Supplementary Information (SI) for Journal of Materials Chemistry A.


**Supplementary Information**

Iodine-Driven Artificial SEI layer for High Performance Lithium Metal Batteries in $SO_2$-based Electrolyte

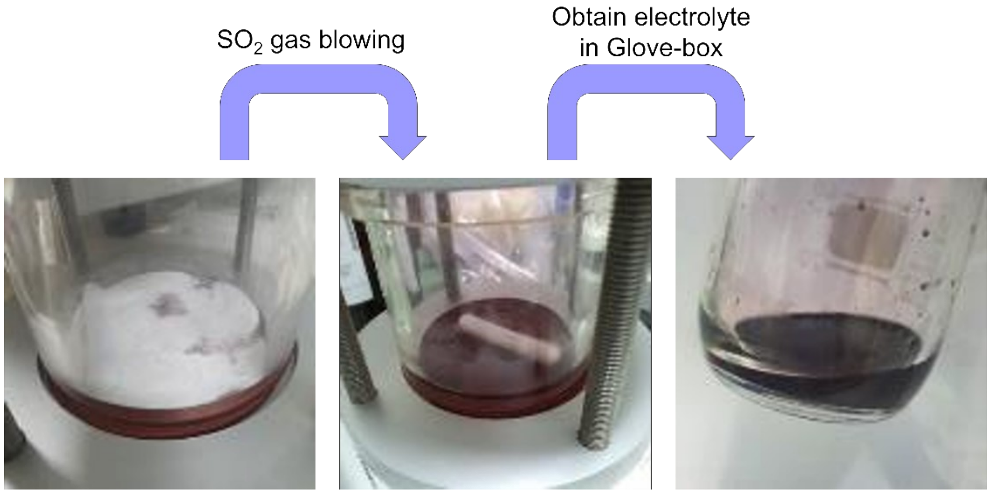


**Fig. S1.** Digital photographs of synthesis process for $I_2$-containing $LiAlCl_4$-$3SO_2$ electrolyte.

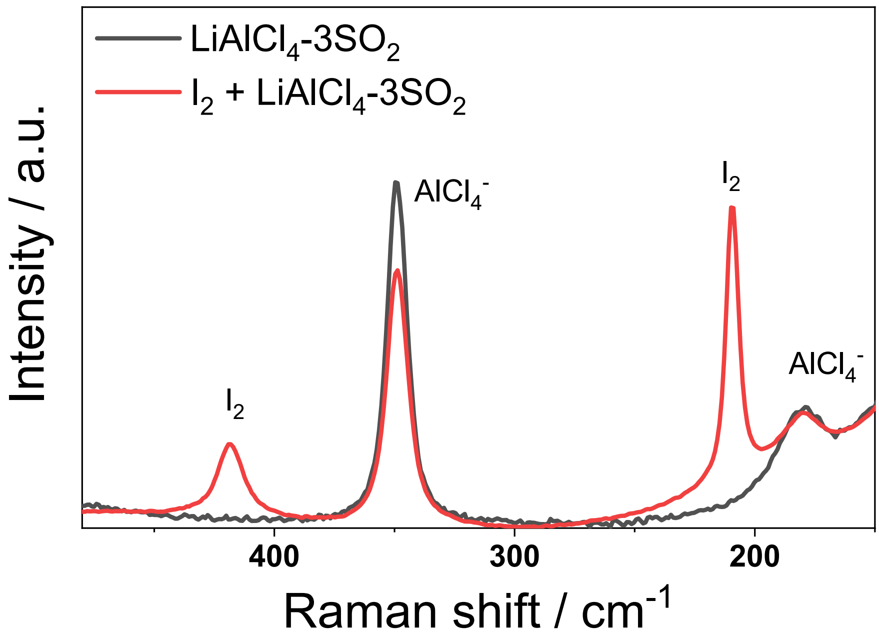


**Fig. S2.** Raman spectra of $LiAlCl_4$-$3SO_2$ and $I_2$-containing $LiAlCl_4$-$3SO_2$ electrolytes.

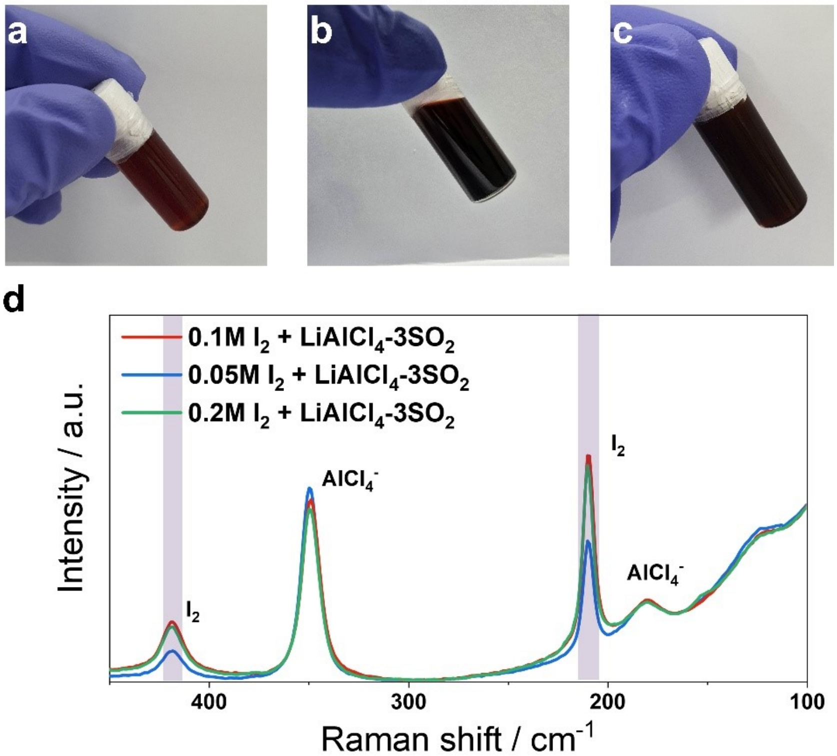


**Fig. S3.** (a–c) Comparison of digital photographs of iodine-containing $LiAlCl_4$–$3SO_2$ electrolytes with different LiI levels: (a) 0.05M (light purple), (b) 0.10M (dark wine), and (c) 0.20M (dark wine; similar color to 0.10M). (d) Normalized Raman spectra of the corresponding electrolytes.

