Supporting Information

Highly stable Lithium plating by a hybrid electrolyte additive in lithium-sulfurized polyacrylonitrile Battery

Yi Shuai,a Zeping Zhang,b Kanghua Chen*,ab Jin Loua and Yu Wangb

aLight Alloy Metal Research Institute, Central South University, Changsha 410083, China
bState Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China

AUTHOR INFORMATION

Corresponding Author

*E-mail: kanghuachen@csu.edu.cn

1.Experimental Section

Materials Synthesis

The S@PAN are prepared as reported and was used for preparing electrode as follows: the slurry was prepared by mixing S@PAN, acetylene black, and CMC in a mass ratio of 7:2:1, and stirred with deionized water, then the slurry was coated onto aluminum foil using doctor blade and dried under vacuum, then punched into 18 mm disks as the working electrode. The typical S@PAN loading is about 6-7 mg·cm$^{-2}$.

KNO$_3$ (aladdin) was dried at 90°C in vacuum overnight before use. The neat electrolyte is 1 M LiPF6 in ethylene carbonate/dimethyl carbonate (EC/DMC/EMC), which obtained from fusai corporation and used without further drying. The control electrolyte (FEC+KNO$_3$) was prepared by adding 25 vol.% FEC and 0.1M KNO$_3$ into the neat electrolytes and stirring overnight, and the FEC electrolyte was added only 25 vol.% FEC.

Materials Characterizations

Morphological was obtained by using scanning electron microscope (SEM). The composition of the Li-deposited Cu foil was determined by energy dispersive X-ray spectroscopy.
**Electrochemical measurement**

The CR2032-type coin cells were assembled in an Ar-filled glove and tested using LAND-CT2001A testers. The Li-S@PAN battery is conducted with the limited electrolyte (7 μl/mg S@PAN), in which, S@PAN is used as cathode and lithium metal foil as anode, while Celgard 2400 used as the separator. Cyclic voltammetry (CV) was conducted on a CHI660e electrochemical workstation at a scanning rate of 0.5 mV s⁻¹, and AC impedance of symmetric lithium cells were measured over the frequency range from 0.1 MHz to 1 Hz. All the electrochemical measurements were carried out in a dry atmosphere at 25 °C.

**2. Supporting Figures**

![Graph](image)

**Figure S1** EDX signals of the deposited Li metal from Li-S@PAN battery after 5 cycles

As shown in Fig. S2a and S2b, after lithium plating, clear dendritic growth is observed in the neat electrolyte and the electrode is fully filled with tenuous lithium dendrites, while no obvious lithium dendrites exist in the cell containing FEC+KNO₃ (Fig. S2e and S2f). Meanwhile, after lithium stripping, obvious fractured lithium dendrite residues remain on the copper foil for the neat electrolyte, while no obvious lithium dendrites exist on the copper foil for the FEC+KNO₃ electrolyte (Fig. S2c and S2g). The growth of lithium dendrites not only poses a danger of the separator becoming pierced, causing a short circuit in the battery, but also constantly depletes the electrolyte until it will no longer meet the necessary demands for charging and discharging the Li-S@PAN battery. Besides, as shown in Fig. S2d and S2h, the lithium layer for the neat electrolyte is fluffy and has a thickness of about 79 mm after stripping. However, for the FEC+KNO₃ electrolyte, the lithium layer thickness is merely 27% (about 21 mm) of that of the neat electrolyte and the cross section remains pyknotic. It is clear that the FEC+KNO₃ additive promotes the formation of a stable SEI surface and keeps the battery stable for a perfect electrochemical charge/discharge performance.
Figure S2 Surface morphology of lithium plating/stripping for Li-Cu cell: (a, b) the neat electrolyte at 1 mA cm$^{-2}$ for 2 h after Li plating and (c) after Li stripping; (e, f) the FEC+KNO$_3$ electrolyte 1 mA cm$^{-2}$ for 2 h after Li plating and (g) after Li stripping; (d, h) the cross-section morphologies of Li metal anode with neat electrolyte and with FEC+KNO$_3$ electrolyte.

3. Reference