Electronic Supplementary Information

Semiliquid Electrolytes with Anion-Adsorbing Metal-Organic Frameworks for High-Rate Lithium Batteries

Li Shen*, Xinru Li, Xing Lu, Dejia Kong, Alexis Fortini, Chen Zhang, and Yunfeng Lu*

Department of Chemical and Biomolecular Engineering, University of California, Los Angeles, 420 Westwood Plaza, Los Angeles, California, 90095, United States

*Correspondence and requests for materials should be addressed to: L. S., Y. L. (email: <u>lishen@ucla.edu</u>, <u>luucla@ucla.edu</u>)

Synthesis of UiO-66-NH₂. The MOF (UiO-66-NH₂) was synthesized based on a facile hydrothermal method according to a reported literature. Typically, 5 mmol 2– aminoterephthalic acid (NH₂-BDC), 3 mmol ZrCl₄ and 22.4 mmol HCl (35 wt-%) were added into 150 mL dimethylformamide (DMF) for 30 minutes continuously stirring. The excessive ligands ratio over metal salt and addition of concentrated HCl were intended for modulating the growth Zr cluster nodes as well as obtaining highly crystalline products, especially for UiO-66-NH₂. The transparent mixture after fully dissolution was transferred into a 250 mL glass bottle at pre-heated 120 °C for 21 hours. The pale-yellow precipitates were collected *via* centrifugation and thoroughly washed by DMF (3 times) and methanol (3 times).

Materials characterization. SEM images were acquired by Nova 230 Nano SEM at acceleration voltage of 10 kV. The XRD patterns were collected by Rigaku powder X-ray diffractometer (XRD), operating at 30 kV/15 mA with K α radiation (λ = 1.54 Å). N₂adsorption and desorption isotherms were obtained by ASAP 2020 plus (Micrometrics) at 77 K, the corresponding pore size distribution was derived from Density Function Theory (DFT) models. Before each isotherm, the samples were subject to degas at 150 °C overnight to remove guest molecules condensed in the pores. Infrared spectra were performed on a Fourier transform infrared (FTIR) spectrophotometer (Jasco 420) using transmission mode. For XPS studies, the cycled Li|Li cells were dissembled in glovebox, the harvested Li electrodes were then sealed in a transporter and immediately transferred to high-vacuum chamber of XPS (AXIS Ultra DLD). The obtained spectra were calibrated by C 1s peak at 284.8 eV and fitted to Gaussian-Lorentzian functions for peak deconvolutions.

Electrochemical characterization. 1 M LiClO₄ in PC (LPC) liquid electrolytes were homemade by dissolving LiClO₄ (Sigma, 99.99%) in PC (Sigma) with 5 vol-% additives of fluoroethylene carbonate (FEC). Before preparation, drying of LiClO₄ salts in vacuum oven (150 °C) overnight was conducted to remove trace amount of moisture.1 M LiPF₆ in EC/DEC (weight ratio of 1:1) and 1M LiTFSI in DOL/DME (volume ratio of 1:1) are commercially available and used as received (BASF). The activation of MOF was carried out by thermal activation at 200 °C under dynamic vacuum. 0.2MOF-LE were prepared by combining every 0.2 mg activated MOF with 1 μ L LE. The well-dispersion of MOF in LE was achieved by rigorous magnetic stirring of the mixture. For FTIR studies on LE confined within MOF, flow–free powders (LE@MOF) were collected by vacuum filtration of 0.2MOF-LE.

The ionic conductivity of 0.2MOF-LE and LE were measured by sandwiching electrolyte

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saturated glass fibers (Whatman, GF/C) between two stainless steel electrodes in coin cell configuration. The glass fiber separators were tailored into disks with identical diameter (D) and varying thickness (L) between 180 and 210 μ m. The resistances (R) of electrolyte were obtained by EIS (Solartron) and respective conductivity (σ) is approximated by calculating (4L/ π RD²). The temperature dependent conductivities were collected by equilibrating coin cells in a convection oven (VWR) at various temperatures. The results were linearly fitted into Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/RT)$ and activation energies (E_a) were derived from the sloping of lines (coefficient of determination r²>0.99).

