

Electronic Supplementary Information (ESI)

Asymmetric behaviour of Li/Li symmetric cells for Li metal batteries

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Experimental Section

Electrochemical characterization. Lithium bis(fluorosulfonyl)imide (LiFSI) was purchased from Enchem Co., Ltd, South Korea. 1,2-dimethoxyethane (DME, 99.9%, Sigma Aldrich) was used after drying with molecular sieves (4 Å). The amount of water in DME was less than 10 ppm, which was measured by Karl-Fischer titrator. 1.3 M LiPF₆ in EC:DEC (battery grade, EC:DEC = 3:7 vol%) was purchased from Soulbrain Co., Ltd, South Korea. The electrochemical performance of Li/Li symmetric cells were examined using 2032 coin-type cells, where Li metal (Honjo Metal, Japan) was approximately 700 μm in thickness. Polyethylene separators were used for all electrochemical experiments except for the measurement of short-circuit time (T_{sc}). Whatman GF/C glassfibre filter papers were used as separators for the measurement of T_{sc}. Coin cells were assembled in Ar-filled glove box where the amounts of O₂ and H₂O were less than 0.1 ppm. For the reassembly of symmetric cells using initially plated and initially stripped Li metal electrodes, cells were disassembled in the Ar-filled glove box, followed by washing Li metal electrodes with DME solvent to remove residual electrolytes.

The electrochemical performance of Li metal-ion full cells was evaluated with coin cells consisting of a LiCoO₂ cathode, a Li metal anode (150 μm in thickness, Honjo Metal, Japan), and an electrolyte of 1.3 M LiPF₆ in EC/DEC = 3/7 (v/v). To prepare the LiCoO₂ cathode, a slurry comprising LiCoO₂ (80 wt %), Super P (10 wt %), and a poly(vinylidene fluoride) (PVdF) binder (10 wt.%) was coated on a Al current collector. The electrodes were dried at 120°C in a vacuum oven overnight, and the loading mass was approximately 5.0 mg cm⁻². Galvanostatic experiments were carried out between 3.0 and 4.2 V (vs. Li/Li⁺) at a 1C rate. For the reassembly of Li metal-ion full cells using initially plated and initially stripped Li metal electrodes, Li/Li symmetric cells were disassembled after stripping and plating in the Ar-filled glove box, followed by reassembling with LiCoO₂ cathodes.

Electrochemical impedance spectroscopy (EIS) was measured using Li/Li symmetric cells with an amplitude of 5 mV over a frequency range of 0.006 to 1 MHz. EIS spectra were obtained with SP-150 potentiostat (Bio-Logic, USA) and analysed with EC-Lab software.

Material characterization. The morphologies of Li metal electrodes were examined using field emission scanning electron microscopes (FE-SEM) equipped with energy dispersive X-ray spectroscopy (EDS), JSM-7800F Prime (JEOL Ltd, Japan) and Auriga (Zeiss, Germany). The cross-sectional images were obtained with focused ion beam (FIB)-SEM, Scios (Hitachi, Japan).