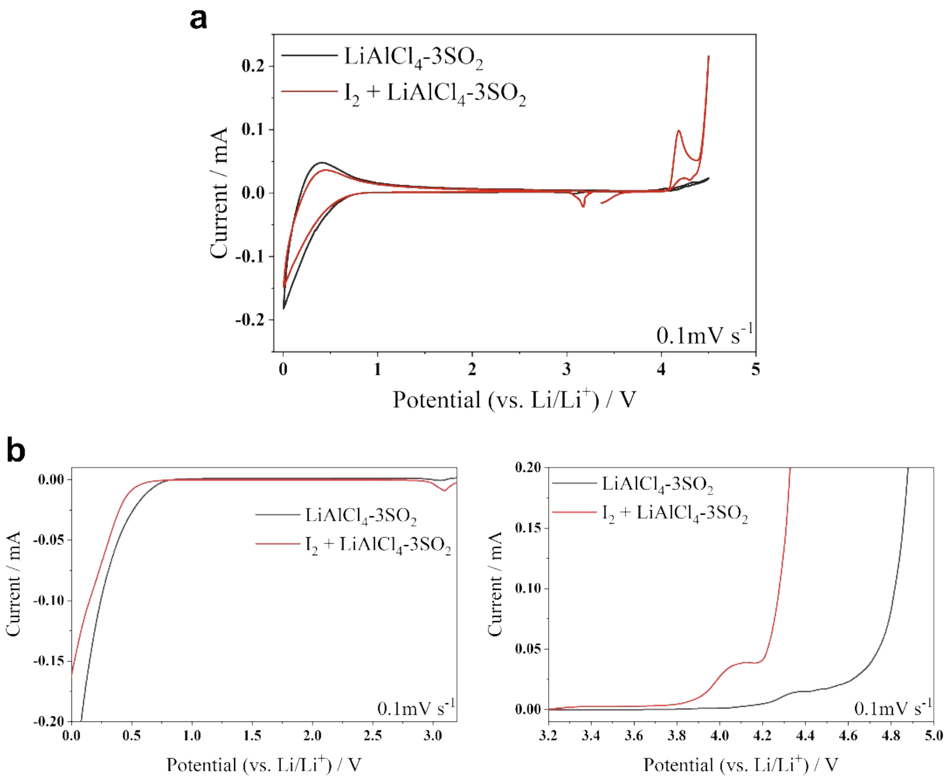


**Fig. S4.** (a) Cyclic voltammetry (CV) and (b) linear sweep voltammetry (LSV) of $LiAlCl_4$-$3SO_2$ and $I_2$-added $LiAlCl_4$-$3SO_2$ electrolytes.

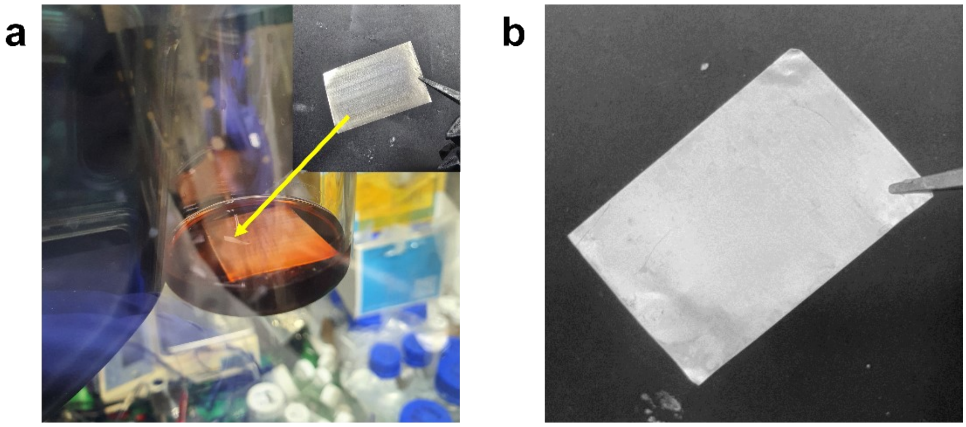


**Fig. S5.** (a) Digital photograph showing dipping process of pristine lithium metal (inset) and (b) lithium metal after the dipping process in $I_2$-containing $LiAlCl_4$-$3SO_2$.

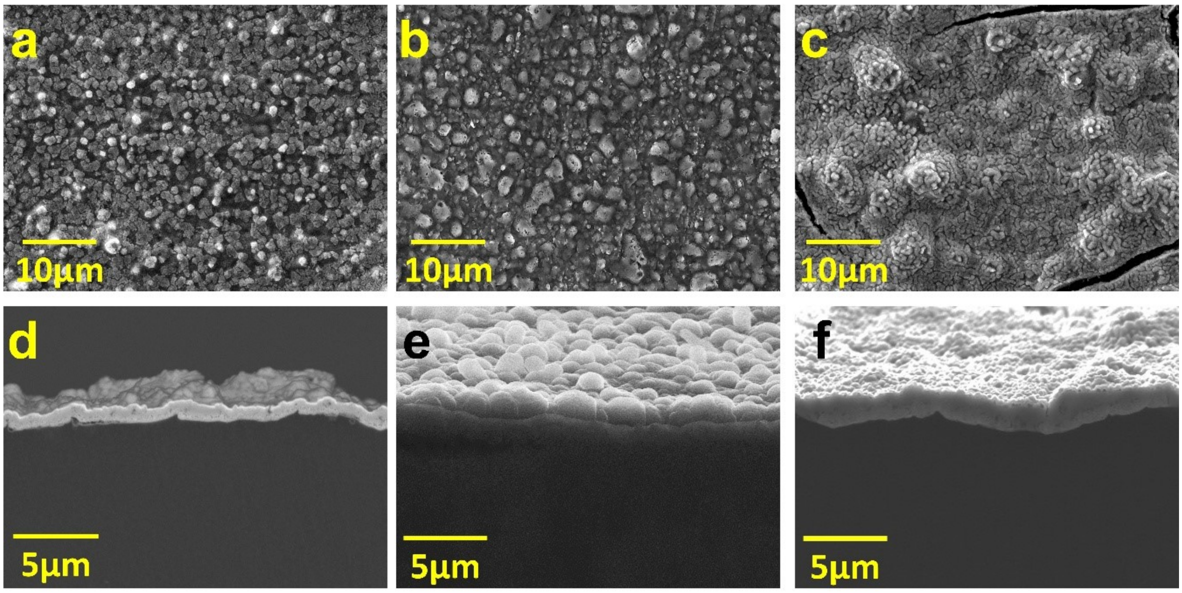


**Fig. S6.** Top-view SEM images of lithium metal after dipping in iodine-containing $LiAlCl_4$–$3SO_2$ electrolytes with different LiI levels: (a) 0.05M, (b) 0.10M, and (c) 0.20M. Cross-sectional SEM images of the corresponding dipped lithium electrodes: (d) 0.05M, (e) 0.10M, and (f) 0.20M.