Li⁺ transference number was evaluated by a potentiostatic polarization method coupled with EIS technique in Li|Li cells. Typically, the cells were subject to a micropotential (V, 20 mV) polarization in period of 30 minutes, yielding the initial current (I₀) and steady-state current (I_{ss}). To exclude the impact of interfacial evolution, the interfacial resistance before (R_{int⁰}) and after (R_{int^{ss}}) polarization were determined by EIS. The t_{Li}⁺ could thereby be calculated by the formula: $t_{Li+} = I_{ss}(V-I_0R_{int}^0)/(I_0(V-I_{ss}R_{int}^{ss}))$.

CV tests were performed in a two-electrode configuration using coin type cells (CR2032), where lithium disks were utilized as reference/counter electrodes and stainless-steel plates (SS) were used as the working electrodes. Electrolyte-saturated PP separators (MTI) were sandwiched between two electrodes. The tests were performed between –0.2 and 5 V (*vs.* Li/Li⁺) at 1 mV s⁻¹ (Biologic).

Li stripping and plating tests were conducted by Li|Li symmetric cells, where LE and 0.2MOF-LE with equivalent amount of 30 μ L were used as electrolytes. The cells were performed under 0.25 mA cm⁻² by time interval of 1 hour. To evaluate the compatibility of electrolytes with commercial electrode including LiFePO₄ (LFP) and LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ (NCM). Home-made electrodes were prepared by a conventional blade coating method. Slurries were prepared by homogeneously mixing active materials, carbon black (CB), and polyvinylidene fluoride (PVdF) based on a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP). The slurries were coated on aluminum foil and dried in vacuum oven at 80 °C. The loading of active LFP is ~2 mg cm⁻² and NCM is ~6 mg cm⁻². LFP|Li and NCM|Li cells were assembled in glove box (O₂ < 0.5ppm) using 30 μ L electrolytes and propylene-based separators (Celgard). The upper cutoffs for LFP|Li (1C=170 mA g⁻¹) and NCM|Li (1C=160 mA g⁻¹) are set at 4 V and 4.3 V, respectively. The cycling tests were carried out in ambient environment and the temperature fluctuation is ±3 °C.



Figure S1. Activated and simulated XRD patterns of MOF.



Figure S2. SEM image of activated MOF.



Figure S3. N₂ adsorption/desorption isotherms of MOF (inset: pore size distribution derived from a Density Functional Theory model).



Figure S4. FTIR spectra of as-synthesized and activated MOF (UiO-66-NH₂).



Figure S5. Measurement of Li⁺ transference number for (a) 0.2MOF-LPC, (b) 0.2MOF-LPF, (c) LFS and (d) 0.2MOF-LFS.



Figure S6. Temperature-dependent ionic conductivity and thermal activation energy for LPC-/LPF-based electrolytes.



Figure S7. Temperature-dependent ionic conductivity and thermal activation energy for LFS-based electrolytes.



Figure S8. Rate performance of LiFePO₄|Li cells.



Figure S9. Representative voltage-capacity plots (500^{th} , 1500^{th} 2500th) from long-term galvanostatic cycling of LiFePO₄|Li cells.



Figure S10. SEM images of cycled LiFePO₄ harvested from LiFePO₄ |Li cell (5C, 1250 cycles).



Figure S11. XRD pattern of cycled LiFePO₄ electrode harvested from LiFePO₄|Li cell using 0.2MOF-LPC (5C, 1250 cycles).



Figure S12. Infrared spectra of cycled Li from Li Li cells (0.25 mA cm⁻², 100 h).



Figure S13. SEM images of post-cycle Li electrode from Li | Li cells (0.25 mA cm⁻², 100 h). Notes: the Li cycled in LPC exhibits rough and mossy morphology, which results from the uneven Li stripping/plating and growth of dendritic Li. In comparison, the Li cycled in 0.2MOF-LPC displays uniform and flat surface without protuberances, verifying that anion-adsorbing MOF particles benefit building up smooth interfaces.



Figure S14. Nyquist plots of post-cycle Li|Li cells (0.25 mA cm⁻², 100 h). Note: the diameter of one semicircle at high frequency represents resistance of SEI film (R_f) and the extrapolated one at relatively low frequency is indicative of charge transfer resistance (R_{ct}). The sum of R_f and R_{ct} is defined as interfacial resistance (R_{int}). The cell cycled in 0.2MOF-LPC shows much smaller R_{int} than the one in LPC (23 *vs.* 56 Ω), which is in line with the smaller overpotential observed in the cell using 0.2MOF-LPC.