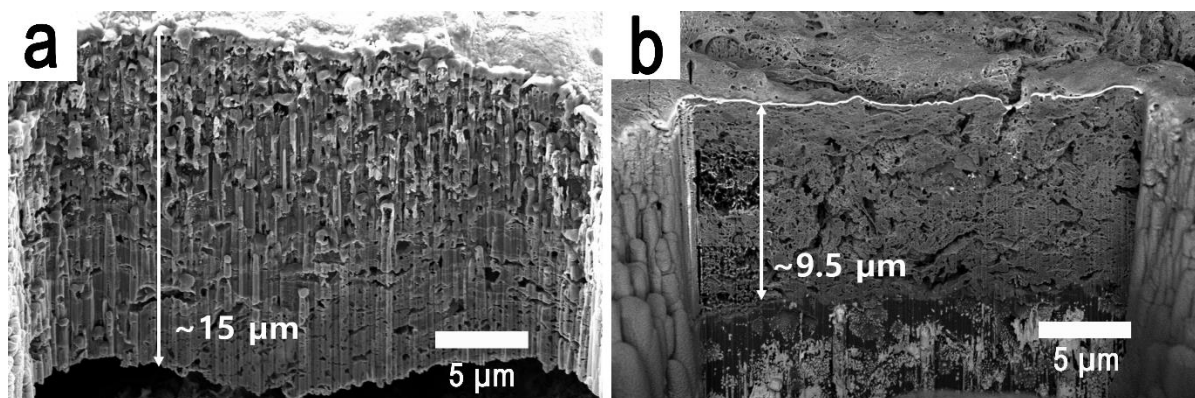


Fig. S1 Cross-sectional SEM images of (a) working and (b) counter electrodes in a Li/Li symmetric cell after 100 cycles. The current density of $\pm 0.5 \text{ mA cm}^{-2}$ was applied for each 0.5 h cycle.

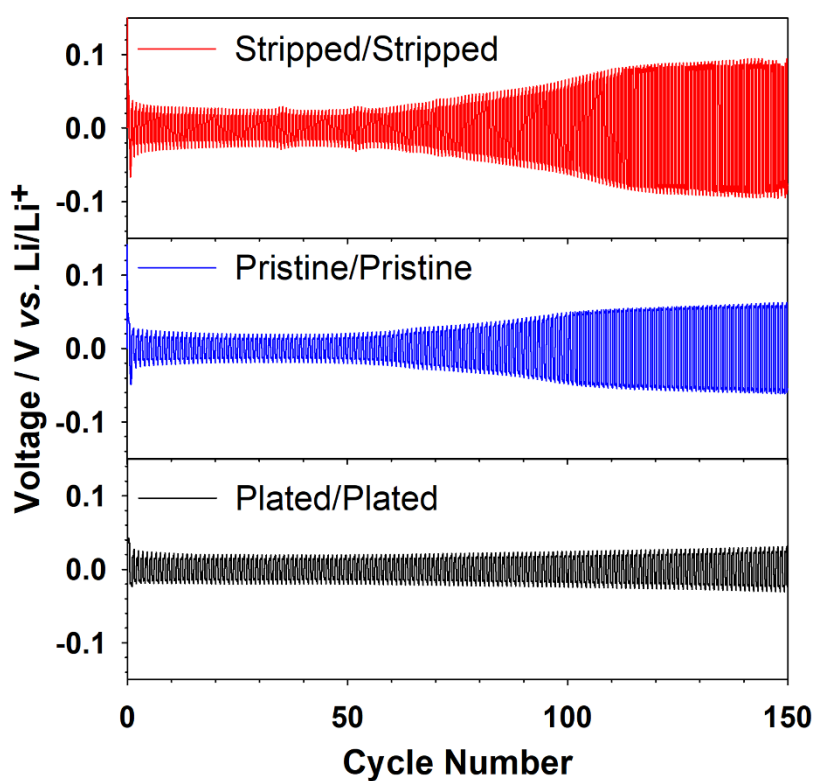


Fig. S2 Voltage profiles of various Li/Li symmetric cells with an areal capacity of 1 mA h cm^{-2} at areal current density of 2 mA cm^{-2} . (red: stripped Li/stripped Li, blue: pristine Li/pristine Li, black: plated Li/plated Li). Each stripped and plated Li metal electrode was obtained after applying a current density of 0.5 mA cm^{-2} for 2 h.

