Supporting Information

A Single-Ion Conducting UiO-66 Metal–Organic Framework Electrolyte for All-Solid-State Lithium Batteries

Hui Yang[a], Botong Liu[a], Joeseph Bright[b], Sujan Kasani[b], Jianhui Yang[b], Xiangwu Zhang[c], Nianqiang Wu[a][b]*

[a] Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA 01003-9303, United States

[b] Department of Mechanical and Aerospace Engineering, West Virginia University, Morgantown, West Virginia, 26506, United States

[c] Fiber and Polymer Science Program, Department of Textile Engineering, Chemistry and Science, Wilson College of Textiles, North Carolina State University, Raleigh, NC 27695-8301, United States

*Corresponding Author: Tel: (413)-545-6175, E-mail: nianqiangwu@umass.edu

Experimental Procedures

Materials

Terephthalic acid and 2-bromoterephthalic acid were purchased from Sigma Aldrich. Zirconium (IV) chloride ($ZrCl_4$), sodium p-styrenesulfonate, palladium(II) acetate, and sodium diphenylphosphinobenzene-3-sulfonate (TPPMS) were purchased from TCI. All other reagents were used as received.

Synthesis of UiO-66 framework

In a typical reaction, 0.35 mmol of terephthalic acid, 0.35 mmol of $ZrCl_4$ and 4 mL of Dimethylformamide (DMF) were placed in a Teflon lined autoclave and heated at 120 ^oC for 24 h. The microcrystalline powders were then isolated by centrifugation and heated at 100 ^oC for 1 h. Residual DMF and terephthalic acid precursors were removed from the microcrystalline UiO-66 by methanol rinsing (3 × 15 mL), soaking for 3 d in methanol, and subsequent heating at 150 ^oC for 5 h.

Synthesis of UiO-66-Br framework

In a typical reaction, 2-bromoterephthalic acid (0.35 mmol) along with $ZrCl_4$ (0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 ^oC for 24 h. The microcrystalline powders were then isolated by centrifugation and heated at 100 ^oC for 1 h. Residual DMF and terephthalic acid precursors were removed from microcrystalline UiO-66-Br by methanol rinsing (3 × 15 mL), soaking for 3 d in methanol, and subsequent heating at 150 ^oC for 5 h.

Synthesis of Sodium 4- styrenesulfonate on UiO-66 framework (UiO-66-NaSS)

To a 100 mL of 3-neck round bottom flask equipped with a nitrogen inlet and a condenser, UiO-66-Br (310 mg), sodium p-styrenesulfonate (206.2 mg, 1 mmol), palladium(II) acetate (12.3 mg, 0.054 mmol), triphenylphosphine (7.2 mg, 0.027 mmol),and sodium carbonate (342 mg, 3.2 mmol) were charged into the flask. Dry DMF (75 mL) was added to the nitrogen-flushed flask with stirring followed by heating at 120 °C for 12 h. DMF was then rotary evaporated, and the residual precipitate was washed by ethanol.

Synthesis of Lithium 4- styrenesulfonate on UiO-66 framework (UiO-66-LiSS)

Lithium 4-styrenesulfonate grafted UiO-66 framework was synthesized via ion exchange method. The molar ratio of poly(sodium 4- styrenesulfonate) (UiO-66-NaSS):$LiOH \cdot H_2O$ was 1:2. UiO-66-NaSS and $LiOH \cdot H_2O$ were added into dimethyl sulfoxide (DMSO) gradually while the temperature was maintained at 30 ^oC in the glass reactor equipped with a nitrogen inlet, a reflux condenser, an additional funnel, and a mechanical stirrer. The mixture was stirred for 12 h at 90 ^oC. Then the final product was isolated by filtration and washed successively with ethanol to remove any impurity such as residual LiOH and NaOH. The product was then dried in a vacuum oven at 60 $^{\circ}C$ for 24 h.