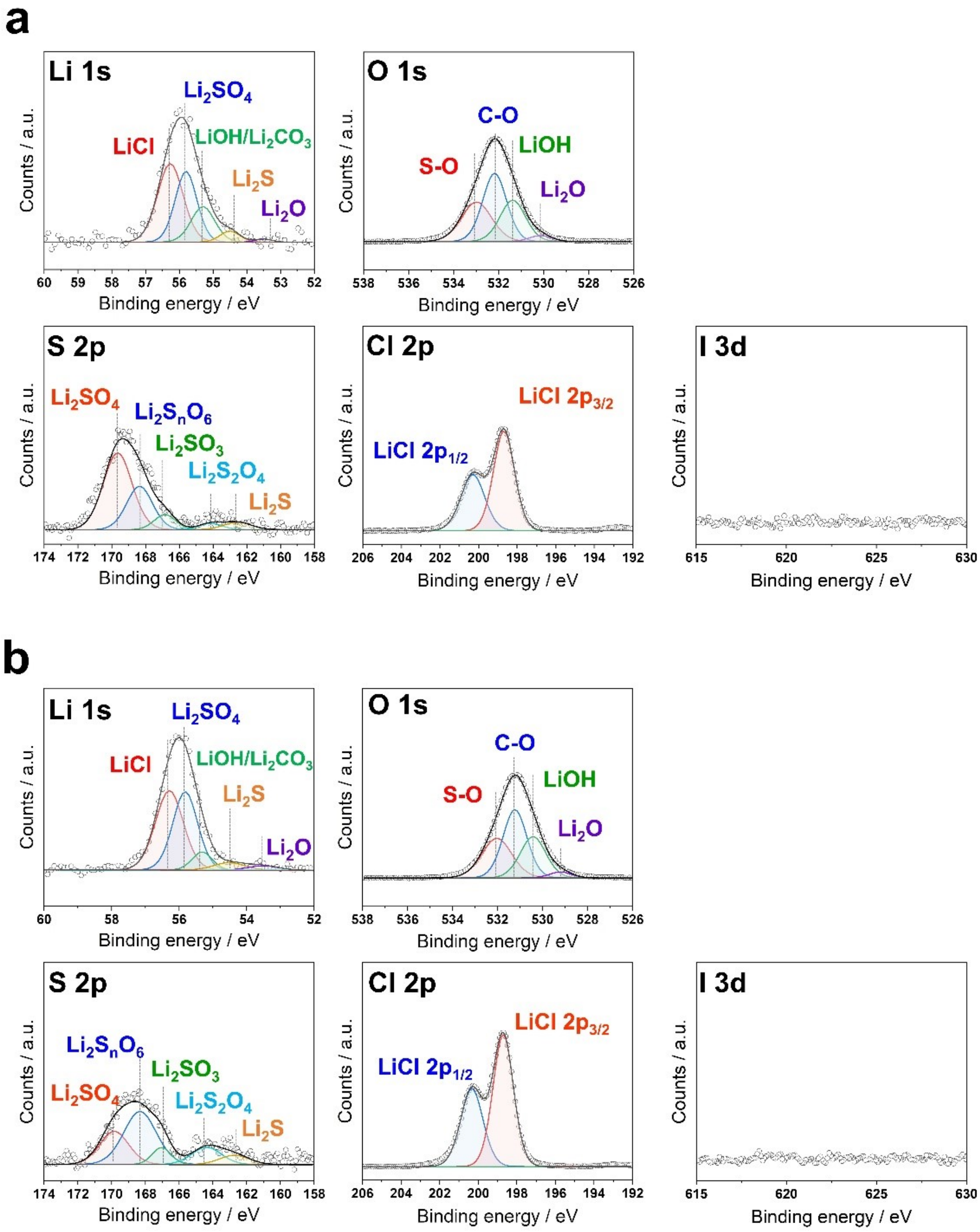


**Fig. S7.** XPS spectra (Li 1s, O 1s, S 2p, Cl 2p, and I 3d regions) of lithium electrodes after dipping in iodine-containing $LiAlCl_4$–$3SO_2$ electrolytes with different LiI levels: (a) 0.05M and (b) 0.20M.

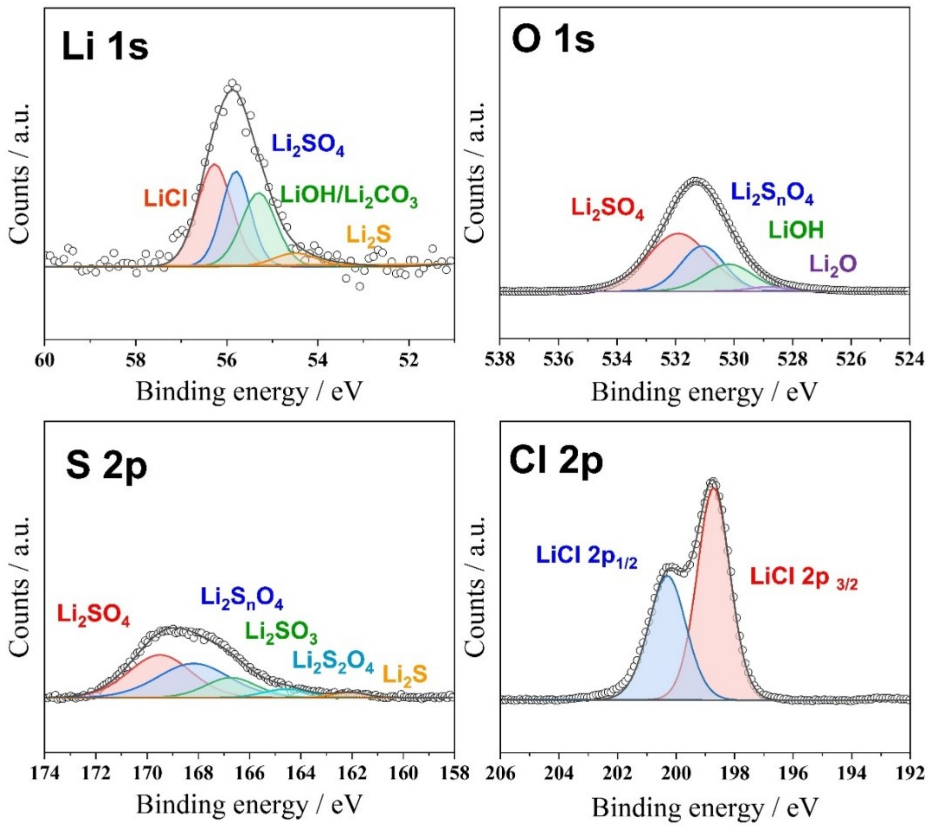


**Fig. S8.** Surface XPS spectra of Li 1s, O 1s, S 2p, and Cl 2p, at lithium metal surface after dipping with $LiAlCl_4$-$3SO_2$ electrolyte.