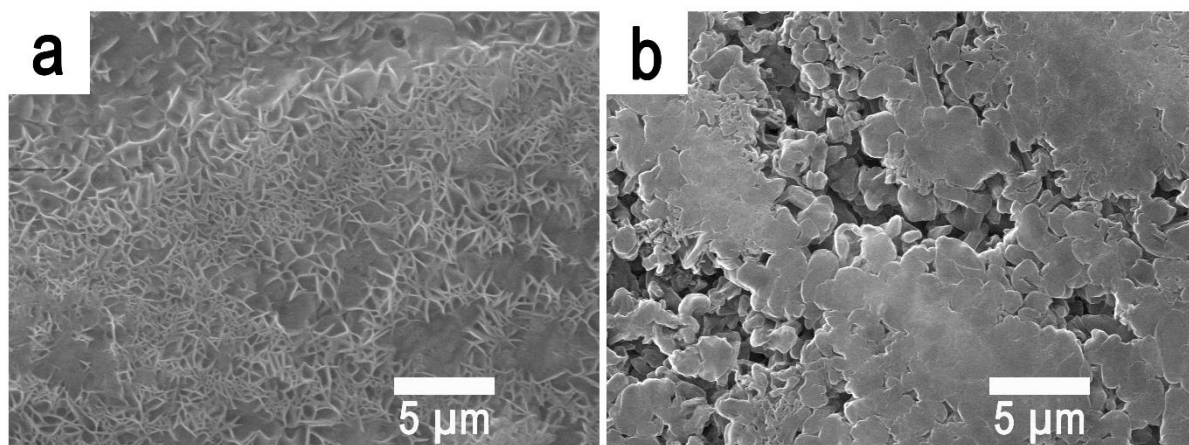


Fig. S3 Scanning electron microscope (SEM) images of Li metal electrodes after (a) initial stripping and (b) initial plating with a capacity of 1 mA h cm^{-2} at areal current density of 0.5 mA cm^{-2} . 1.3 M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) = 3/7 (v/v) was used as an electrolyte.