Characterization

The morphology of the samples was characterized by field-emission scanning electron microscopy (FE-SEM). FESEM images were taken with a JEOL JSM-7600 at an accelerating voltage of 15 kV. The crystallographic and chemical structures were characterized by an X-ray diffractometer (XRD, Rigaku DIII Ultima with Cu Kα radiation). All Raman spectra were

acquired with a portable B&W Tek i-Raman Plus. Fourier transform infrared (FT-IR) spectra were obtained under the attenuated total reflection (ATR) mode with Thermo Nicolet 6700 spectrometer. X-ray photoelectron spectroscopy (XPS) was measured with Physical Electronics PHI 5000 Versa Probe system. The binding energy (BE) of XPS spectra was calibrated as reference to the binding of adventitious carbon at 284.80 eV.

The ionic conductivity of the composite electrolyte was measured by electrochemical impedance spectroscopy (EIS) using a Solartron® 1260 in a frequency range of 1 Hz to 1 MHz. The electrolyte membrane was sandwiched between two stainless steel plates. The Li^+ transference number (t_{Li+}) was determined by the chronoamperometry test using symmetric lithium cells at an applied DC voltage of 10 mV. EIS was also performed before and after the DC polarization with the frequency ranging from 1 MHz to 1 Hz. The t_{Li+} value was calculated by Bruce's equation:

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})} \qquad \text{(S1)}$$

where ΔV is the polarization voltage, I_0 is the initial current, I_{ss} is the steady state current, R_0 is the initial total resistance, and R_{ss} is the steady state total resistance.

The electrochemical window of the electrolyte was measured using a liner sweep voltammetry (LSV) mode in the range of 0-6 V at a sweep rate of 10 mV/s. For the LSV test, the electrolyte membrane was sandwiched between the stainless-steel working electrode and the lithium metal foil (as a counter and reference electrode).

Cell assembly and electrochemical testing

The symmetric Li|MOF electrolyte|Li cell was assembled using Li foil as the electrodes in an argon-filled glove box. The symmetric cell was periodically charged and discharged for 1

hour at different current densities of 0.2, 0.5 and 1 mA cm^{-2} at 25 °C. The symmetric Li||Li half-cell with liquid electrolyte $LiPF_6$ and Celgard 2400 separator was used as a control, which was charged and discharged at current density of 0.5 mA cm^{-2}.

The MOF electrolyte membrane was fabricated for electrochemical testing of Li||$LiFePO_4$ CR2032 solid-state full cells. The UiO-66-LiSS MOF powder was mixed with polyvinylidene fluoride (PVDF) with a weight ratio of 3:1 in DMF solution, the mixture was stirred overnight. The uniform mixture was then cast on a Teflon plate to form a membrane separator under 120 ^{o}C. The membrane was then immersed in anhydrous propylene carbonate and ethylene carbonate solutions for 72 h before use. $LiFePO_4$ cathode was prepared by grinding 70% $LiFePO_4$ (LFP), 20% carbon black and 10% polyvinylidene fluoride (PVDF) in N-methyl-2- pyrrolidone (NMP) into uniform slurry. The prepared slurry was coated on an aluminum foil and dried in vacuum at 80 °C for 12 h. Then the LFP cathode and lithium foil were assembled with MOF membrane in CR2032 coin cell in the glovebox. The charge/discharge experiments were carried out between 2.7 and 4.2 V at room temperature.