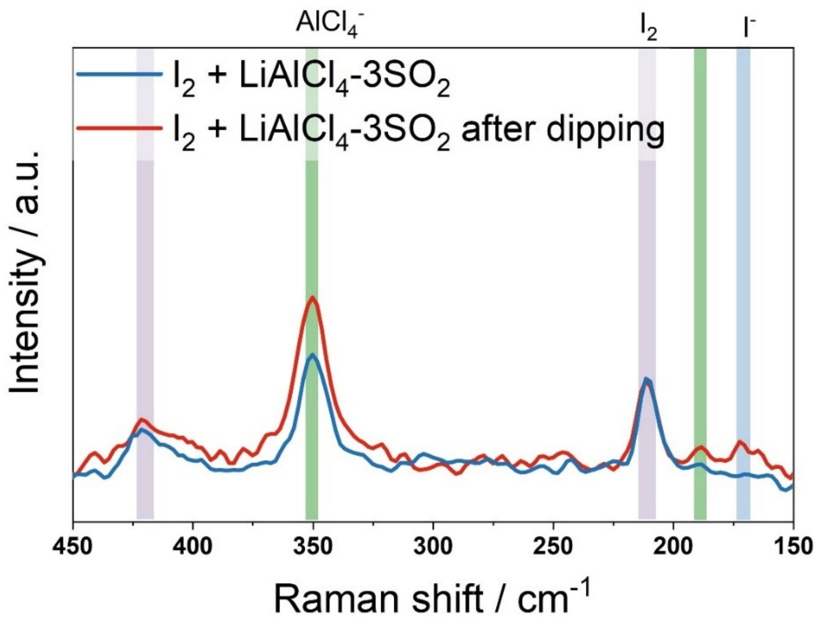


**Fig. S9.** Ex situ Raman spectra of the $I_2$–Li–$SO_2$ electrolyte before and after lithium dipping.

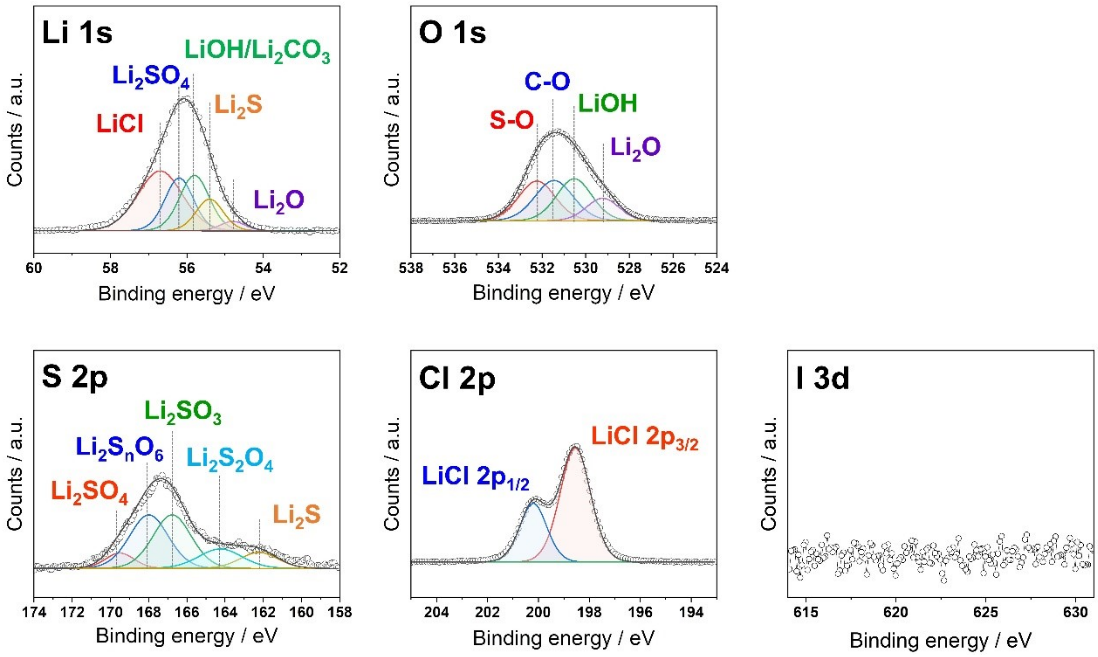


**Fig. S10.** XPS spectra of lithium metal after sequential surface treatment involving initial dipping in the pristine Li–$SO_2$ electrolyte followed by treatment in the $I_2$–Li–$SO_2$ electrolyte.

