Supporting Information

A "Flotation" Strategy for Tailoring Solid Electrolyte Interphase of 3D Composite Li Anode

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Experimental Section

Materials

$Zn(CH_3COO)_2 \cdot 2H_2O$, CH_3CSNH_2, NH_4F, NaH_2PO_2, hexamethylenetetramine ($C_6H_{12}N$) anhydrous ethanol and N-methyl-2-pyrrolidone (NMP) were purchased from Xilong Chemical Co., Ltd. (Shantou, China). $Zn(NO_3)_2 \cdot 6H_2O$ was purchased from purchased from Sinopharm Chemical Reagent Co. Ltd. Carbon cloth (CC), Li foil, LiFePO$_4$ (LFP) and carbon black and polyvinylidene fluoride binder (PVDF) were purchased from Guangdong Canrd New Energy Technology Co.,Ltd. Electrolytes were purchased from DoDoChem.

Synthesis of carbon cloth covered with lithophilic ZnO nanoarrays (ZnO/CC). The carbon cloth (3×5 cm^2) is immersed in Zn(Ac)$_2$ ethanol solution, followed by drying at 160 ° C for 15 minutes. This process is repeated three times. The ZnO nanorods are obtained by hydrothermal treatment. Then the ZnO seeds decorated carbon cloth is immersed in aqueous solution containing zinc nitrate hexahydrate (25 mM) and methenamine (25 mM), and keep at 90°C for 24 h. Then the carbon cloth is washed several times with DIW and vacuum drying at 60°C.

Synthesis of ZnF$_2$ decorated ZnO/CC (ZnF$_2$/ZnO/CC). ZnO/CC is immersed in NH_4F ethanol solution (25 mM), and keep at 90°C for 3 h. Then the carbon cloth is washed

several times with anhydrous ethanol and vacuum drying at 60°C.

Synthesis of ZnP$_x$ decorated ZnO/CC (ZnP$_x$/ZnO/CC). ZnO/CC is placed at the downstream of furnace with excess sodium hypophosphite at the center of the tube furnace, and two porcelain boats were separated with a distance of 2-4 cm. Then ZnP$_x$ is formed via a phosphating process under slow Ar flow at 300 °C for 30 min with a heating rate of 5 °C min^{-1}.

Synthesis of ZnS decorated ZnO/CC (ZnS/ZnO/CC). The ZnO/CC is immersed in CH$_3$CSNH$_2$ aqueous solution, and keep at 90°C for 3 h. Then the carbon cloth is washed several times with DIW and vacuum drying at 60°C.

Material Characterization. The morphologies of all the samples were characterized by scanning electron microscope ((SEM, Zeiss Gemini 500) and transmission electron microscope (TEM, Talos F200s). X-ray diffraction (XRD) patterns were recorded by an X-ray diffractometer (Bruker D8 Advance, 60 kV) using Cu Kα (λ=1.5406 Å) as radiation. X-ray photoelectron spectroscopy (XPS) analysis was performed on a spectrometer (Escalab 250Xi, Thermo Fisher Scientific) using Al Kα as the excitation source.

Electrochemical Measurements. All the electrochemical performances were evaluated by assembling 2032-type coin cells in the argon-filled glove box with O_2 and H_2O content below 0.1 ppm. The composite Li anodes are prepared through a facile molten infusion method. The average mass of composite Li anodes is 72.4 mg. According to the mass changes of hosts before and after Li coating, the average areal mass loading mass percentage of Li in the in the hosts is calculated to be ~17.2 mg cm^{-2} and 47.5%,

