Supporting Information

AlF_3-modified carbon nanofibers as multifunctional 3D interlayer for stable lithium metal anode

Cheng Guo [a], Huijun Yang [a], Ahmad Naveed [a], Yanna Nuli [a], Jun Yang [a], Yuliang Cao [b], Hanxi Yang [b], Jiulin Wang*[a]

[a] Shanghai Electrochemical Energy Devices Research Center, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China
[b] College of Chemistry and Molecular Science, Wuhan University, Wuhan 430072, China.

Experimental Section

Preparation of the AlF_3@CNF interlayer

AlF_3@CNFs were prepared by electrospinning and subsequent carbonization. AlF_3 (99.9%, Aladdin) powders were firstly treated by ball milling to get smaller crystal size. Afterwards, AlF_3 powders (20% in weight in PAN) with diameter of submicron were dispersed via ultrasonic in dimethylformamide (DMF, 99.9%, Aladdin). After uniformly dispersing the AlF_3 powder, Polyacrylonitrile (PAN, Aldrich, MW=150,000) was dissolved in as-prepared dispersion (10% in weight in DMF) at 70 °C and was used as the precursor for electrospinning. During the fiber fabrication, the flow rate maintained at 1 mL h^{-1}, and a high voltage of 16 kV was applied between the tip and collector (distance: 15 cm). Finally, a white thin film was collected from the aluminum foil on a drum and was calcinated at 700 °C for 1 h under argon flow. The thickness of the whole AlF_3@CNF interlayer can be easily controlled by the electrospinning process. In this study, the interlayer is thin (ca. 100 μm) and ultralight (ca. 1.8 mg cm^{-2}).

Preparation of the CNF interlayer

The preparation process of the carbon nanofiber (CNF) was similar to the method used for the AlF_3@CNF interlayer. The difference is that the CNF interlayer was obtained without AlF_3 powders added. The CNF interlayer was placed on the top of Cu foil to form a new modified electrode (denoted as Cu-CNF).

Preparation of the Cu-AlF_3/PAN400 electrode

The protective layers were obtained using AlF_3 powders mixed with pre-dissolved PAN solution (10% in weight in DMF), with a weight ratio of 8:2. The slurry was coated on the copper foils. After removing the solvent at 80°C under vacuum, the layers were heated in furnace under argon flow at 400°C for 2 hours.

Electrochemical measurements

The CR2016 coin-type cells were assembled in an Ar-filled glove box for all electrochemical tests. The Celgard 2400 membrane was used as the separator and the solution of 1M $LiPF_6$ in EC/DMC (v/v=1;1) with 10 wt% FEC was used as the electrolyte. For the Coulombic efficiency test, the cells were firstly cycled between 0.01-1.2V at 1 mA for 3 cycles to stabilize the SEI. Cyclic voltammogram measurement (CV) was performed using a CHI760E Electrochemical Workstation

(Shanghai, China) between -0.1 V and 1 V at the scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy (EIS) was measured on an Autolab Workstation (PGSTAT302N, Metrohm) with the frequency ranging from 100 kHz to 0.01 Hz. For full cells, the preparation of S@pPAN cathode materials has been reported in our previous work[1]. The cathode electrodes were prepared by casting a water slurry containing S@pPAN, Super P and carbonyl-β-cyclodextrin binder in a weight ratio of 8:1:1 onto carbon-coated Al foil[2]. The cathodes were cut into discs with a diameter of 12 mm and dried at 60°C before use. The cathode loading was about 1.8 mg cm^{-2}. All electrochemical tests were measured at 25°C.

Materials characterization

For the field emission scanning electron microscopy (SEM, Nova NanoSEM 230, FEI company, USA) analysis, the interlayers after different cycles were first taken out from disassembled cells in an Ar-filled glove box, and then gently rinsed with DMC to remove residual lithium salts and electrolyte. Afterwards, the interlayers were sealed in an Ar-filled container and transferred to the SEM chamber without exposed to air. Powder X-ray diffraction (XRD, D8 Advance, Bruker Corp., Germany) was conducted using Cu-Kα radiation (λ=0.15418 nm) at 40 kV. The thickness of the interlayer was all measured using a micrometer caliper (IP 65, Mitutoyo company, Japan). The resistivity of the whole interlayer was measured using a four-point-probe tester (SB100A-21), and the thickness of the interlayer is 100μm.

