Supporting Information

**AlF₃-modified carbon nanofibers as multifunctional 3D interlayer for stable lithium metal anode**

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

*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.

Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2018
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, Polyanionitrile (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-K\(\alpha\) radiation (\(\lambda=0.15418\) 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 100\(\mu\)m.
**Fig. S1** SEM images of AlF₃ powder (a) before and (b) after ball milling.

**Fig. S2** Schematic illustration of the synthesis procedure of the AlF₃@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% AlF₃@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$^{-2}$. 

8
Table S1. Mechanical properties of the PAN fibers treated at various temperatures\[^3\].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>120</th>
<th>300</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s Moduli (GPa)</td>
<td>4</td>
<td>11</td>
<td>10</td>
<td>11</td>
<td>27</td>
<td>47</td>
</tr>
<tr>
<td>Materials/electrode</td>
<td>Components of electrolytes</td>
<td>Capacity (mAh cm$^{-2}$)</td>
<td>Current density (mA cm$^{-2}$)</td>
<td>Cycle life (h)</td>
<td>Coulombic efficiency (%)</td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>---------------------------</td>
<td>---------------------------</td>
<td>-----------------------------</td>
<td>----------------</td>
<td>-------------------------</td>
<td></td>
</tr>
<tr>
<td>3D glass fiber @Cu$^4$</td>
<td>1 M LiTFSI in DOL and DME with 2% LiNO$_3$</td>
<td>0.5</td>
<td>1</td>
<td>67h</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>3D oxidized PAN Nanofiber @Cu$^5$</td>
<td>1 M LiTFSI in DOL and DME with 2% LiNO$_3$</td>
<td>1</td>
<td>1</td>
<td>240h</td>
<td>97.9%</td>
<td></td>
</tr>
<tr>
<td>PAN fiber array @Cu$^6$</td>
<td>1 M LiTFSI in DOL and DME with 2% LiNO$_3$</td>
<td>1</td>
<td>1</td>
<td>500h</td>
<td>97.4%</td>
<td></td>
</tr>
<tr>
<td>Interconnected hollow Carbon @Cu$^7$</td>
<td>1 M LiTFSI in DOL and DME with 1% LiNO$_3$ and Li$_2$S$_8$ additives.</td>
<td>1</td>
<td>1</td>
<td>300h</td>
<td>97.5%</td>
<td></td>
</tr>
<tr>
<td>3D Graphene@Ni Scaffold$^8$</td>
<td>1 M LiTFSI in DOL and DME with 2% LiNO$_3$</td>
<td>1</td>
<td>1</td>
<td>200h</td>
<td>92%</td>
<td></td>
</tr>
<tr>
<td>LiF with PAN binder @Cu$^3$</td>
<td>1 M LiPF$_6$ in EC and DEC with 5% FEC</td>
<td>1</td>
<td>1</td>
<td>400h</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$@PMMA coating layer@Cu$^9$</td>
<td>1 M LiPF$_6$ in EC and DEC with additives</td>
<td>2</td>
<td>1</td>
<td>~200h</td>
<td>87% (After 100 cycles)</td>
<td></td>
</tr>
<tr>
<td>VGCF@GF$^{10}$</td>
<td>1 M LiPF$_6$ in EC and DEC with 5% VC</td>
<td>2.5</td>
<td>0.5</td>
<td>965h</td>
<td>91.1% (After 100 cycles)</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>1 M LiPF$_6$ in EC and DMC with 10% FEC</td>
<td>1</td>
<td>1</td>
<td>900h</td>
<td>97.2%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>8</td>
<td>1</td>
<td>740h</td>
<td>97.3%</td>
<td></td>
</tr>
</tbody>
</table>
References