Results

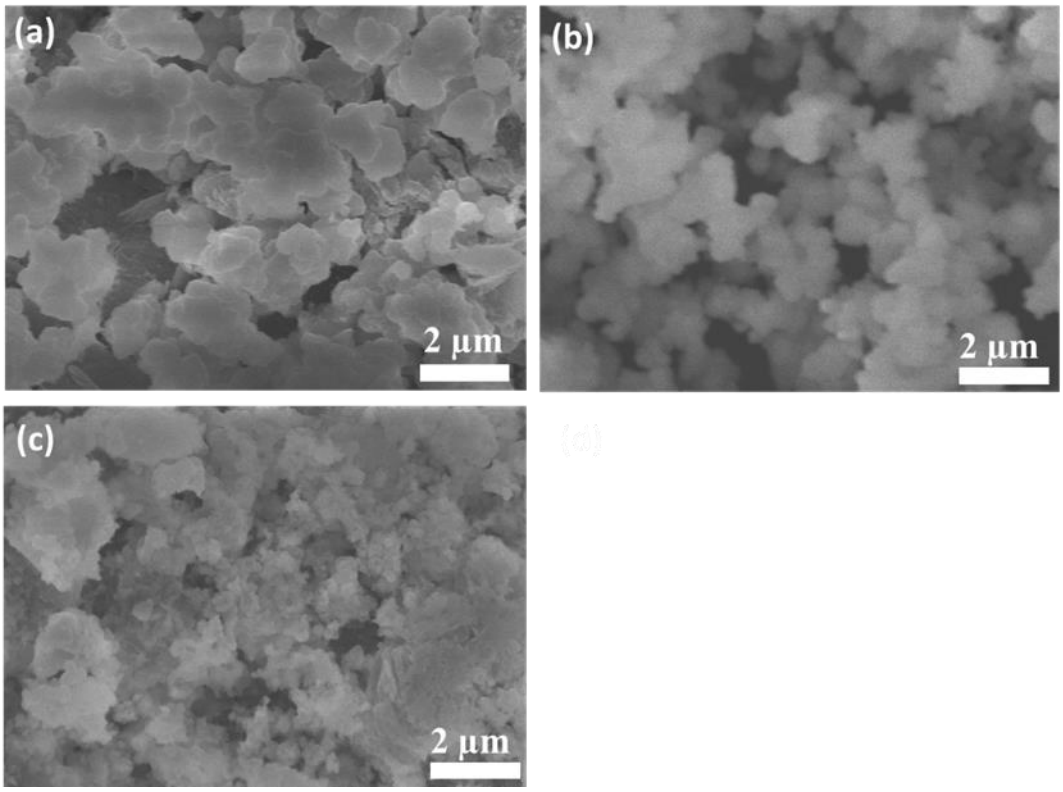

Figure S1. SEM images of UiO-66-Br, UiO-66-NaSS, and UiO-66-LiSS.

