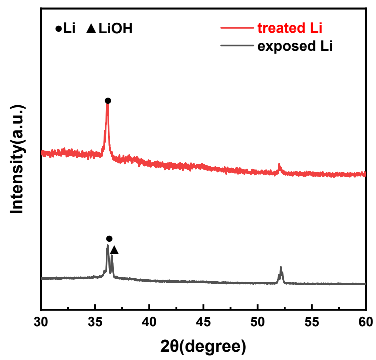

Fig. S14 XRD patterns of cycled exposed Li and treated Li.

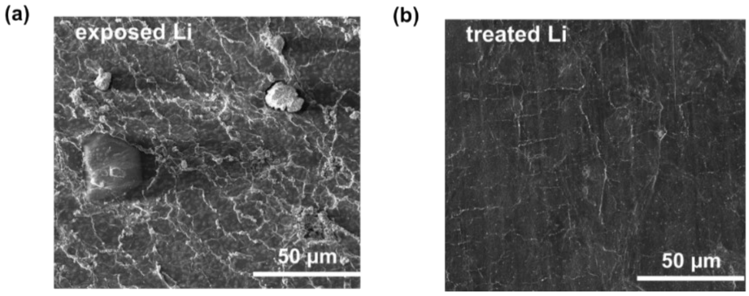

Fig. S15 Cross-sectional view SEM images of cycled (a) exposed Li foils and (b) treated Li foils in the Li-Li cells.

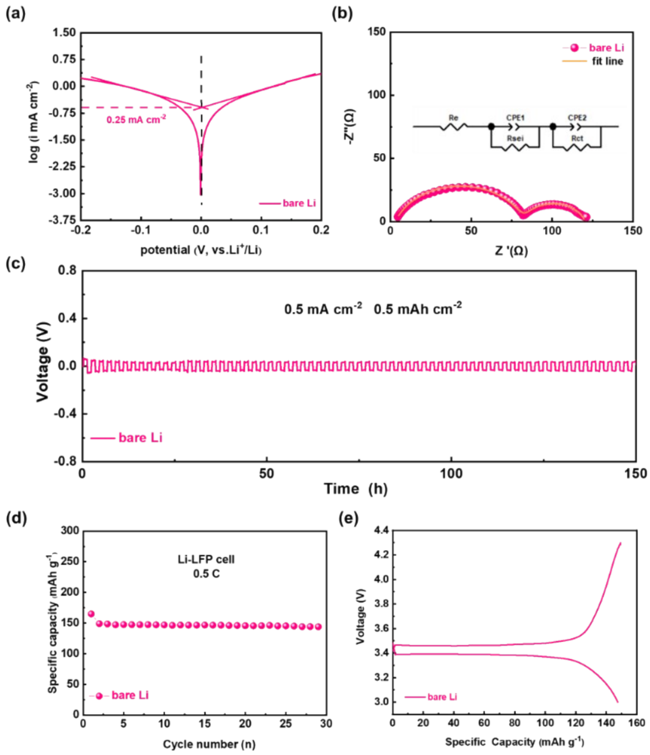

Fig. S16 (a) Tafel curves and (b) EIS plots of Li-Li cells using bare Li. Cycling performance of (c) Li-Li symmetric cells (0.5 mA cm^{-2}, 0.5 mAh cm^{-2}) and (d) Li-LFP cells (0.5 C, 1 C= 170 mA g^{-1}) using bare Li. (e) The corresponding discharge/charge curves of Li-LFP cells.

References

1 L. Suo, Y.-S. Hu, H. Li, M. Armand and L. Chen, *Nat Commun*, 2013, **4**, 1481.

2 R. Xu, Y. Xiao, R. Zhang, X. Cheng, C. Zhao, X. Zhang, C. Yan, Q. Zhang and J. Huang, *Adv. Mater.*, 2019, **31**, 1808392.