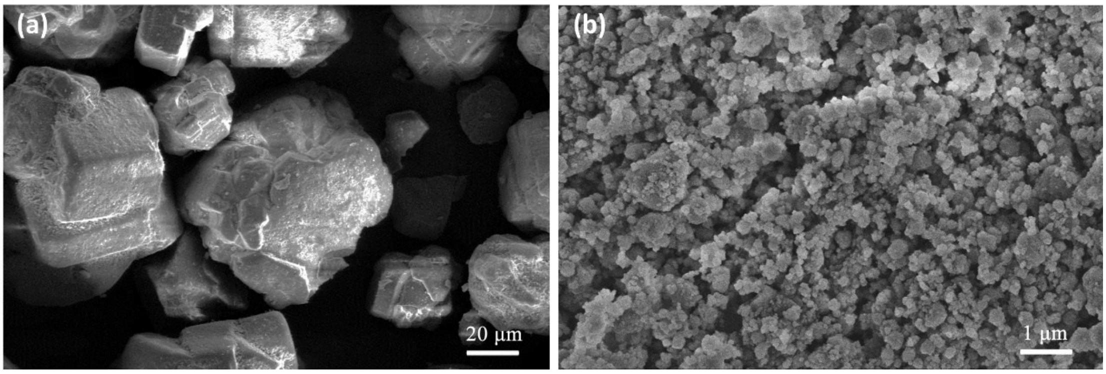

Fig. S1 SEM images of AlF_3 powder (a) before and (b) after ball milling.

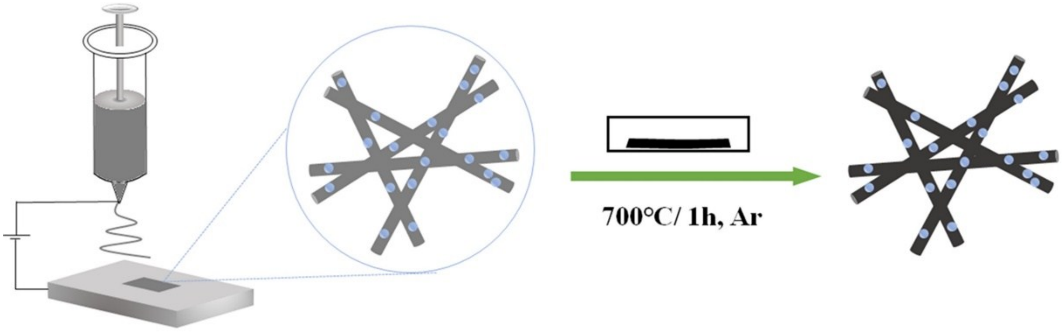

Fig. S2 Schematic illustration of the synthesis procedure of the AlF_3@CNFs.

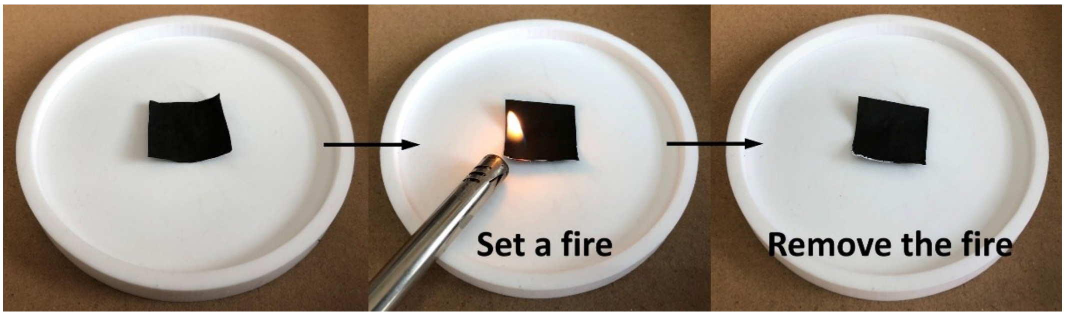

Fig. S3 The nonflammability test of the AlF_3@CNF.