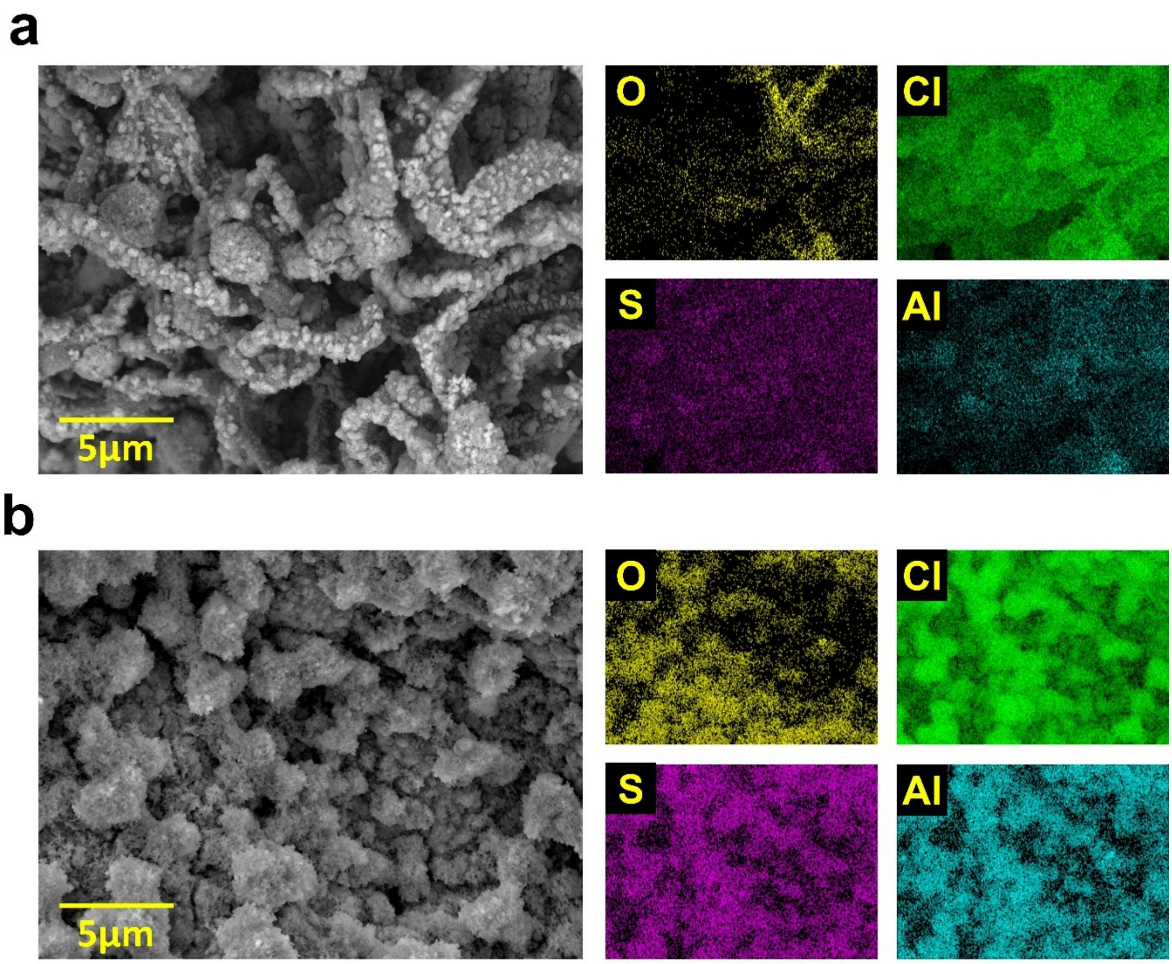


**Fig. S11.** SEM images and EDS elemental mapping of cycled lithium electrodes after Li//Li cycling at 3 mA cm$^{-2}$ and 5 mA h cm$^{-2}$ using (a) pristine lithium and (b) $I_2$-modified lithium. Corresponding EDS maps of O, S, Cl, and Al are shown to identify electrolyte-derived interphase products.

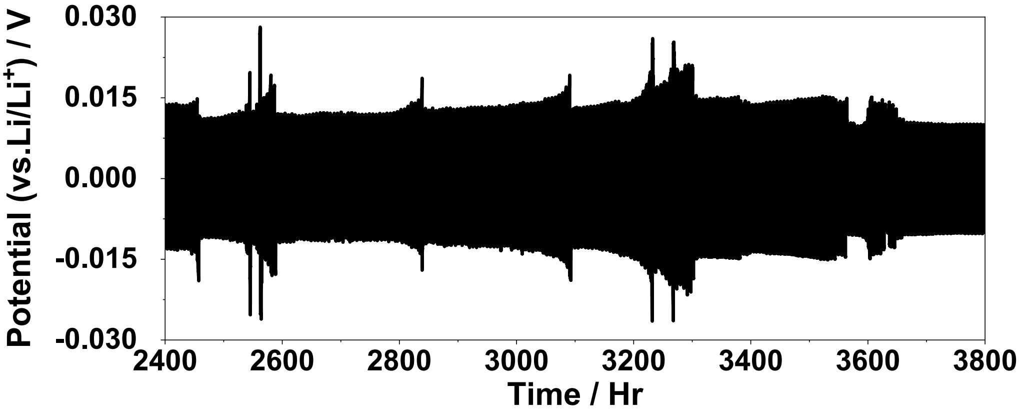


**Fig. S12.** Amplified electrochemical performance of Li//Li symmetric cells with pristine lithium electrode at current densities of 1 mA $cm^{-2}$ with areal capacity of 3 mA h $cm^{-2}$ during 400 cycles to 630 cycles.

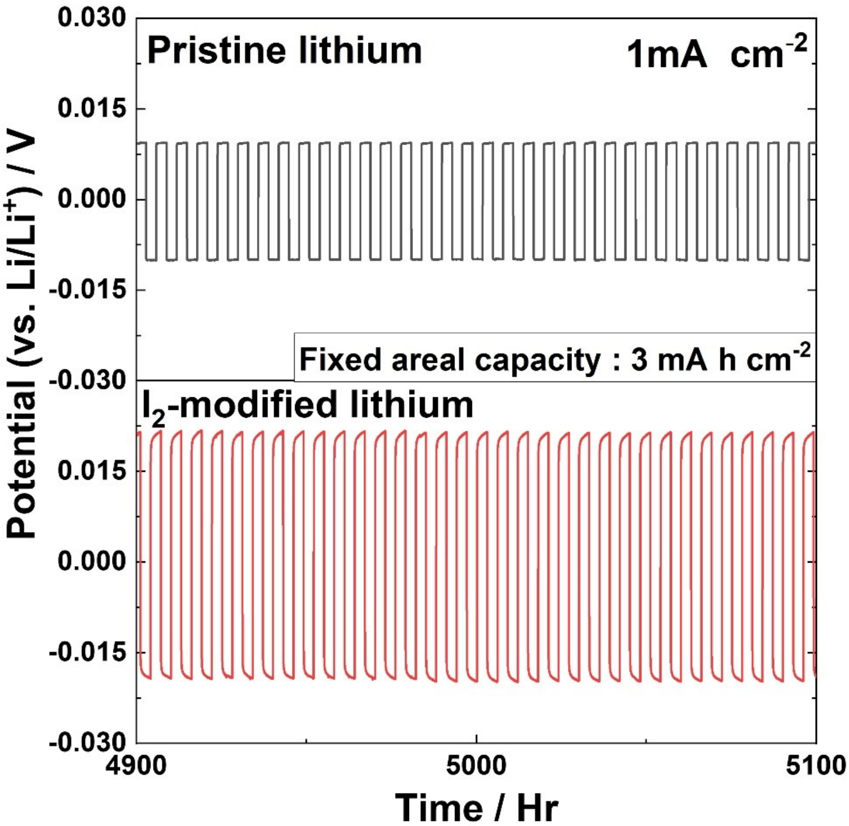


**Fig. S13.** Amplified electrochemical performance of Li//Li symmetric cells with pristine lithium electrode at current densities of 1 mA $cm^{-2}$ with areal capacity of 3 mA h $cm^{-2}$ during 400 cycles to 630 cycles.

