Supporting Information

Scalable solid solution strengthened Li-Ag alloy anode for high-energy-density lithium batteries

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Experimental Section

Fabrication of the Li-Ag Alloy Composite Foils.

The alloy ingot preparation process was carried out in an Ar-filled glovebox with H_2O and O_2 content below 0.1 ppm. High-purity Li metal (China Energy Lithium Co., Ltd.) was first placed in a nickel crucible and heated to ~300 °C in an Ar-filled glovebox. silver powder (Shanghai Aladdin Bio-Chem Technology Co., Ltd., 99%) was then added into molten Li with continuous stirring until silver powder disappeared to give a homogeneous composite. After cooling down to room temperature, Li-Ag composite alloys with different mass ratios were given. The Li-Ag foils were prepared by repeated rolling using a rolling machine (MSK-HRP-1A, Hefei Kejing Materials Technology, Ltd.) in a dry room (relative humidity, RH<5%).

Characterizations.

X-ray diffraction (XRD) patterns were recorded on a Bruker D8-Focus equipped with a Cu Kα radiation (λ=0.15418 nm). The morphology of the samples was investigated using scanning electron microscope (SEM, Hitachi S4800, Japan) under an accelerated voltage of 5.0 kV. The bending stretching test and tensile strength measurement were conducted in a dry room (RH<5%). The tensile strength measurement was carried out using an SR-50N tester with a loading rate of 1 mm min^{-1}. The size of the tested sample was demonstrated in figure 2a and S7.

Coin-Type Cell Fabrication and Electrochemical Measurements

Li-Ag alloy composite foils with different Ag ratios were punched into disks with 16 mm in diameter for coin cell fabrication. $LiCoO_2$ cathode has an average active loading of ~5.1 mg cm^{-2} and 10.3 mg cm^{-2}. NCM90 cathode has an average active loading of ~22.5 mg cm^{-2}. CR2430-type coin cells were assembled using a ceramic-coated polyethylene (PE) separator of 20 μm in an Ar-filled glovebox. A high-concentration electrolyte (the molar ratio of LiFSI:DME:TTE is 1:1.6:1.6) was selected as electrolyte for cell assembly. Galvanostatic charge/discharge measurements were evaluated on a standard battery tester (LAND CT2001A). The $LiCoO_2$ full cells were cycled at different current rates between 3.0 and 4.3 V. The NCM90 full cells were cycled at different current rates between 2.7 and 4.3 V. Electrochemical impedance spectroscopy (EIS) and were recorded on Solartron Metrology cell test system 1400 at an amplitude of 10 mV with a frequency ranging from 10^6 Hz to 0.1 Hz. Tafel plots of symmetric cells were obtained by linear sweep voltammetry (LSV) testing between -0.17 and 0.17 V at a scan rate of 1 mV s^{-1}.

Pouch Cell Fabrication and Electrochemical Measurements

The 15.8 Ah pouch cells were fabricated in dry-rooms using 50 μm Li metal anodes or Li-Ag alloy anodes, 20 μm ceramic-coated polyethylene (PE) separators, NCM90 cathode with an average active loading of ~22.5 mg cm^{-2} (4.5 mAh cm^{-2}) and 1.8 g Ah^{-1} electrolyte. The cycling performance was measured on a LAND CT2001A battery test system. The pouch cells were cycled between 2.7 and 4.3 V at 0.1 C charge and 0.2 C discharge rates.

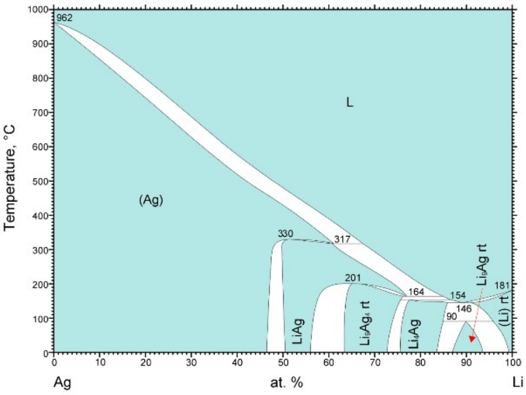

Figure S1 Binary phase diagrams of the Li−Ag alloy (source: https://materials.springer.com/)

Figure S2 Digital photographs of the process of preparing Li-Ag alloy foil.

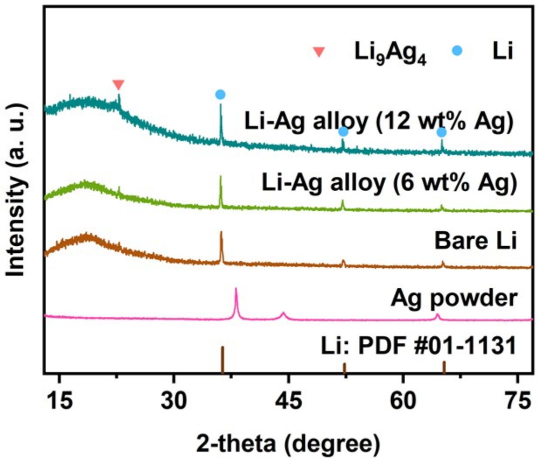

Figure S3 XRD pattern of Ag powder, Li, Li-Ag alloy with different mass ratios.

