Supplementary Information

Long life-span of Li-metal anode enabled by a protective layer

based on the pyrolyzed N-doped binder network

Zhenggang Zhang,^{a,d,f} Zhe Peng,^a* Jieyun Zheng,^b Susu Wang,^{a,c} Zixuan Liu,^a Yujing Bi,^a

Yousi Chen,^{a,c} Gang Wu,^e Hong Li,^b Ping Cui,^a Zhaoyin Wen,^d* and Deyu Wang^a*

a. Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

b. Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China.

c. National Engineering Laboratory for Carbon Fiber Preparation Technology, Ningbo 315201, China.

d. CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China.

e. Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, 309 Furnas Hall, Buffalo, New York 14260-4200, United States.

f. University of Chinese Academy of Sciences, Beijing, 100049, China.

Corresponding Authors

E-mail:

- (Z. P.) pengzhe@nimte.ac.cn;
- (Z. W.) zywen@mail.sic.ac.cn;
- (D. W.) wangdy@nimte.ac.cn.

Supplementary Figures



Fig. S1 Capacities of pyrolyzed PAN at various temperatures, for the 1st, 2nd and 50th cycles. The working electrodes are pyrolyzed PAN:SP:PVdF (8:1:1), the counter electrodes are Li foils, and the electrolyte is 1 M LiPF_6 in EC:DEC:EMC (1:1:1).



Fig. S2 Digital photos of the electrodes with porous layers prepared at various temperatures.



Fig. S3 Charge-discharge curvy of the 1st Li plating/striping cycle in the electrodes with porous layers prepared at various pyrolysis temperatures.



Fig. S4 Coulombic efficiency of Li plating/stripping in the electrode with porous layer prepared at 700 °C.



Fig. S5 SEM images of the electrodes with porous layers prepared at various temperatures.



Fig. S6 XRD pattern and SEM image of the used LiF powders in this work, with a typical size of 20-30 μ m. The well-defined XRD pattern justifies the high material purity.



Fig. S7 Cross-sectional SEM images of the PAN-based porous layer formed at 400 °C with nano-sized Al_2O_3 powders, (a) before and (b) after cycling.



Fig. S8 (a) SEM image and (b) digital photo of the PAN layer prepared at 120 °C; (c) digital photo of the PAN layer pyrolyzed at 400 °C, with serious pulverizations.



Fig. S9 SEM images of the PAN binder networks prepared at (a) 120 °C and (b) 400 °C, using LiCl to replace LiF in the porous layers followed by the removal in water.



Fig. S10 (a) TG curves of PVDF and PAN; (b) Coulombic efficiencies of Li plating/stripping in the electrodes with porous layers based on PVDF binders prepared at various pyrolysis temperatures.



Fig. S11 C 1s XPS spectrum of a typical SEI layer formed on Li metal in carbonatebased electrolyte (LiPF₆ in EC:DEC).



Fig. S12 Charge-discharge capacities of the Cu-LiFePO₄ cells with/without the porous layer prepared at 400 °C, the investigated Cu electrodes are directly paired with LiFePO₄ cathodes to construct the "anode-free" batteries. The mass loading of (LiF+PAN400) is ~ 0.35 mg cm⁻², on the Cu foil.