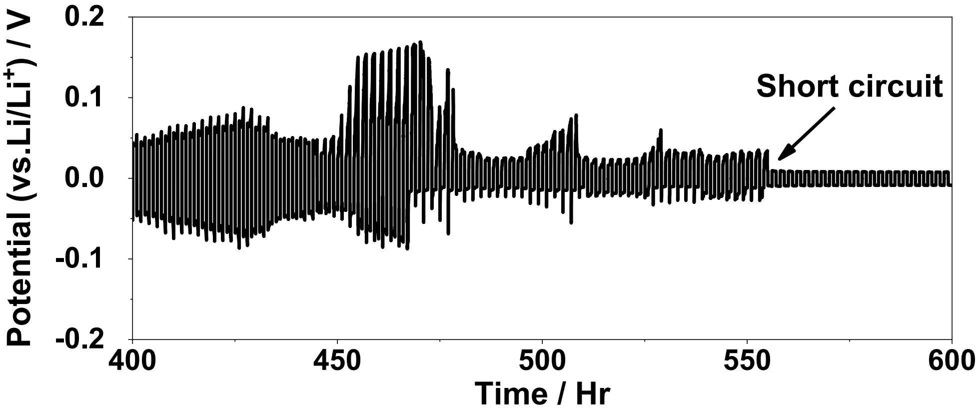


**Fig. S14.** Amplified electrochemical performance of Li//Li symmetric cells with pristine lithium electrode at current densities of 3 mA $cm^{-2}$ with areal capacity of 3 mA h $cm^{-2}$.

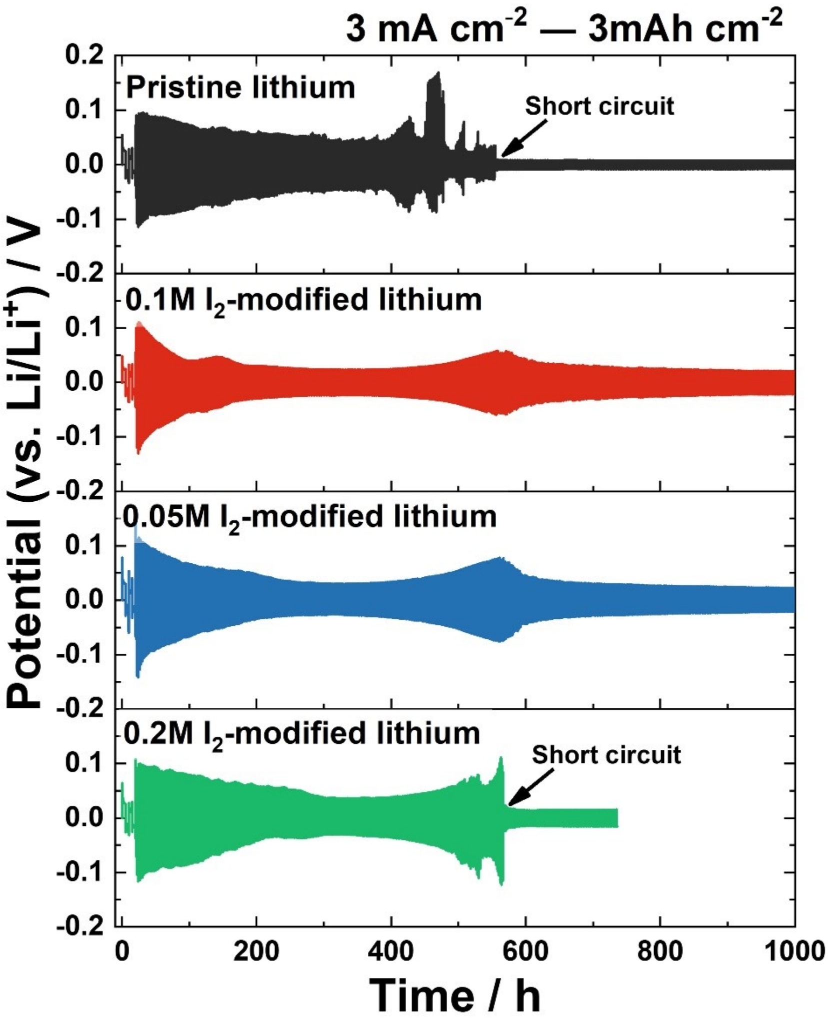


**Fig. S15.** Galvanostatic Li//Li symmetric-cell cycling profiles measured at 3 mA $cm^{-2}$ with a fixed areal capacity of 3 mA h $cm^{-2}$ for pristine lithium and modified Li electrodes using iodine-containing electrolytes with different LiI levels (0.05M, 0.10M, and 0.20M).

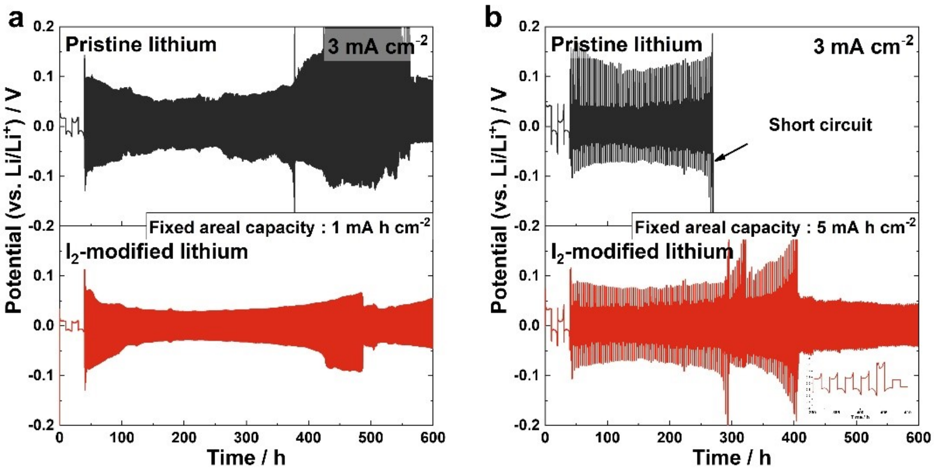


**Fig. S16.** Voltage profiles of Li symmetric cells using pristine lithium and $I_2$-modified lithium at a current density of 3 mA cm$^{-2}$ with a fixed areal capacity of (a) 1 mA h cm$^{-2}$ and (b) 5mA h cm$^{-2}$.