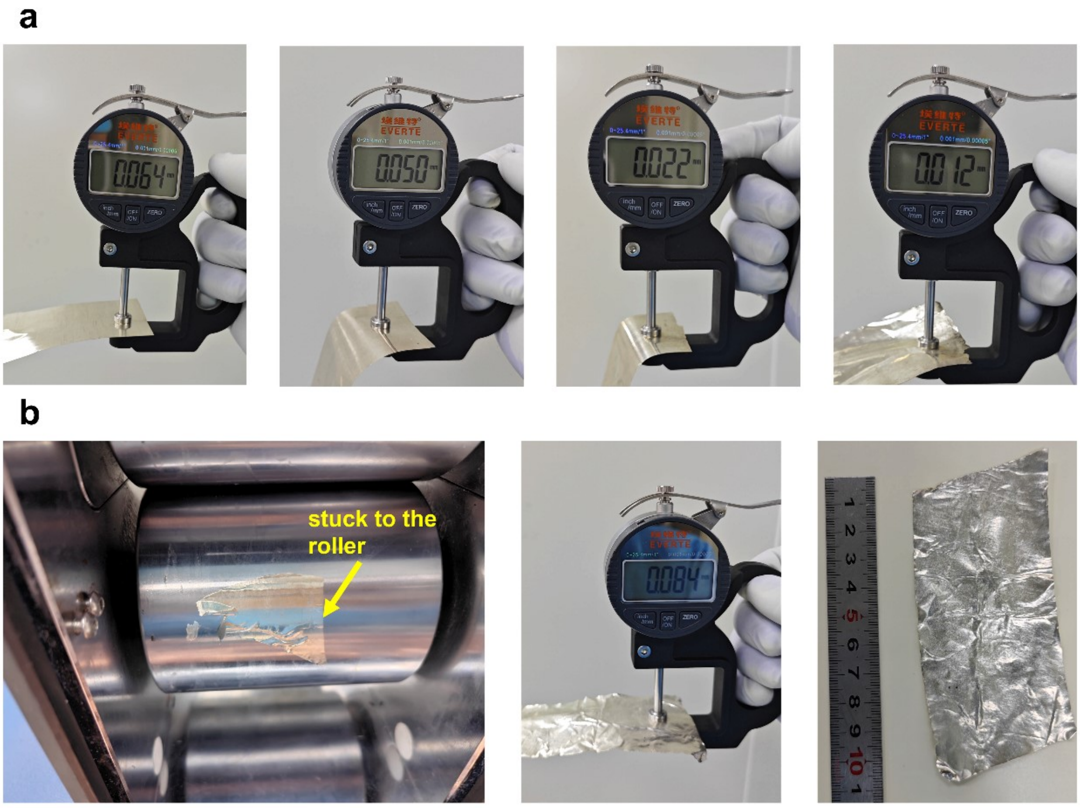

Figure S4 (a) Digital photographs of Li-Ag alloy foil with different thicknesses. (b) Digital photographs of bare Li foil stuck to the stainless-steel roller with a thickness below 100 μm.

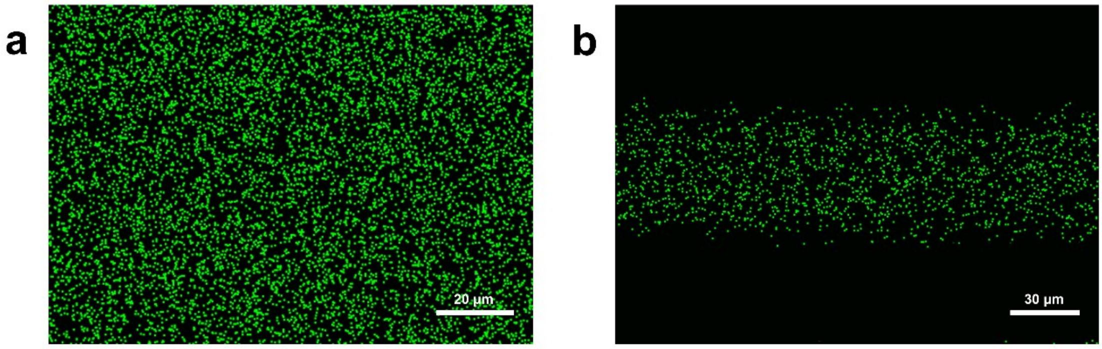

Figure S5 (a) EDS mapping images of the (a) top-view and (b) cross-sectional SEM images of 40 μm-thick Li-Ag alloy foil.