respectively. The LiFePO$_4$ (LFP) cathodes was made by blending LFP, carbon black and polyvinylidene fluoride binder (PVDF) with a weight ratio of 8: 1: 1 (9: 0.5: 0.5 for high load) to form a slurry. The slurry was then blade-coated on the aluminum foils and dried in a vacuum oven at 60 °C for 12 h. The load of LFP was 3.2 mg cm^{-2} and 13.2 mg cm^{-2} for low load and high load, respectively. The N/P values under low and high LFP loads of the full cells can be calculated to be about 241.25 and 58.48, respectively. Carbon cloth (CC) and Li foils were use as the counter electrodes for Li|CC half cells. 50 μL of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, v:v=1:1) solution with 2 wt% LiNO$_3$ additive was used in Li|Cu cell and symmetric Li|Li cell. For full cells, the bare Li, Li@ZnO/CC, Li@ZnF$_2$/ZnO/CC, Li@ZnP$_x$/ZnO/CC, and Li@ZnS/ZnO/CC were used as the anodes and Celgard 2400 was used as the separator. 60 μL of 1.0 M LiPF6 in ethylene carbonate/diethyl carbonate solution (EC/DEC, v:v=1:1) with 10% fluoroethylene carbonate (FEC) and 1% vinylene carbonate (VC) was added in the full cell. The E/C values of the full cells under low and high LFP loads are calculated to be 110.29 and 26.74 μL mAh^{-1}, respectively. The electrochemical impedance spectroscopy (EIS) measurements and Tafel curve were conducted by using a Chenhua CHI 660E. Galvanostatic charge/discharge tests were performed on a LAND CT2001C battery tester system.
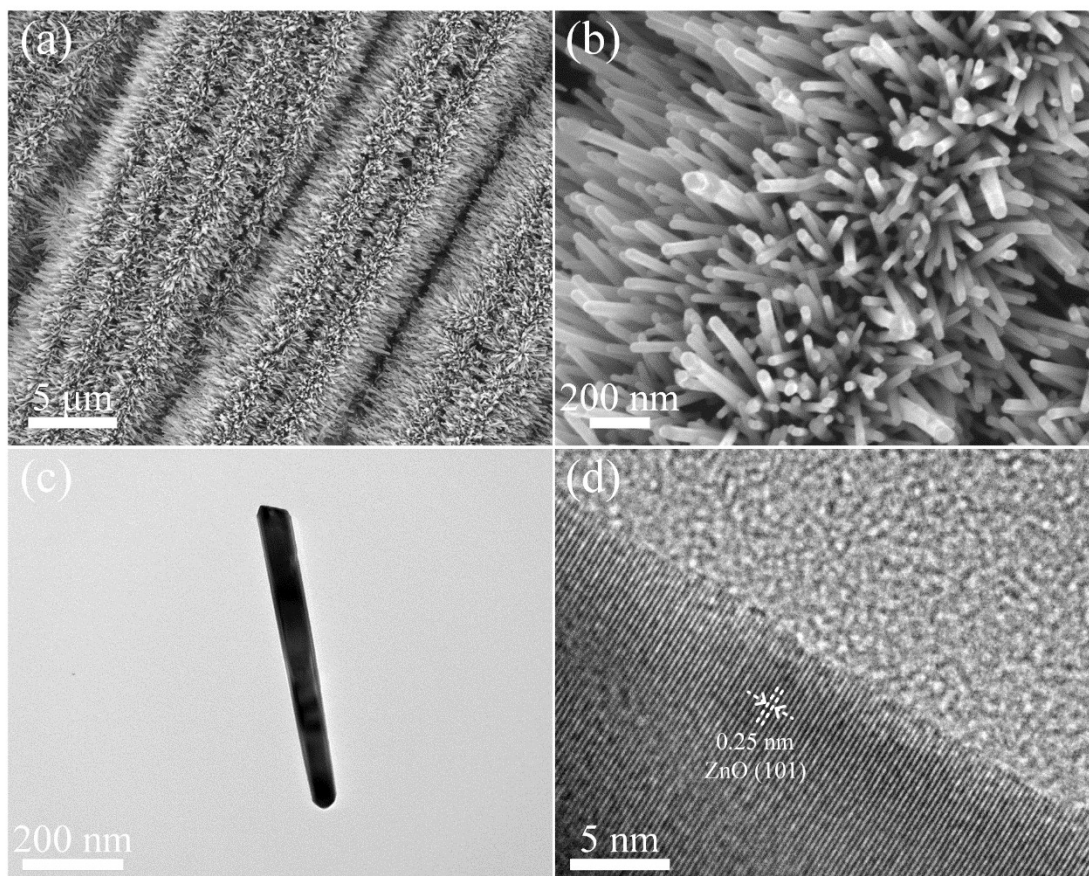
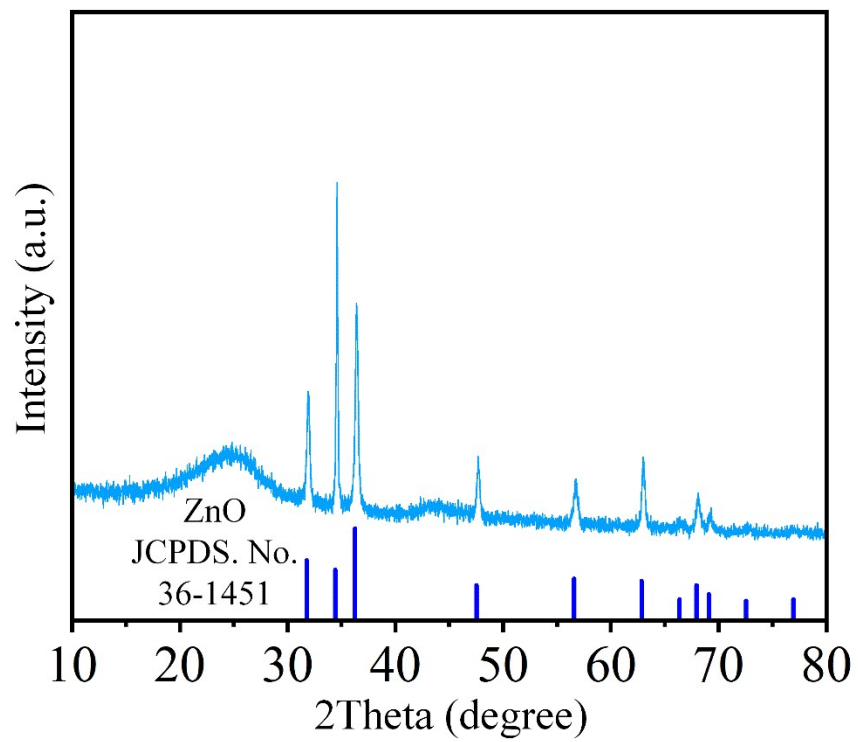Fig. S1 (a, b) SEM images of ZnO/CC, (c)TEM and (d) HRTEM images ZnO nanorod
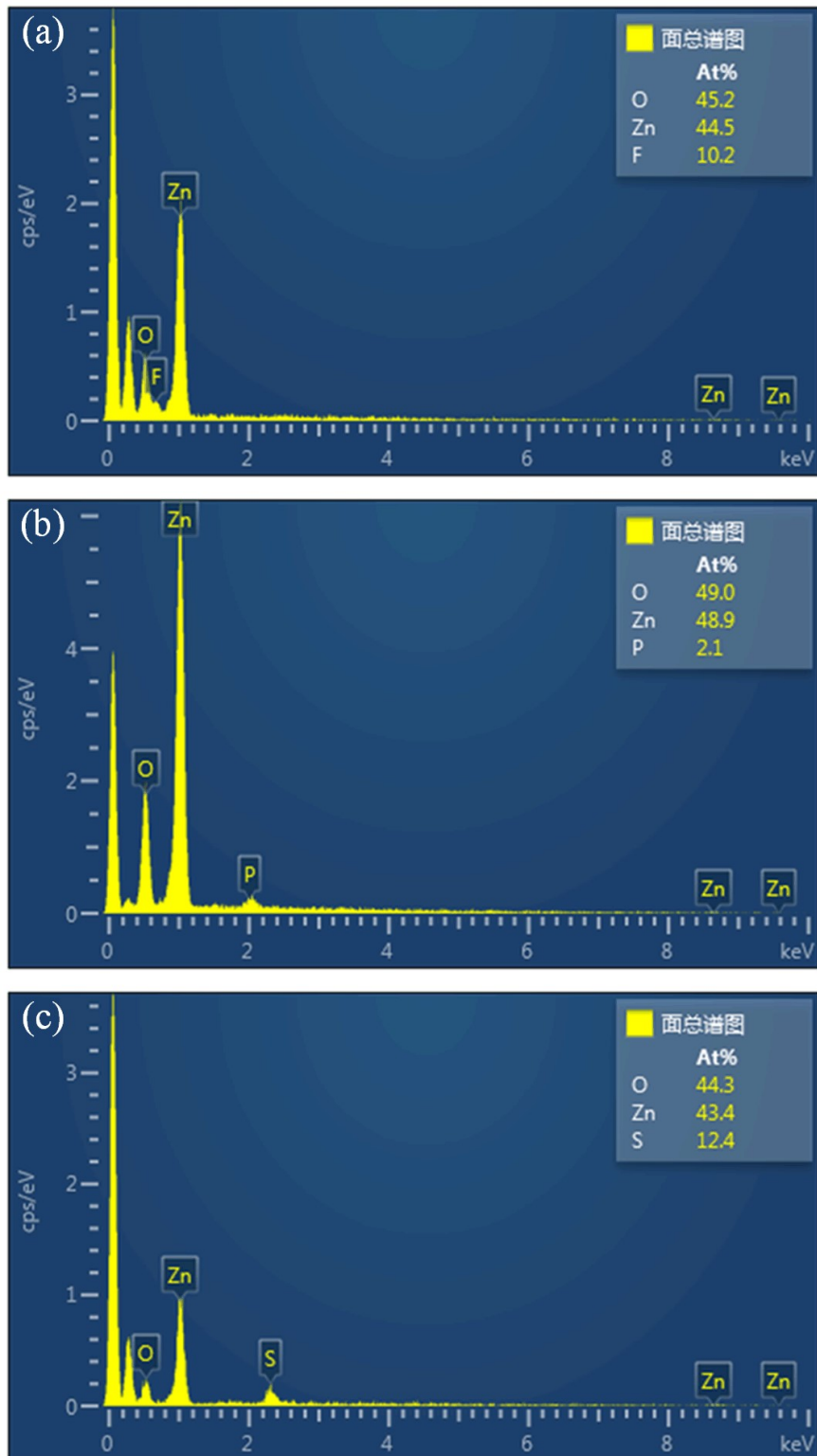
Fig. S2 XRD pattern of ZnO/CC