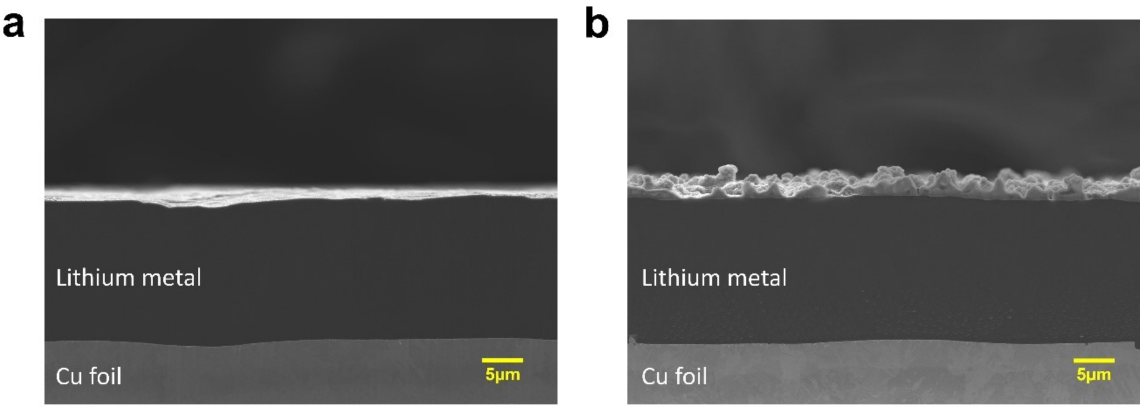


**Fig. S17.** Cross-sectional SEM images of thin lithium metal (18 μm) electrodes of (a) pristine lithium electrode and (b) $I_2$-modified lithium electrode.

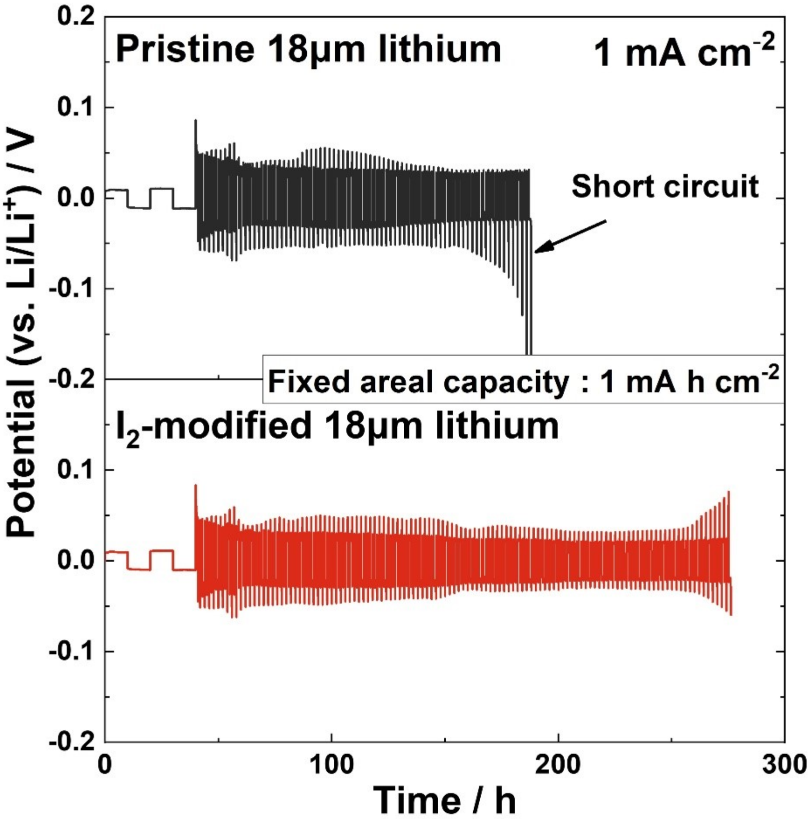


**Fig. S18.** Electrochemical performances of thin-lithium (18 μm) Li//Li symmetric cells using pristine and $I_2$-modified lithium at a current density of 1 mA $cm^{-2}$ with a fixed areal capacity of 1 mA h $cm^{-2}$.

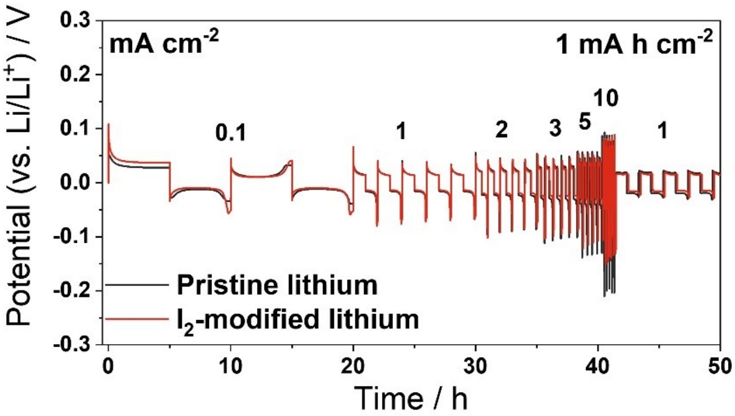


**Fig. S19.** Rate capability of Li//Li symmetric cells using pristine lithium and $I_2$-modified lithium electrodes in the $LiAlCl_4$–$3SO_2$ electrolyte. The cells were cycled at a fixed areal capacity of 1 mA h cm$^{-2}$ while the current density was sequentially increased from 0.1 to 10 mA cm$^{-2}$ and then returned to 1 mA cm$^{-2}$.

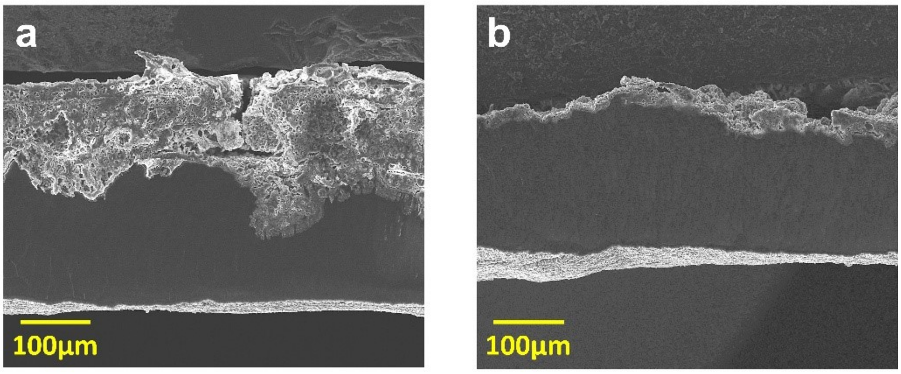


**Fig. S20.** Low-magnification cross-sectional SEM images of cycled lithium electrodes of (a) pristine lithium and (b) $I_2$-modified lithium after 50 cycles.