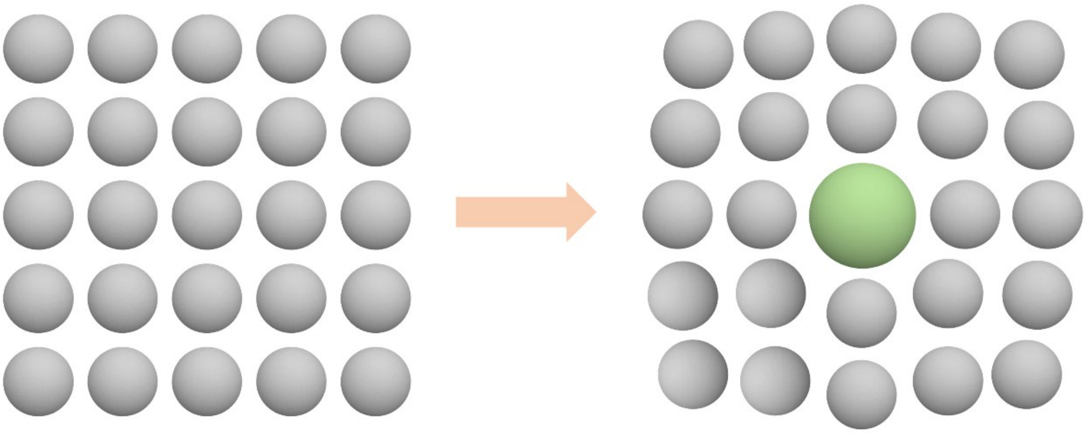

Figure S6 Schematic illustration of solid solution strengthening induced by Li-Ag alloy.

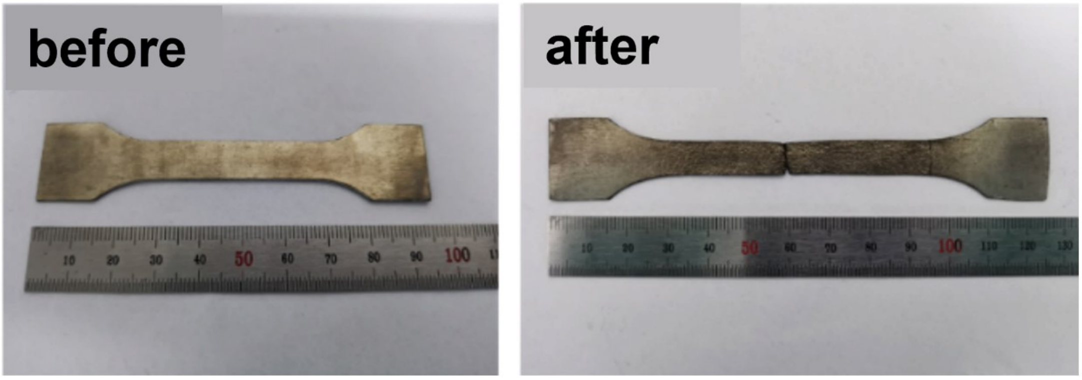

Figure S7 Digital photographs of the Li-Ag alloy strip before and after the tensile performance test.

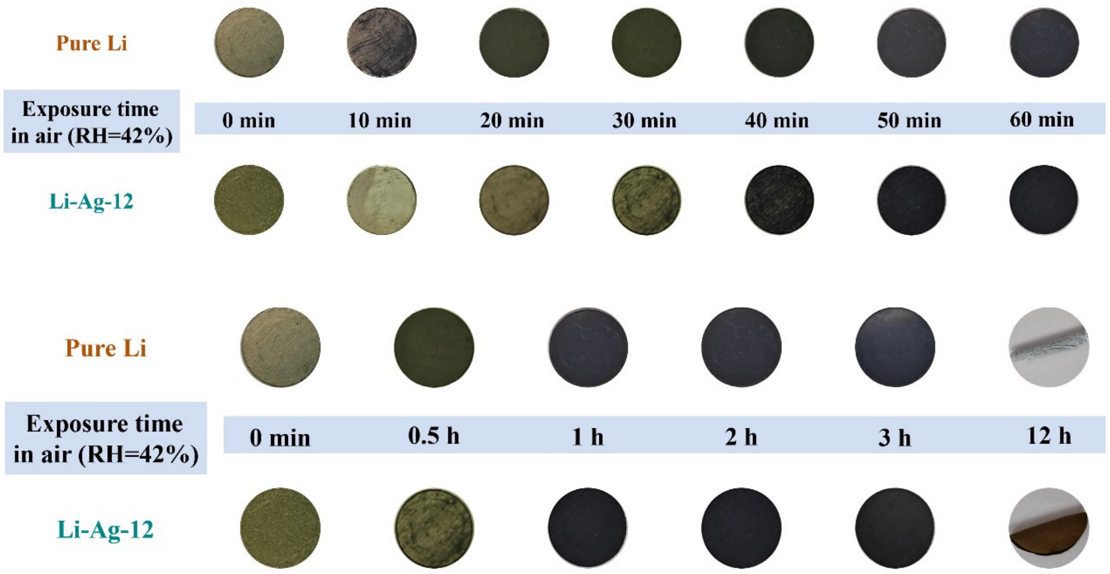

Figure S8 Digital photographs of the bare Li and Li-Ag-12 electrodes exposed to the ambient air with relative humidity of 42% for various times.

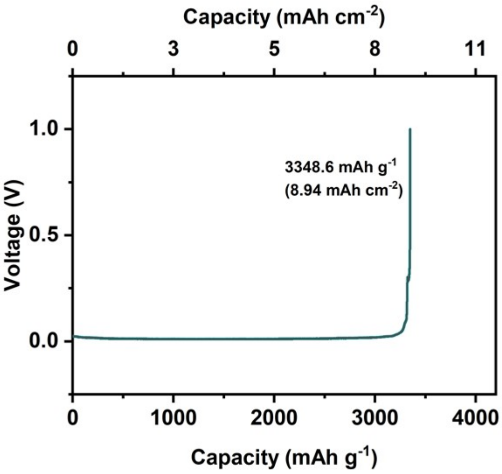

Figure S9 The Li stripping curve of the Li-Ag-12 electrode charged to 1 V versus Li^+/Li.