Fig. S3 A typical EDS spectrum of ZnF$_2$/ZnO/CC, ZnP$_x$/ZnO/CC and ZnS/ZnO/CC with composition listed in the inset table.
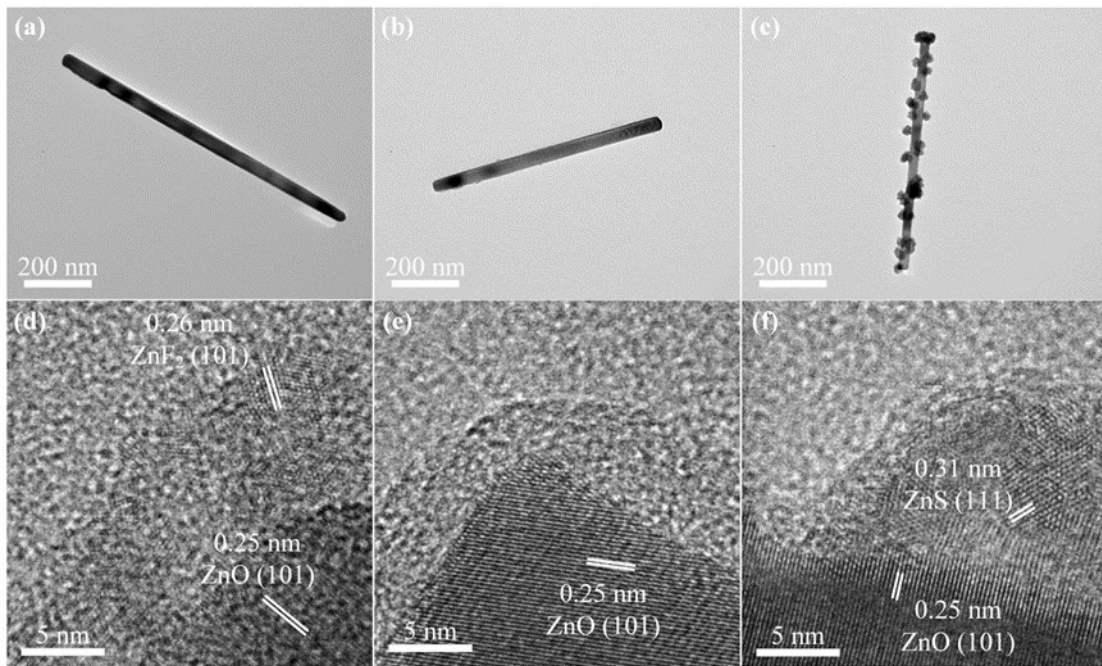
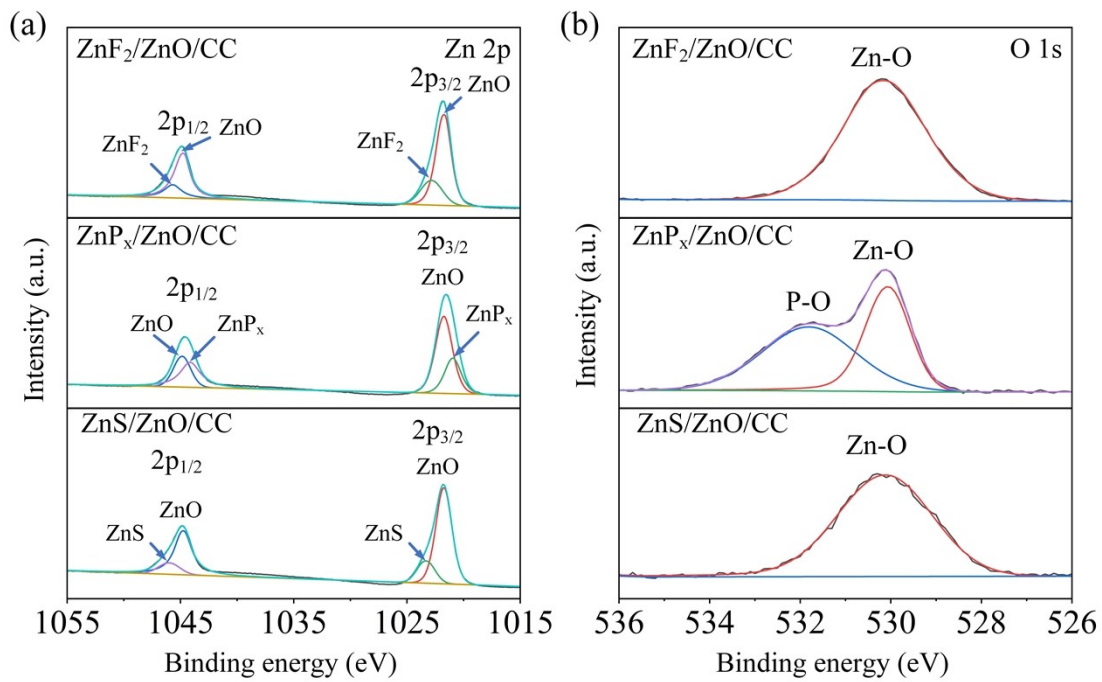Fig. S4 TEM and HRTEM images. (a, d) ZnF_2/ZnO/CC, (b, e) ZnP_x/ZnO/CC, (c, f) ZnS/ZnO/CC.

Fig. S5 (a) Zn 2p and (b) O1s XPS XPS spectra of $ZnF_2/ZnO/CC$, $ZnP_x/ZnO/CC$ and $ZnS/ZnO/CC$.

Fig. S6 Photographs of the evolution of ZnO/CC to Li@ZnO/CC composite through thermal infusion process of molten Li.
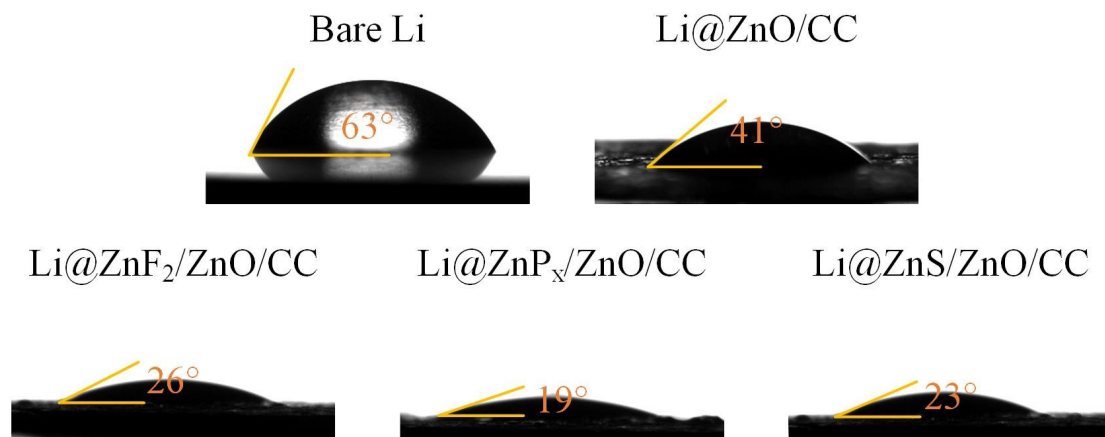
Bare Li   Li@ZnO/CC

63°   41°

Li@ZnF$_2$/ZnO/CC   Li@ZnP$_x$/ZnO/CC   Li@ZnS/ZnO/CC

26°   19°   23°

Fig. S7 Contact angle between the electrolyte and different Li anodes.