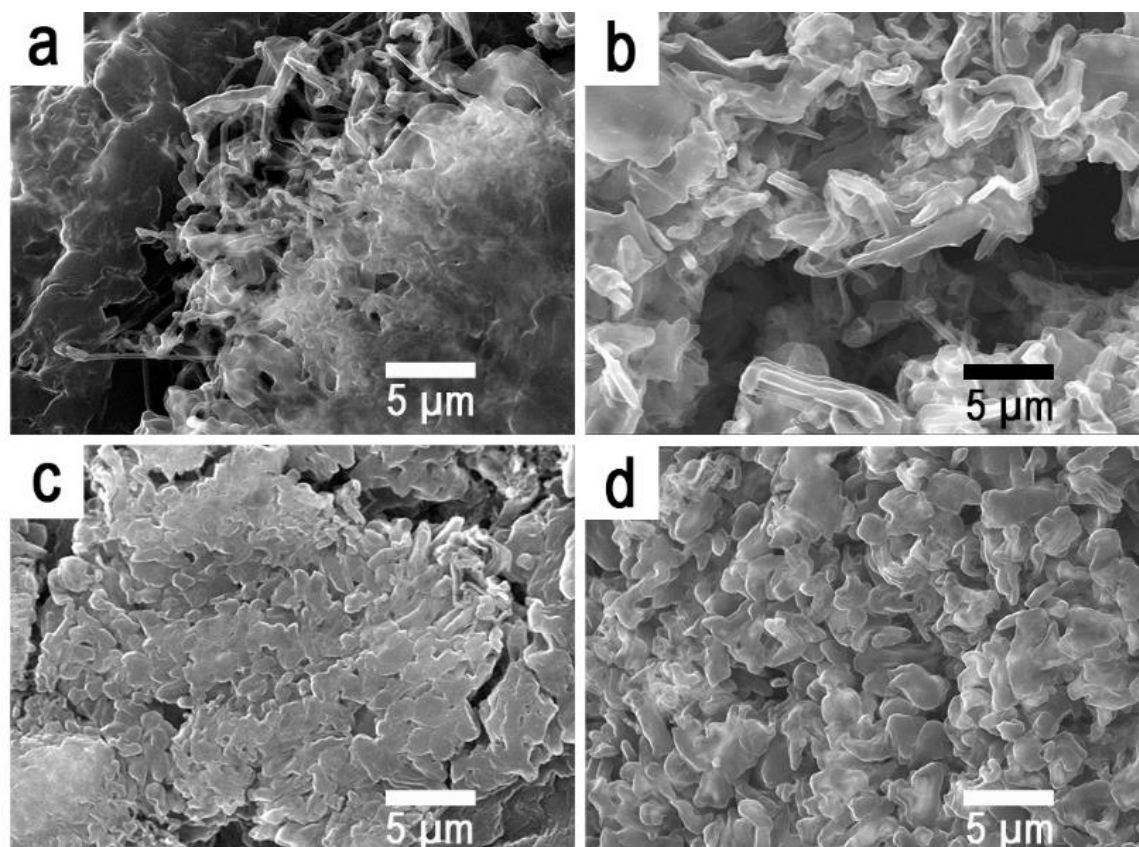


Fig. S4 SEM images of (i) initially stripped Li metal electrodes after additional Li plating with a capacity of (a) 1 mA h cm^{-2} and (b) 3 mA h cm^{-2} ; (ii) initially plated Li metal electrodes after additional Li plating with a capacity of (c) 1 mA h cm^{-2} and (d) 3 mA h cm^{-2} . The current density was $\pm 0.5 \text{ mA cm}^{-2}$. 1.3 M LiPF_6 in ethylene carbonate (EC)/diethylene carbonate (DEC) = 3/7 (v/v) was used as an electrolyte. Initially stripped and initially plated Li metal electrodes were obtained after applying a current density of 0.5 mA cm^{-2} for 2 h.

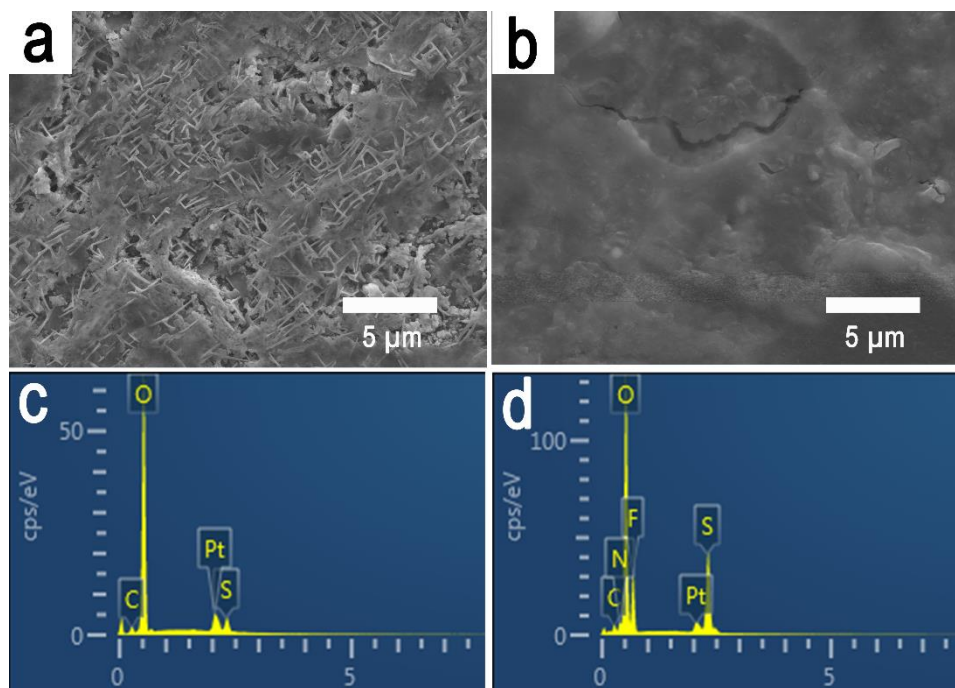


Fig. S5 SEM images of initially stripped Li metal electrodes (a) after and (b) before washing with DME solvent. The corresponding EDS spectra of initially stripped Li metal electrodes (c) after and (d) before washing with DME solvent. Stripped Li metal electrodes were obtained after stripping with a capacity of 1 mA h cm^{-2} .

Table. S1 Quantitative elemental analysis of initially stripped Li metal electrodes before and after washing with DMC solvent using EDS spectra in Fig. S5c and S5d.

Samples	Content of Elements (at%)					Total
	C	N	O	F	S	
After washing (Fig. S5c)	9.3	-	88.5	-	2.2	100.0
Before washing (Fig. S5d)	8.5	6.3	55.7	23.5	6.0	100.0

Author Contributions

Dongho Koo and Kyu Tae Lee conceived the research. Dongho Koo designed the experiments. Bomee Kwon and Jeonghyeop Lee performed SEM analysis. Dongho Koo and Kyu Tae Lee wrote the manuscript. Kyu Tae Lee supervised the project. All authors contributed to the interpretation of the results.