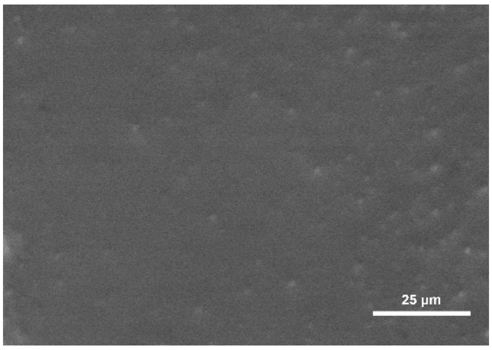

Figure S10 Top-view and of the Li-Ag-12 electrode after Li stripping of 3 mAh cm^{-2}.

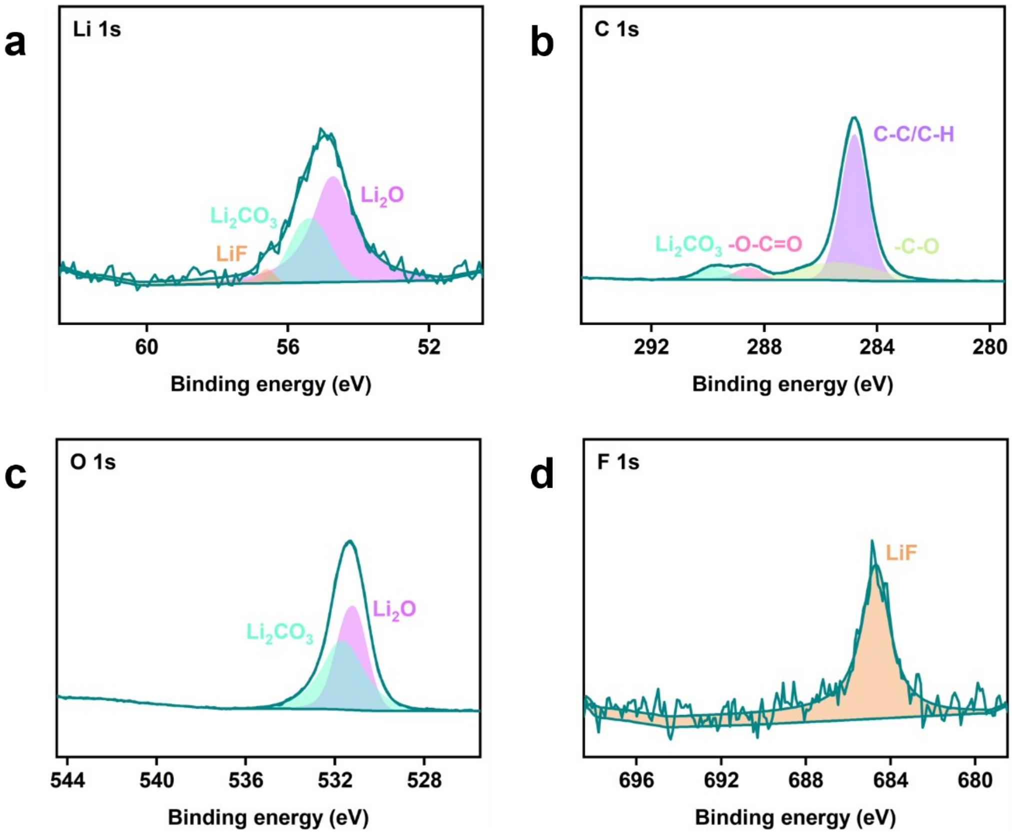

Figure S11 High-resolution XPS spectra of Li 1s, C 1s, O 1s and F 1s of the Li-Ag-12 alloy foil after Li stripping of 3 mAh cm^{-2}.