	R_{ct} (ohm)	
Time	0 h	24 h
Bare Li	57.1	77.2
Li@ZnO/CC	41.2	63.3
Li@ZnF$_2$/ZnO/CC	19.8	18.9
Li@ZnP$_x$ZnO/CC	17.1	17.3
Li@ZnS/ZnO/CC	11.7	11.8
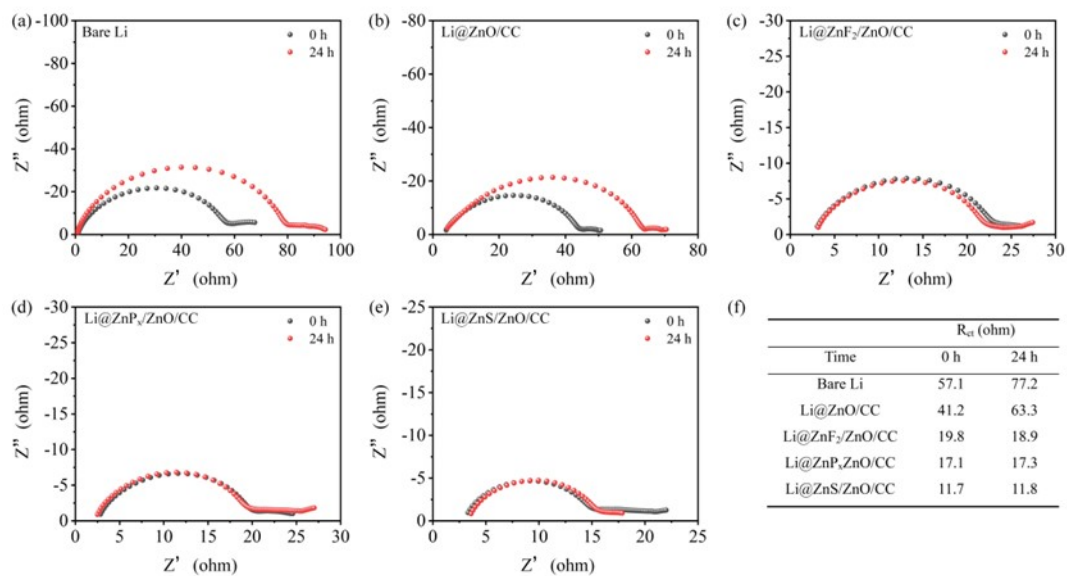
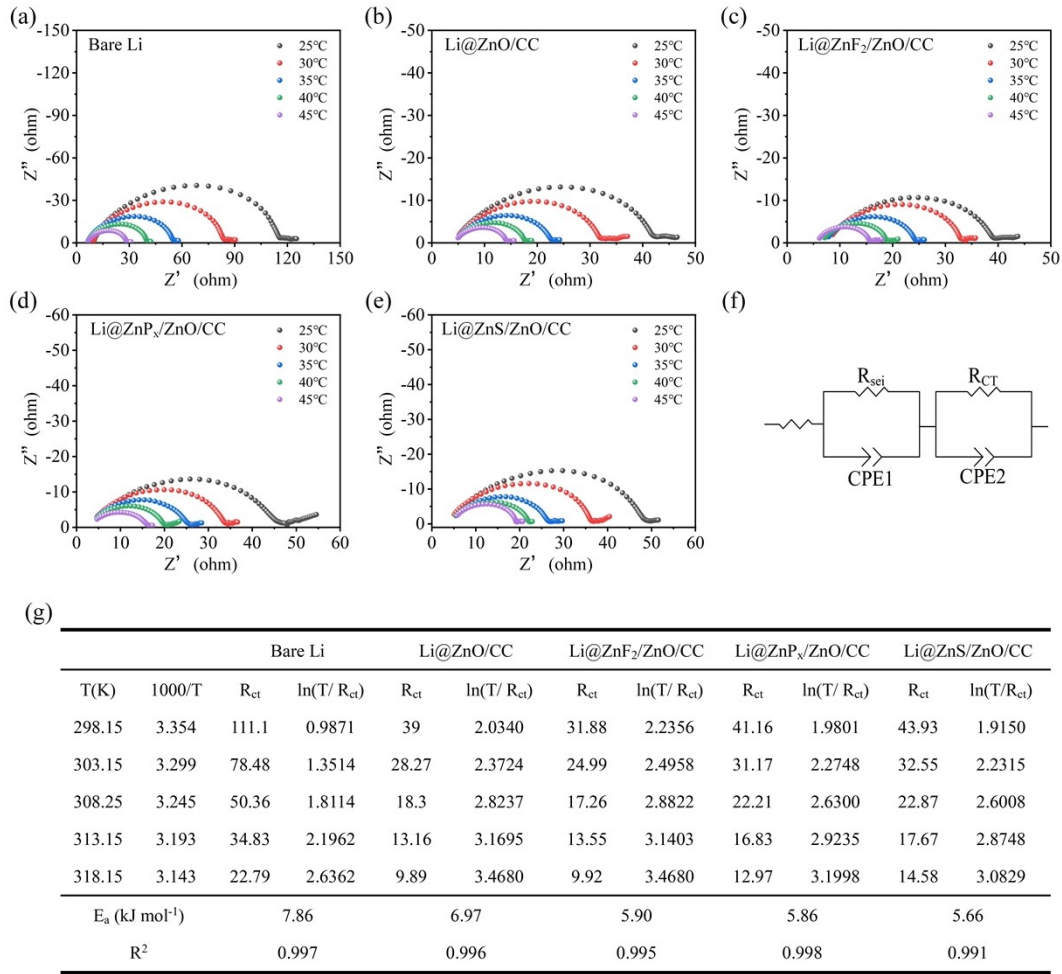Fig. S8 EIS spectra of the symmetric cells with different electrodes after 0 and 24 h.

Fig. S9 Nyquist Plots at various temperatures for symmetric cells with (a) Bare Li, (b) Li@ZnO/CC, (c) Li@ZnF$_2$/ZnO/CC, (d) Li@ZnP$_x$/ZnO/CC, (e) Li@ZnS/ZnO/CC. (f) the equivalent circuit model used for fitting, (g) Corresponding values of RSEI under various temperatures.