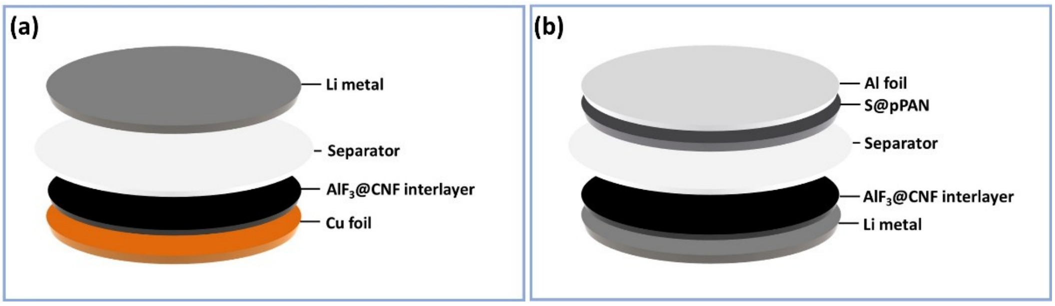

Fig. S4 Schematic diagram of the configurations used for modified electrode with AlF_3@CNF interlayers: (a) Cu-AlF_3@CNF with Li metal as the counter electrode; (b) Li-AlF_3@CNF with S@pPAN as the cathode.

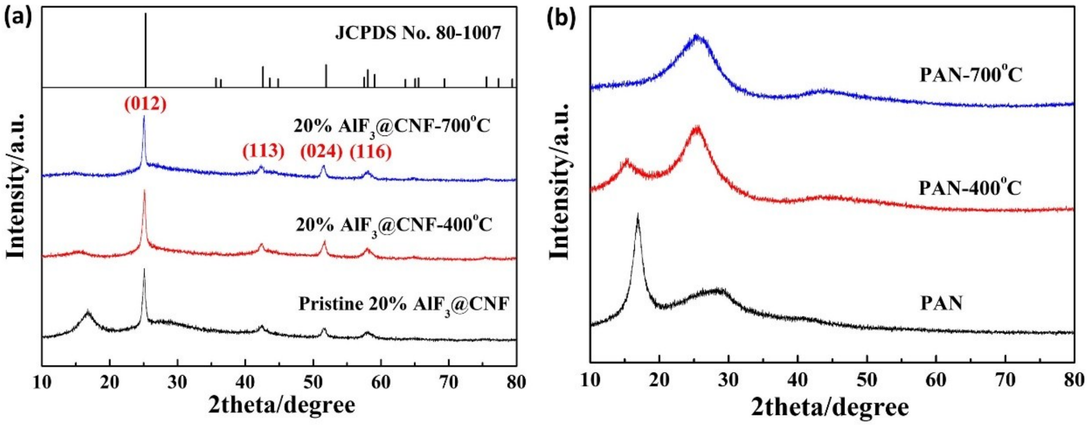

Fig. S5 XRD spectra of (a) 20% AlF$_3$@CNF electrode and (b) PAN powders treated at various temperature.

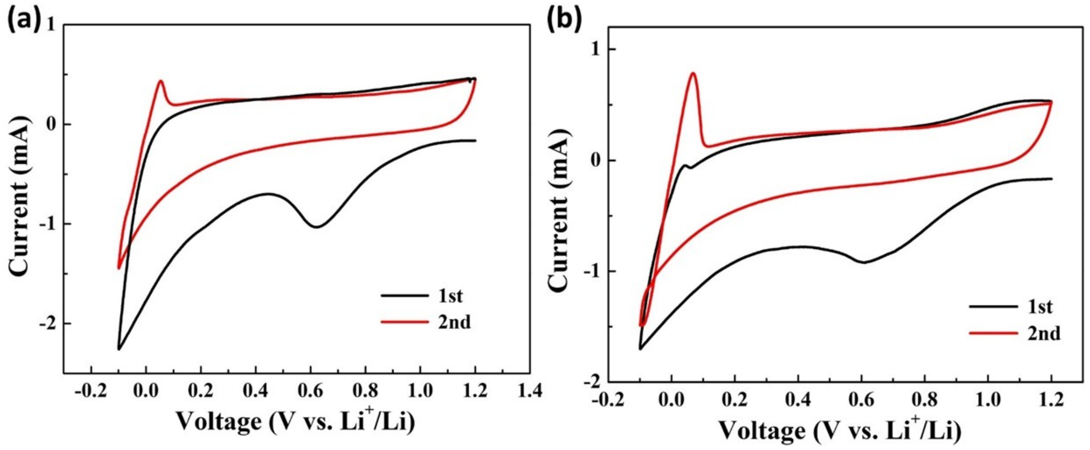

Fig. S6 Cyclic voltammogram of (a) Cu-CNF and (b) Cu-20% AlF$_3$@CNF electrode with Li counter electrode at a sweep rate of 0.1 mV s^{-1}.