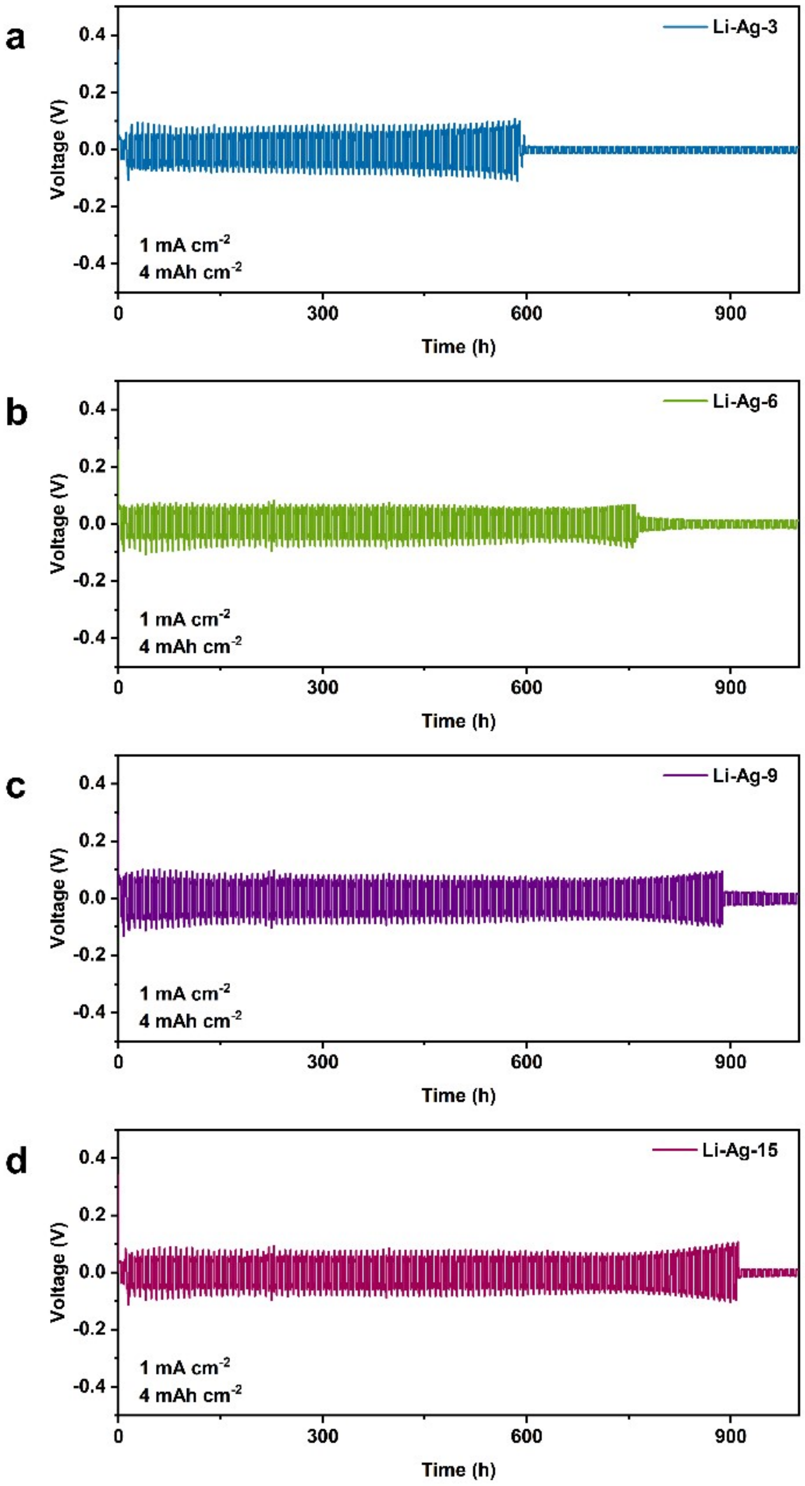

Figure S12 Cycling performance of the symmetric cells for the Li-Ag alloy electrodes with different mass ratios (a) 3 wt% Ag, (b) 6 wt% Ag, (c) 9 wt% Ag, and (d) 15 wt% Ag.

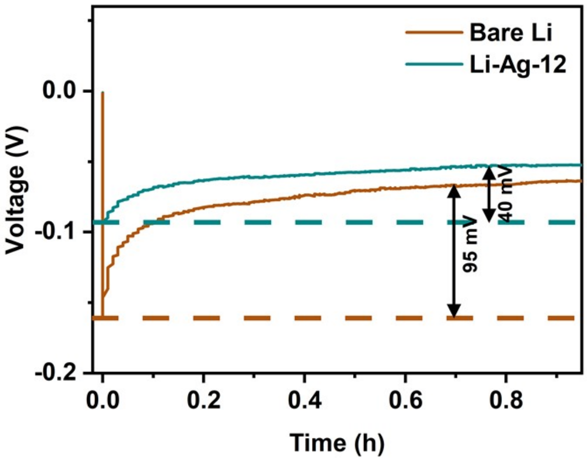

Figure S13 The initial nucleation overpotential of the bare Li and Li-Ag-12 electrodes in symmetric cells.