And the activation energy for Li deposition could be obtained from the well fitted to straight lines using the Arrhenius equation according to the equation:

$$\frac{T}{R_{ct}} = Aexp(-\frac{E_a}{RT})$$

where E$_a$ is the activation energy, T is the absolute temperature, R is the gas constant, R$_{SEI}$ is the SEI film resistance, and A is the pre-exponential factor
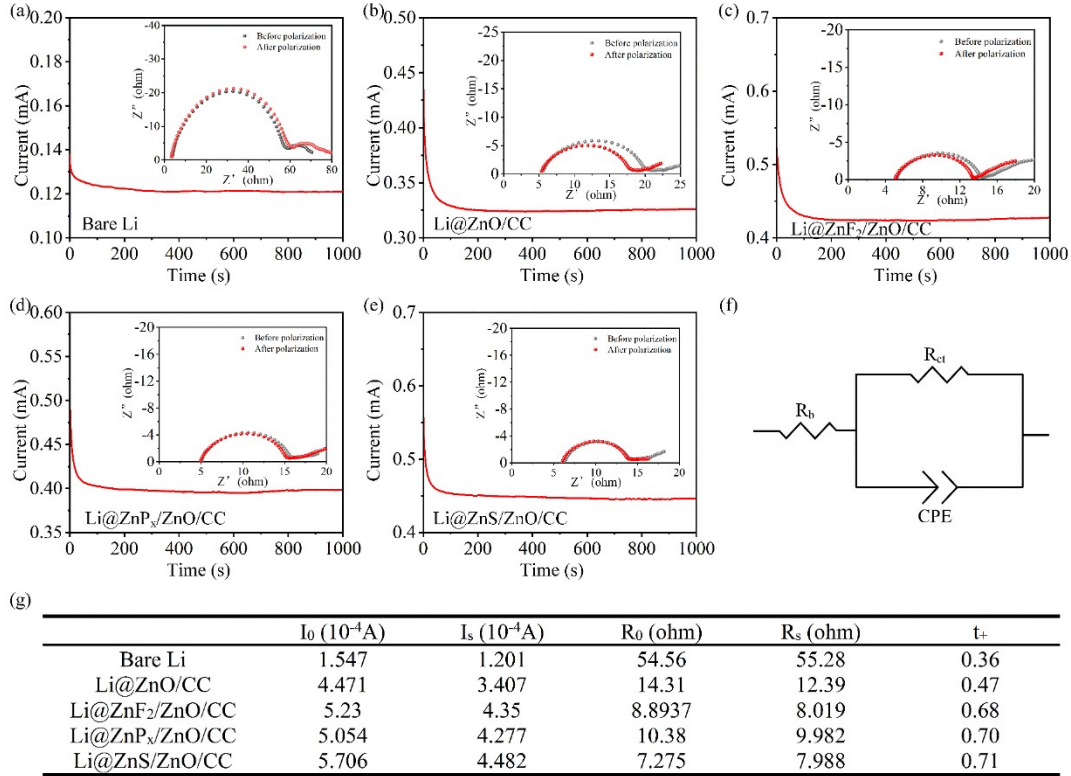
(g)

	I_0 (10^{-4}A)	I_s (10^{-4}A)	R_0 (ohm)	R_s (ohm)	t_+
Bare Li	1.547	1.201	54.56	55.28	0.36
Li@ZnO/CC	4.471	3.407	14.31	12.39	0.47
Li@ZnF$_2$/ZnO/CC	5.23	4.35	8.8937	8.019	0.68
Li@ZnP$_x$/ZnO/CC	5.054	4.277	10.38	9.982	0.70
Li@ZnS/ZnO/CC	5.706	4.482	7.275	7.988	0.71

Fig. S10 (a-e) Current-time plots of the fresh symmetric cells with bare Li, Li@ZnO/CC, Li@ZnF$_2$/ZnO/CC, Li@ZnP$_x$/ZnO/CC and Li@ZnS/ZnO/CC after the application of a constant potential (10 mV). The inserts are the EIS spectra before and after polarization. (f) Equivalent circuit model for fitting, (g) Corresponding values of initial current, steady-state current, initial resistance, steady-state resistance, and Li$^+$ transference number (t$_+$).

The Li$^+$ transference number (t$_+$) was determined by the following equation:

