Electronic Supplementary Information

Anchoring Anions by Metal-Organic Framework-Functionalized Separators for Advanced Lithium Batteries

Li Shen¹, Hao Bin Wu^{2*}, Fang Liu¹, Chen Zhang¹, Shengxiang Ma¹, Zaiyuan Le¹ and Yunfeng Lu^{1*} ¹Department of Chemical and Biomolecular Engineering, University of California, Los Angeles,

420 Westwood Plaza, Los Angeles, California 90095, United States. Email: luucla@ucla.edu

²School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China. Email: hbwu@zju.edu.cn

* To whom all correspondence should be addressed.

Experimental Sections

Preparation of MOG separators.

The MOF precursors were prepared by dissolving NH_2 –BDC (62 mg) and $ZrCl_4$ (80 mg) in mixture of 20 mL DMF and 0.025 mL H_2O . Glass fiber (Whatman, GF/C) disks with a diameter of 18 mm were soaked in MOF precursors. After sonicating for 30 min and aging for overnight, the *in–situ* growth of MOF on GF was carried out in a microwave reactor (900 W) at 120 °C for 20min. After reaction, the yellowish separators were repeatedly rinsed by DMF and Methanol, followed by drying at vacuum oven at 80 °C.

Materials characterizations.

The morphology was examined by SEM using Nova Nano 230 (FEI). Thin layer of gold was coated on samples by plasma sputtering before analysis. Crystalline structure was determined by Rigaku powder XRD using K α radiation (λ = 1.54 Å) run at 30 kV and 15 mA. A Jasco 420 FTIR spectrophotometer was used to collect infrared spectra in transmission mode. The N₂ adsorption/desorption curves were acquired by ASAP 2020 plus (Micrometrics) at 77 K. The surface area was calculated based on the Brunauer–Emmett–Teller (BET) equation from the adsorption branch. The pore size distribution was derived from Density Function Theory (DFT) models. All samples before tests were degassed at 200 °C for 24 h. The TGA was carried out by heating samples in air atmosphere by ramping rate of 5 °C min⁻¹.

Electrochemical characterizations.

The separators were thermally activated at 200 °C under dynamic vacuum to remove residual solvents and generate open metal sites. Liquid electrolyte used is 1 M LiClO₄ in propylene carbonate. All characterizations were performed in coin cell (CR2032) configuration and volume of electrolyte was ~100 ul. The Li⁺ transference number was evaluated by conventional Bruce-Vincent method in lithium symmetric cell. The cells were polarized by a small constant potential (V, 20 mV) for 30 mins, and the corresponding polarization currents including the initial current (I_0) and final steady-state current (I_{ss}) were recorded. Meanwhile, the interfacial resistance before (R_{int}⁰) and after (R_{int}^{ss}) potentiostatic polarization were derived from EIS (Solartron) by alternating current amplitude of 20 mV from 100 kHz to 1 Hz. The Li⁺ transference number was calculated as following equation: $t_{Li+} = I_{ss}(V-I_0R_{int}^0)/(I_0(V-I_{ss}R_{int}^{ss}))$. The ionic conductivity was measured by sandwiching electrolyte saturated separators by two blocking electrodes (stainless steel plates), which is approximated by equation: $\sigma=4L/\pi RD^2$, where σ is conductivity; L and D are thickness and diameter of separator, respectively; R is resistance value from EIS. Activation energy (E_a) from Arrhenius behavior of conductivity ($\sigma = \sigma_0 \exp(-E_a/RT)$) was derived by linear fitting between $\log(\sigma)$ and 1000/T. The measurements were conducted in convection oven (VWR) by equilibrating the cells at various temperatures. The electrochemical stability window was determined by CV using lithium foils as reference/counter electrodes and stainless-steel plates (SS) as the working electrodes. The cells were tested between -0.2 and 5 V at 1 mV s⁻¹ (Biologic).

The polarization of Li⁺ plating and stripping in Li|Li cells were carried out at 1.5 mA cm⁻² for a periodic 2 h. The Coulombic efficiency in Cu|Li cells were obtained by plating at small current density (0.5 mA cm⁻² for 1 h) or high current density (1 mA cm⁻² for 2 h), and stripping to voltage cutoff at 1.2 V (*vs.* Li/Li⁺). LiFePO₄ electrodes were fabricated by mixing LiFePO₄, poly(vinylidene difluoride) and carbon nanootube in mass ratio of 85:10:5 at N-methyl-2-pyrrolidone. The blends were casted on carbon-coated aluminum and dried at 80 °C under vacuum. The thickness or

loading of electrodes were controlled by tuning the slurry viscosity and height of doctor blade. Li₄Ti₅O₁₂ electrodes were prepared in the same manner and the weight ratio between LiFePO₄ and Li₄Ti₅O₁₂ in full cells is 1:1.

Supplementary Figures



Figure S1. (a) Representative structure of UiO-66-NH₂ analogue (UiO-66) showing Zr metal clusters (purple polyhedrons) and bridging ligands (in gray). Micropores are represented by semi-transparent yellow spheres. (b) Scheme showing the possible interaction between anions (green spheres) and open metal sites in abbreviated Zr cluster core (Zr_6O_6) (Zr in purple, O in red).



Figure S2. N_2 adsorption/desorption isotherms of (a) MOF, (b) MOG and (c) GF. Insets show corresponding pore size distribution.



Figure S3. Photographs showing (a) MOG and (b) polypropylene separators after heating at 200 °C under dynamic vacuum (the original size is 18 mm in diameter).



Figure S4. TGA curves of GF and MOG up to 700 °C in air atmosphere.

Activation of defect-free UiO-66-NH₂:

 $Zr_6O_4(OH)_4(NH_2-BDC)_6(s) \rightarrow Zr_6O_6(NH_2-BDC)_6(s) + 2H_2O(g)$

Oxidative decomposition of activated UiO-66-NH₂:

$$Zr_6O_6(NH_2-BDC)_6(s) + 54O_2(g) \rightarrow 6ZrO_2(s) + 48CO_2(g) + 6NO_2(g) + 18H_2O(g)$$



Figure S5. Li⁺ transference number of liquid electrolyte in (a) GF separator and (b) polypropylene (PP) separator.



Figure S6. FTIR spectra of LPC and LPC-saturated MOG.



Figure S7. Lithium deposition/stripping efficiency in Cu|Li cells using GF and MOG at 0.5 mA cm^{-2} and 0.5 mAh cm^{-2} .



Figure S8. Voltage–capacity profiles of LiFePO₄|Li cells at various rates with (a) GF and (b) MOG separators.



Figure S9. Voltage–capacity profiles of LiFePO₄|Li cells with GF and MOG separators from 106th to 109th cycle.



Figure S10. SEM images of Li electrodes collected from cycled LiFePO4|Li cells with (a-b) GF and (c-d) MOG separators (after 100 cycles at 1C).



Figure S11. Voltage–capacity profiles of LiFePO₄ | $Li_4Ti_5O_{12}$ full cells using GF and MOG separators at 1000th cycle and current density of 0.5 C (4 mA cm⁻²).