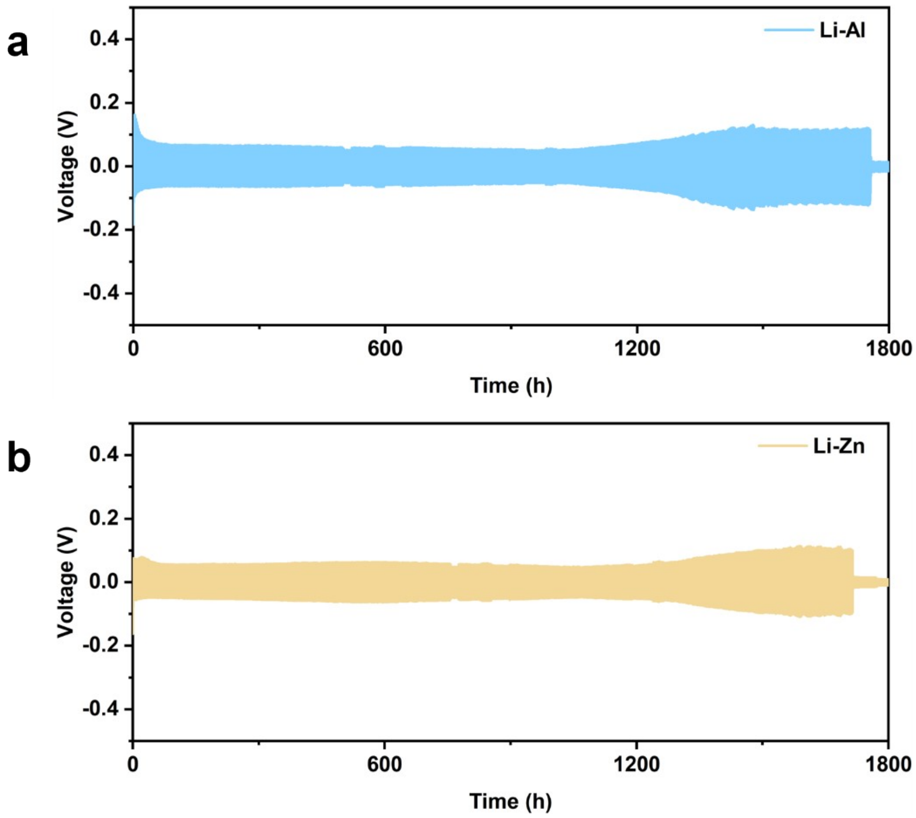

Figure S14 Cycling performance of the symmetric cells for the Li-Al and Li-Zn alloy electrodes at 1 mA cm^{-2} and 1 mAh cm^{-2}

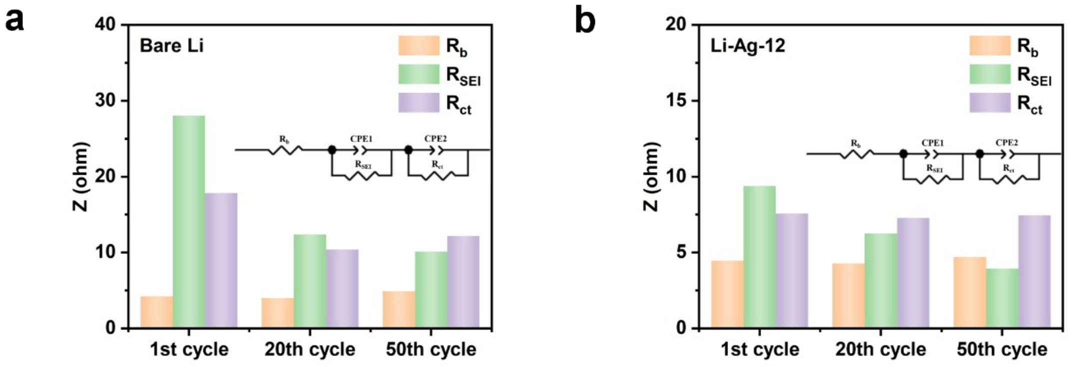

Figure S15 The illustration of resistance from bulk electrolyte, SEI layer (R_{SEI}) and charge-transfer process (R_{ct}) of symmetric cells for (a) bare Li and (b) Li-Ag-12 electrodes after 1, 20 and 50 cycles at 1 mA cm^{-2} and 4 mAh cm^{-2}.

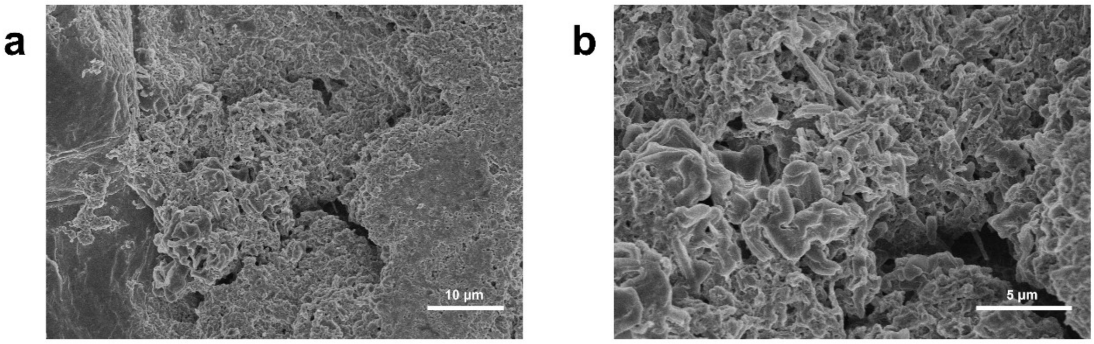

Figure S16 Top-view SEM images of the morphology for the bare Li electrode after 40 cycles at 2 mA cm^{-2} and 1 mAh cm^{-2}.