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV is the constant polarization voltage, I$_0$ and R_0 represent the initial current and resistance, respectively, I_s and R_s are the steady-state current and resistance, respectively.
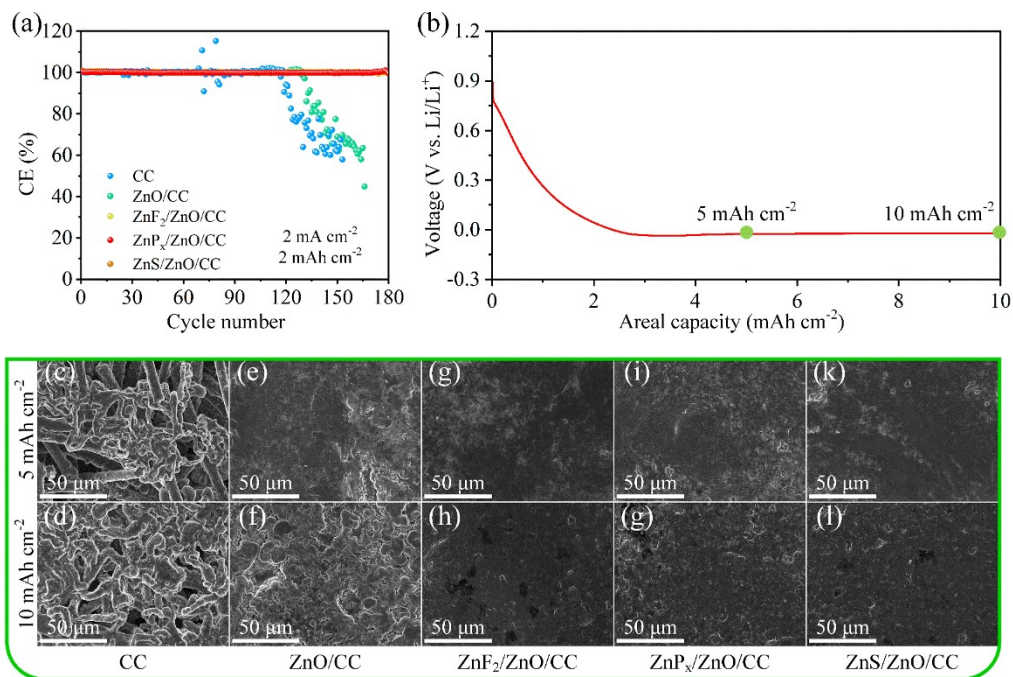
Fig. S11 (a) Coulombic efficiency of CC, ZnO/CC, ZnF_2/ZnO/CC, ZnP_x/ZnO/CC and ZnS/ZnO/CC, (b) Voltage profiles of Li plating at a current density of 1 mA cm^{-2}, (c-l) SEM images of Li plating on (c,d) CC, (e, f) ZnO/CC, (g, h) ZnF_2/ZnO/CC, (i, j) ZnP_x/ZnO/CC and (k, l) ZnS/ZnO/CC with different deposition capacity of 5, 10 mAh cm^{-2} at a current density of 1 mA cm^{-2}.