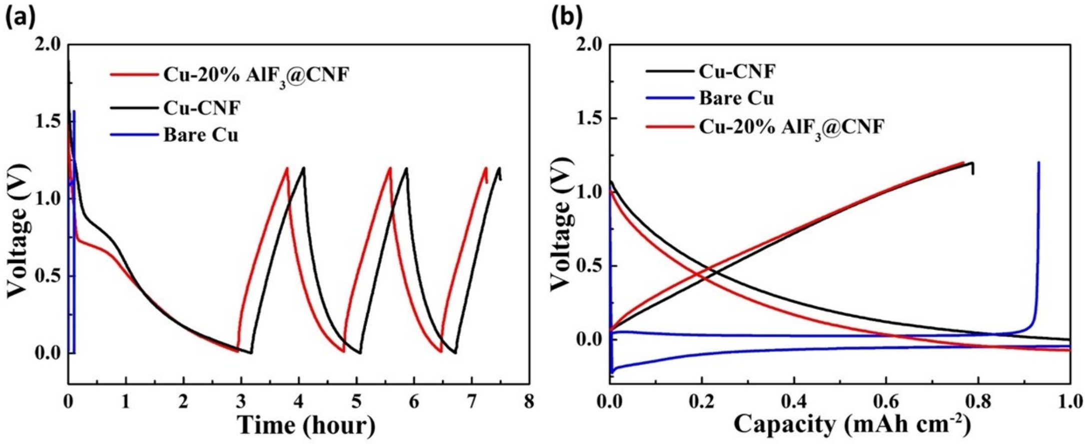

Fig. S7 (a) Voltage profiles during initial activation process of various electrodes. (b) The voltage profiles of the first cycle (after activation) of Bare Cu, Cu-CNF and Cu-20%AlF$_3$@CNF.

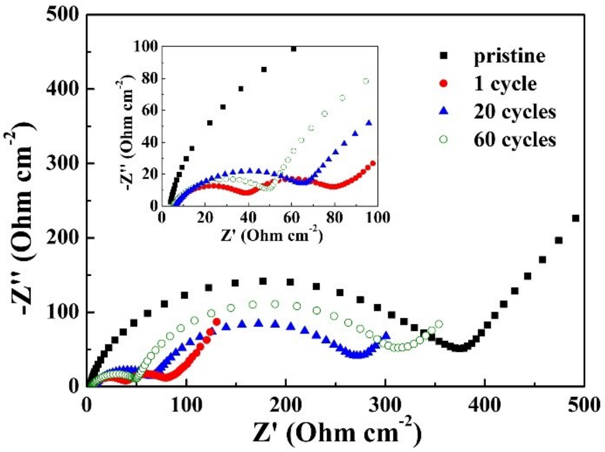

Fig. S8 Nyquist plots of Cu-CNF electrode before and after cycling.