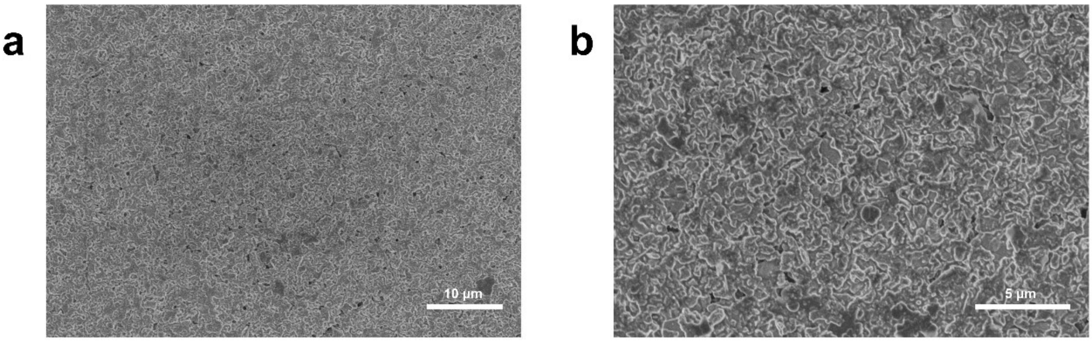

Figure S17 Top-view SEM images of the morphology for the Li-Ag-12 electrode after 40 cycles at 2 mA cm^{-2} and 1 mAh cm^{-2}.

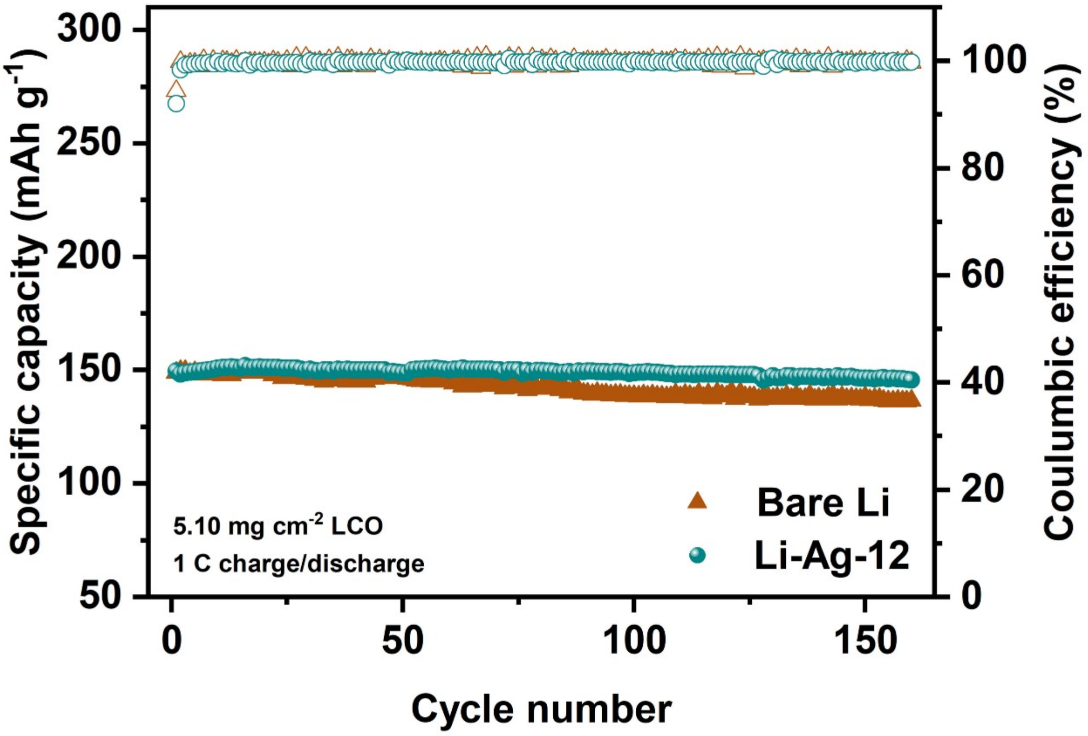

Figure S18 Cycling performances of $LiCoO_2$||bare Li and $LiCoO_2$||Li-Ag-12 full cells with the cathode load of 5 mg cm^{-2} at 1 C.