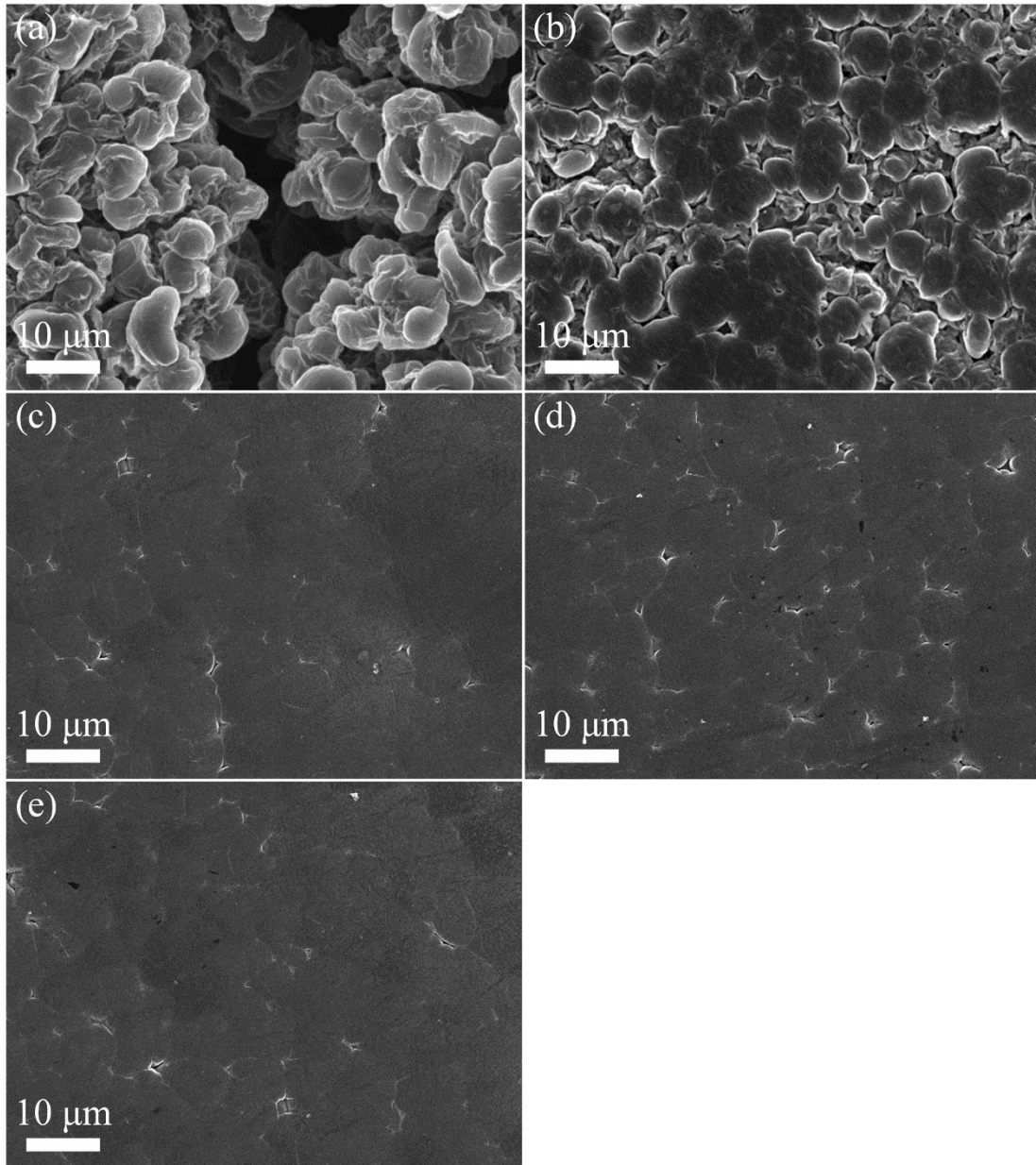
Fig. S12 EX-situ SEM images of (a) bare Li, (b) Li@ZnO/CC, (c) Li@ZnF$_2$/ZnO/CC, (d) Li@ZnP$_x$/ZnO/CC and (e) Li@ZnS/ZnO/CC anodes disassembled from symmetric cell after 100 cycles.
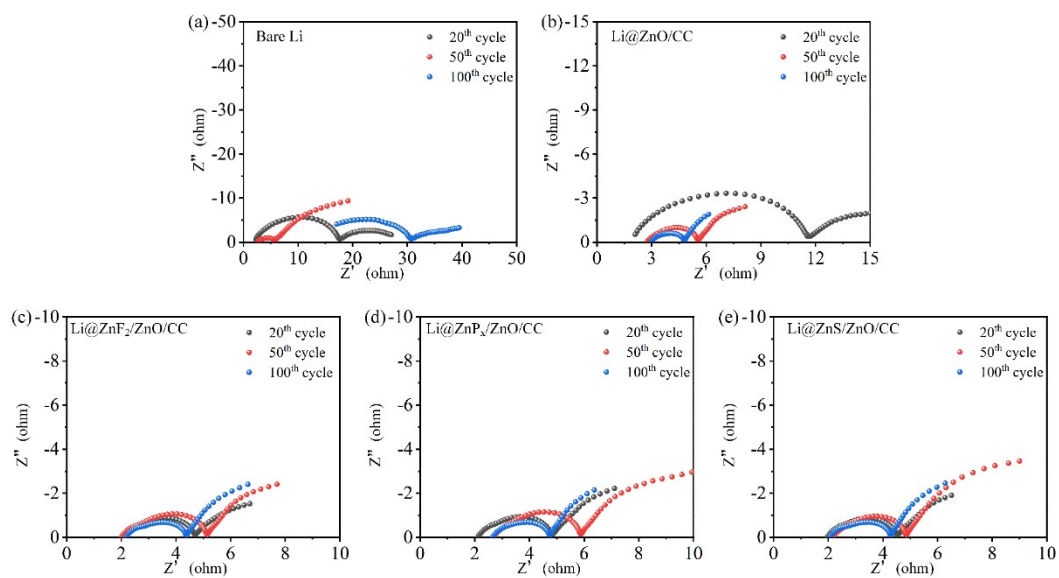
Fig. S13 EIS spectra of the symmetric cells with different electrodes after 20, 50 and 100 cycles at 1 mA cm^{-2} for 1 mAh cm^{-2}.
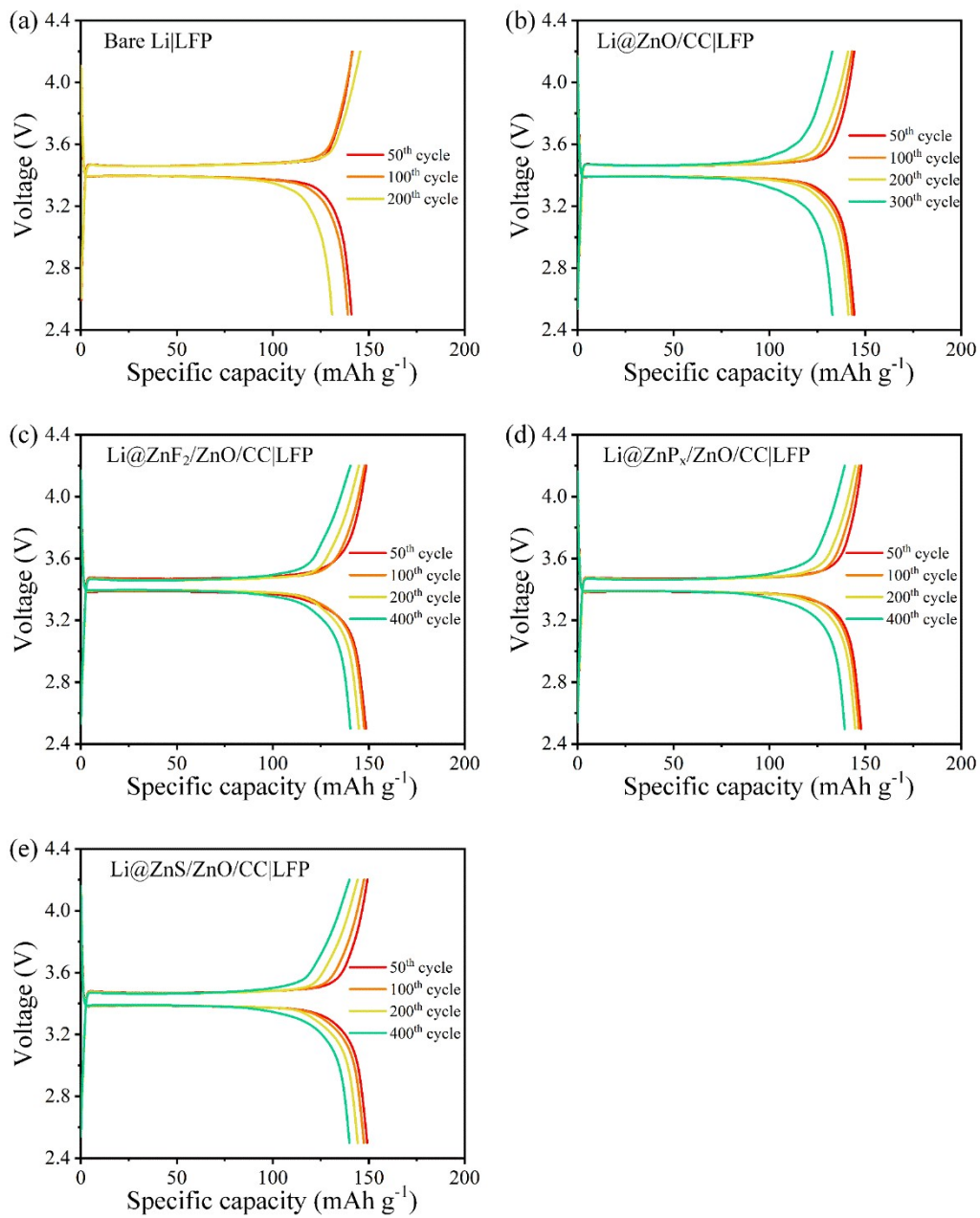
Fig. S14 Voltage profiles of bare Li|LFP, Li@ZnO/CC|LFP, Li@ZnF$_2$/ZnO/CC|LFP, Li@ZnP$_x$/ZnO/CC|LFP, and Li@ZnS/ZnO/CC|LFP full cells at 0.5C.