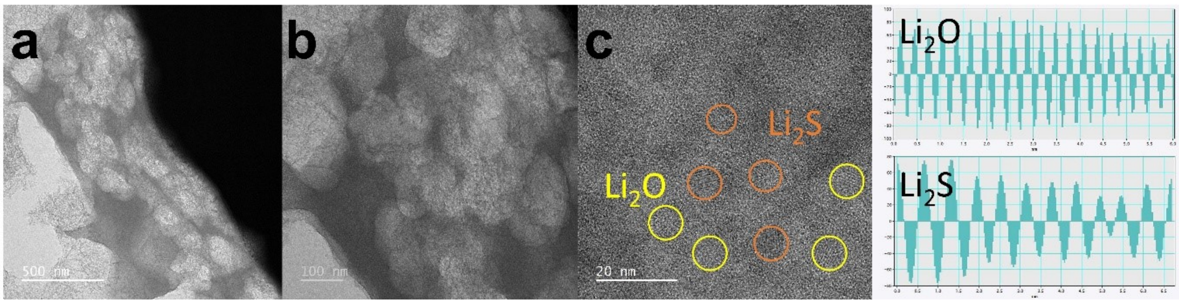


**Fig. S21.** TEM analysis of the $I_2$-modified lithium metal electrode after 2 cycles. (a, b) Low- and (c) high-magnification TEM images with Interlayer d-spacing images of $Li_2O$ and $Li_2S$, respectively.

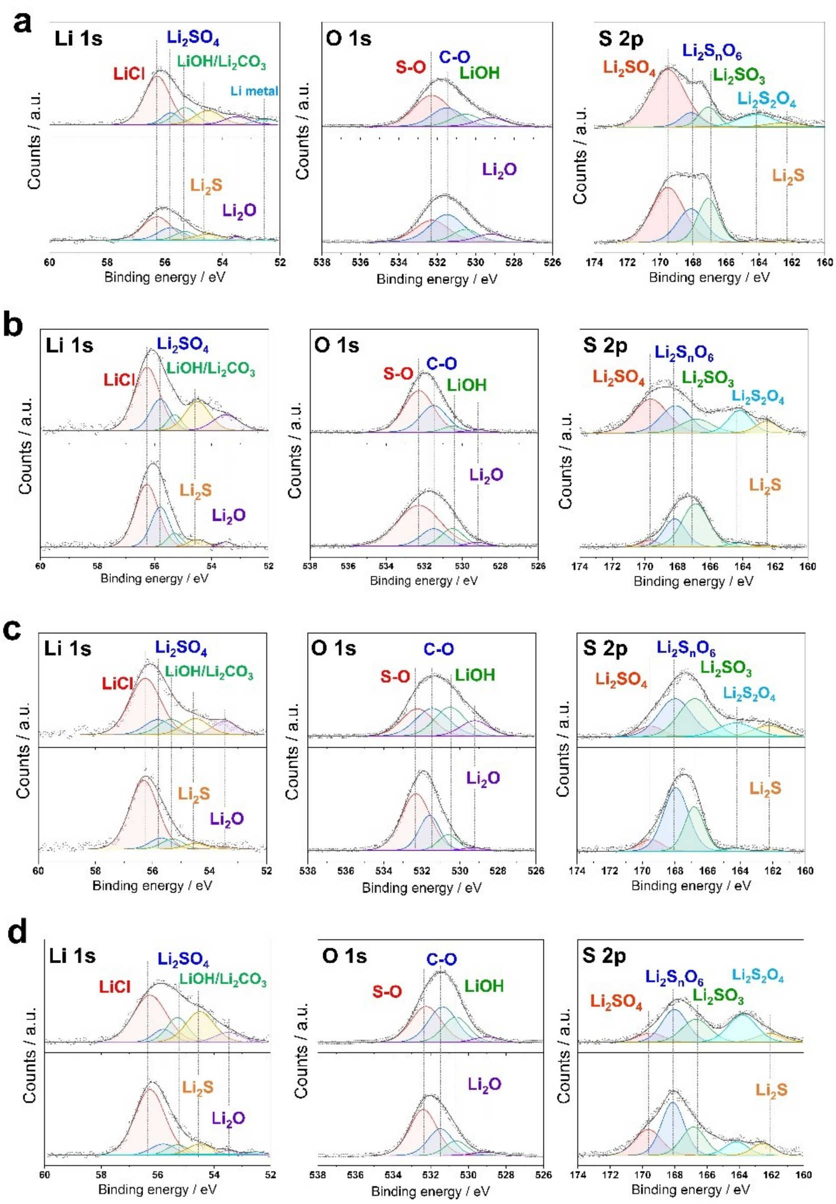

**Fig. S22.** Surface and depth-profiled XPS spectra of cycled lithium electrodes at different cycle numbers. XPS spectra of the Li 1s, O 1s, and S 2p regions collected from lithium electrodes after (a) 10, (b) 20, (c) 50, and (d) 100 cycles (upper for depth-profiled spectra after $Ar^{+}$ sputtering for 120 sec, and the lower for the corresponding surface spectra).

| | R1 | R2 | R3 |
|---|---|---|---|
| **Pristine lithium** | **0.5 Ω** | **34.3 Ω** | **68.1 Ω** |
| **$I_2$-modified lithium** | **0.8 Ω** | **41.9 Ω** | **320.7 Ω** |

**Table S1.** Resistance values (R1, R2, R3) for symmetric Li//Li cells with pristine lithium and $I_2$-modified lithium electrodes in $LiAlCl_4$–$3SO_2$ electrolyte after 12 hours resting at open-circuit voltage. R1 represents the bulk electrolyte resistance, while R2 and R3 correspond to interfacial resistances of SEI and charge transfer processes, respectively.

| | | R1 | R2 | R3 |
|---|---|---|---|---|
| Pristine lithium | 2 cycles | 0.4 Ω | 13.3 Ω | 23.6 Ω |
| | 10 cycles | 0.5 Ω | 17.5 Ω | 28.4 Ω |
| | 50 cycles | 0.2 Ω | 7.9 Ω | 7.0 Ω |
| $I_2$-modified lithium | 2 cycles | 0.6 Ω | 41.9 Ω | 69.5 Ω |
| | 10 cycles | 0.6 Ω | 11.5 Ω | 22.7 Ω |
| | 50 cycles | 0.3 Ω | 8.5 Ω | 10.8 Ω |

**Table S2.** Resistance values (R1, R2, R3) for symmetric Li//Li cells with pristine lithium and $I_2$-modified lithium electrodes in $LiAlCl_4$–$3SO_2$ electrolyte after 2 cycles, 10cycles, and 50 cycles. R1 represents the bulk electrolyte resistance, while R2 and R3 correspond to interfacial resistances of SEI and charge transfer processes, respectively.