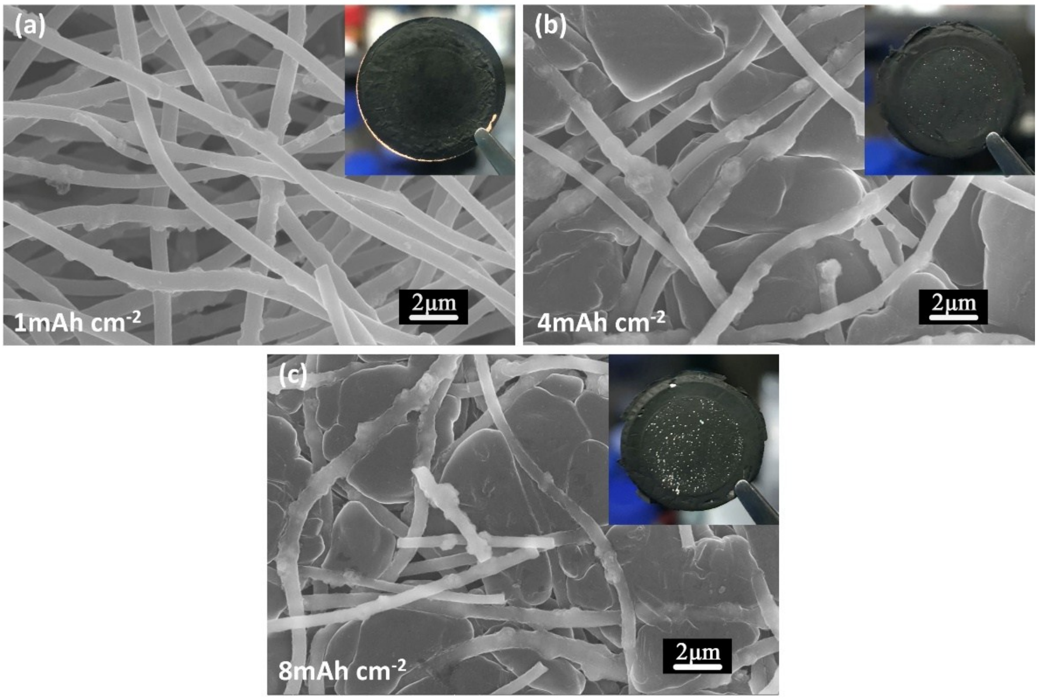

Fig. S9 SEM images of Li deposition on Cu-20% AlF_3@CNF electrode at the current density of 1mA cm^{-2} for different capacities: (a) 1mAh cm^{-2}, (b) 4mAh cm^{-2}, (c) 8mAh cm^{-2}. The inset is the corresponding digital photos.

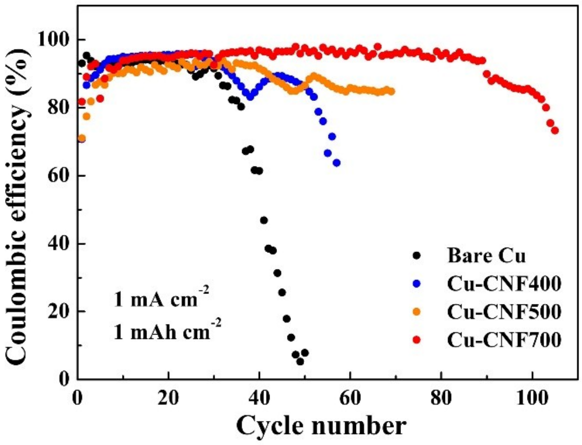

Fig. S10 The comparison of the CE of Li deposition on Cu-CNF electrodes treated at various temperature at 1 mA cm^{-2} for 1 mAh cm^{-2}.

Table S1. Mechanical properties of the PAN fibers treated at various temperatures[3].

Temperature (^oC)	120	300	400	500	600	700
Young's Moduli (GPa)	4	11	10	11	27	**47**

Table S2. Summary of the electrochemical plating/stripping performances in the reported literature.

Materials/electrode	**Components of electrolytes**	**Capacity (mAh cm^{-2})**	**Current density (mA cm^{-2})**	**Cycle life (h)**	**Coulombic efficiency (%)**
3D glass fiber @Cu[4]	1 M LiTFSI in DOL and DME with 2% $LiNO_3$	0.5	1	67h	97
3D oxidized PAN Nanofiber @Cu[5]	1 M LiTFSI in DOL and DME with 2% $LiNO_3$	1	1	240h	97.9%
PAN fiber array @Cu[6]	1 M LiTFSI in DOL and DME with 2% $LiNO_3$	1	1	500h	97.4%
Interconnected hollow Carbon @Cu[7]	1 M LiTFSI in DOL and DME with 1% $LiNO_3$ and Li_2S_8 additives.	1	1	300h	97.5%
3D Graphene@Ni Scaffold[8]	1 M LiTFSI in DOL and DME with 2% $LiNO_3$	1	1	200h	92%
LiF with PAN binder @Cu[3]	1 M $LiPF_6$ in EC and DEC with 5% FEC	1	1	400h	95%
SiO_2@PMMA coating layer@Cu[9]	1 M $LiPF_6$ in EC and DEC with additives	2	1	~200h	87% (After 100 cycles)
VGCF@GF[10]	1 M $LiPF_6$ in EC and DEC with 5% VC	2.5	0.5	965h	91.1% (After 100 cycles)
This work	1 M $LiPF_6$ in EC and DMC with 10% FEC	1	1	900h	97.2%
		8	1	740h	97.3%

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