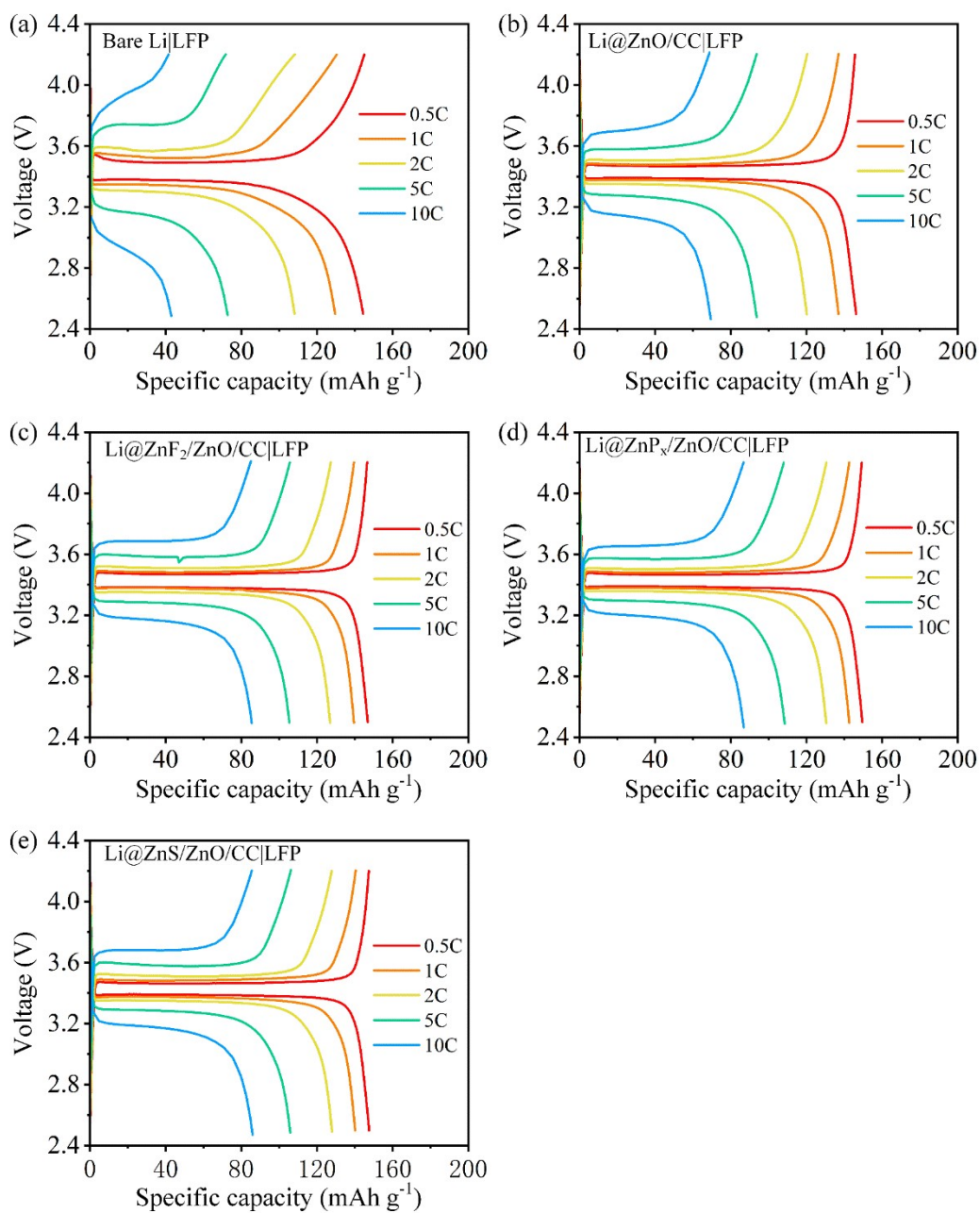
Fig. S15 Voltage profiles of bare Li|LFP, Li@ZnO/CC|LFP, Li@ZnF$_2$/ZnO/CC|LFP, Li@ZnP$_x$/ZnO/CC|LFP, and Li@ZnS/ZnO/CC|LFP full cells at at various rates from 0.5 to 10 C.
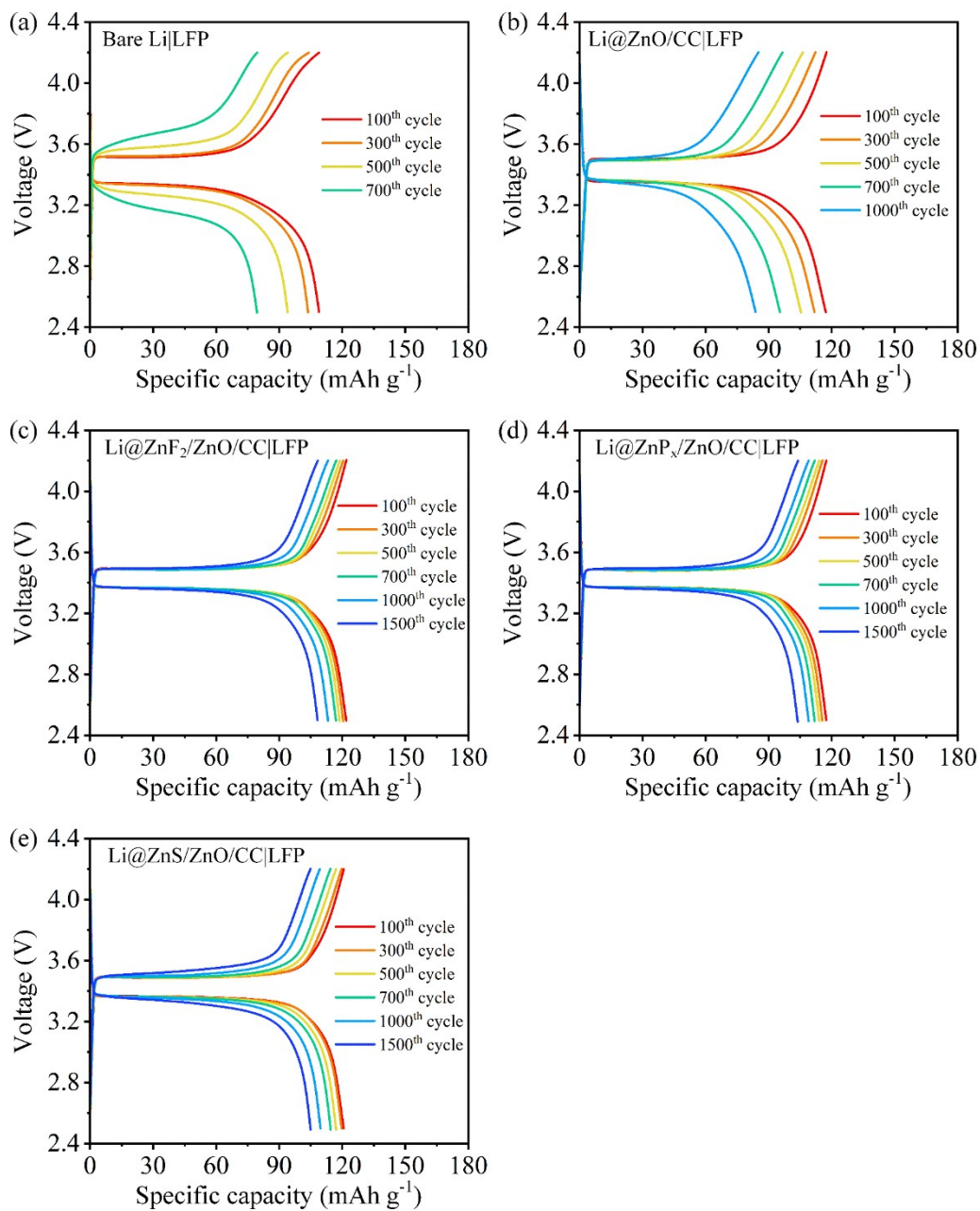
Fig. S16 Voltage profiles of bare Li|LFP, Li@ZnO/CC|LFP, Li@ZnF$_2$/ZnO/CC|LFP, Li@ZnP$_x$/ZnO/CC|LFP, and Li@ZnS/ZnO/CC|LFP full cells at 2C.
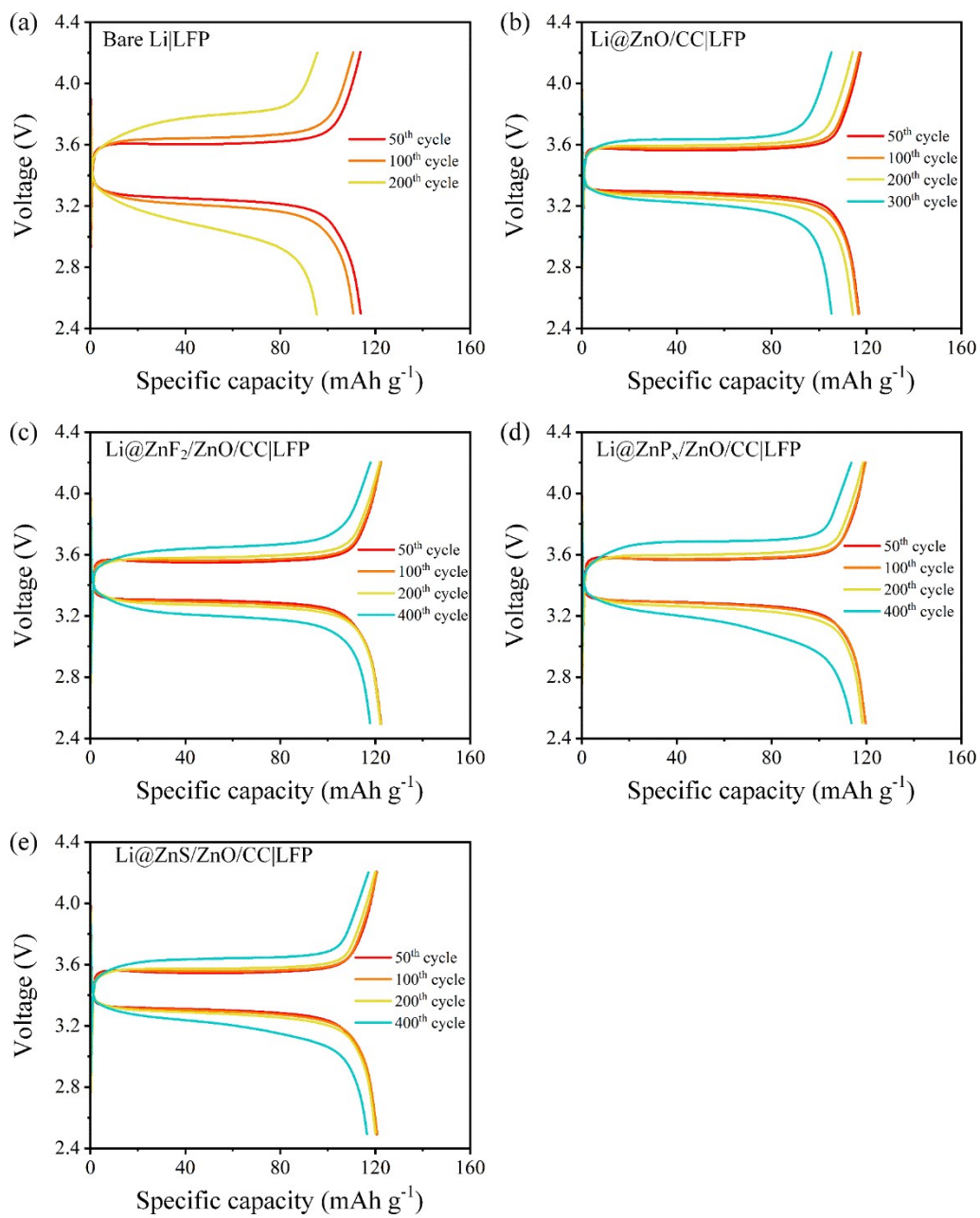
Fig. S17 Voltage profiles of bare Li|LFP, Li@ZnO/CC|LFP, Li@ZnF$_x$/ZnO/CC|LFP, Li@ZnP$_x$/ZnO/CC|LFP, and Li@ZnS/ZnO/CC|LFP full cells at 2C.