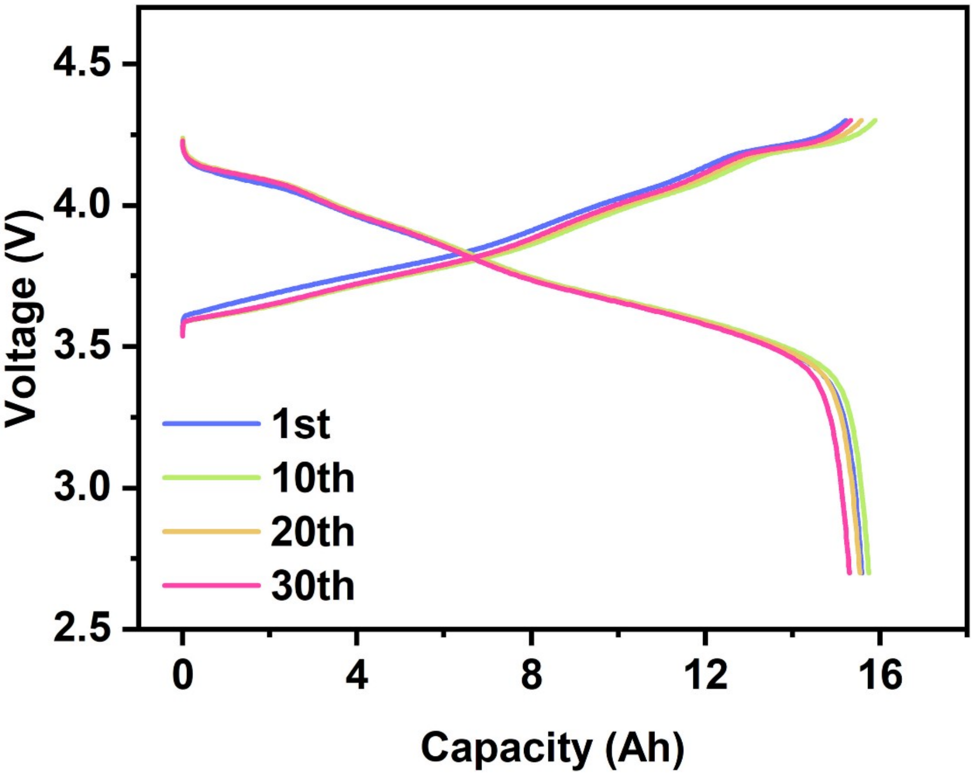

Figure S19 The charge-discharge voltage profiles of 15.8 Ah NCM90||Li-Ag-12 pouch cell.

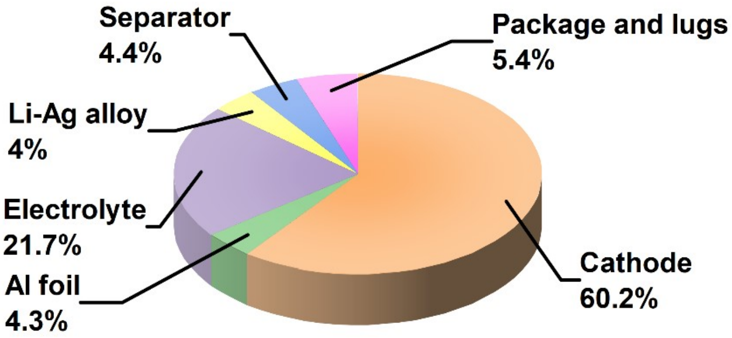

Figure S20 The pie chart of the mass distribution of all components in a pouch cell. The specific energy in this work is calculated by the whole mass in the pouch cell.

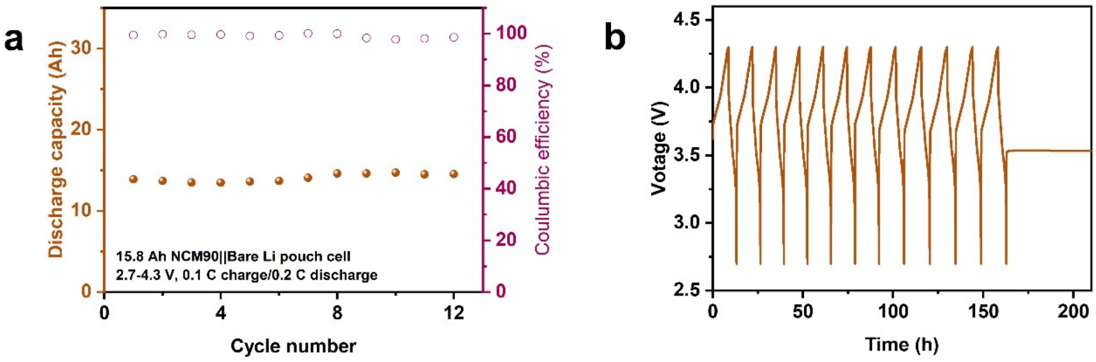

Figure S21 (a) Cycling performance of 15.8 Ah NCM90||bare Li pouch cell. (b) Corresponding voltage-time profiles of 15.8 Ah NCM90||bare Li pouch cell.

Table S1 Detailed mass parameters of the 15.8 Ah pouch cell.

	Parameter	Value	Mass (g)
NCM90 cathode (138*98)	Specific capacity	205 mAh g^{-1}	79.12
	Area weight	22.5 mg cm^{-2}	
	Area capacity single area	~4.5 mAh cm^{-2}	
	Number of layers	13	
Al foil	Thickness	12 μm	5.70
Li-Ag anode (140*100)	Specific capacity	3348.6 mAh g^{-1}	5.23
	Thickness	50 μm	
	Area capacity	8.94 mAh cm^{-2}	
	N/P ratio	1.11	
Separator	Type	Ceramic-coated polyethylene	5.80
	Thickness	20 μm	
Electrolyte	E/C ratio	1.8 g Ah^{-1}	28.44
Package foil	Thickness	153 μm	7.06
Pouch cell	Average voltage	3.75V	131.35
	Capacity	15.8 Ah	
	Weight	131.35g	
	Energy density	451.1 Wh kg^{-1}	

Note: The calculation of N/P ratio is based on the actual capacity of the anodes and cathodes used in the pouch cell. The detailed parameters and the calculation are now presented below:

$$\text{N/P ratio} = \frac{\text{capacity of total anodes}}{\text{capacity of total cathodes}} = \frac{8.94\ \text{mAh cm}^{-2} \times 14\ \text{cm} \times 10\ \text{cm}}{4.5\ \text{mAh cm}^{-2} \times 13.8\ \text{cm} \times 9.8\ \text{cm} \times} = 1.11$$