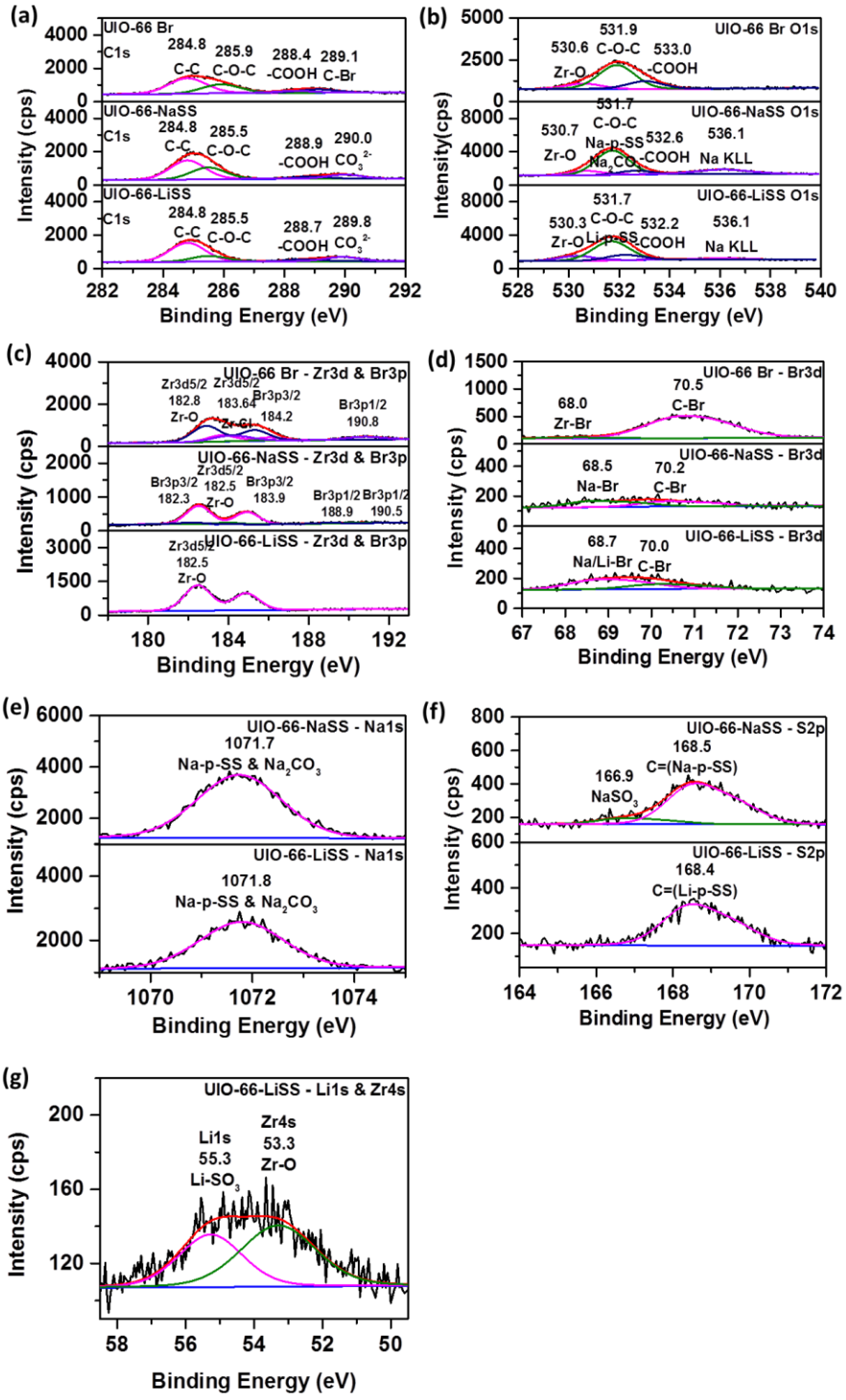

Figure S2. XPS spectra of UiO-66-Br, UiO-66-NaSS, and UiO-66-LiSS.

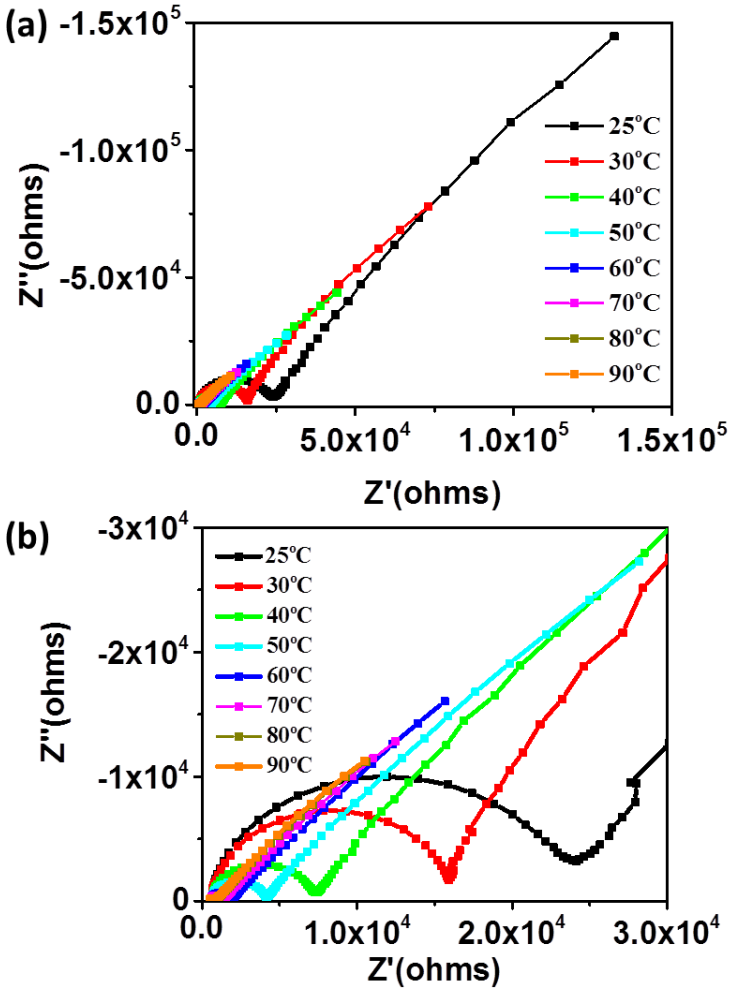

Figure S3. Electrochemical impedance spectroscopy of UiO-66-LiSS measured at (a) room temperature to 90 °C, (b) zoom spectra of (a).

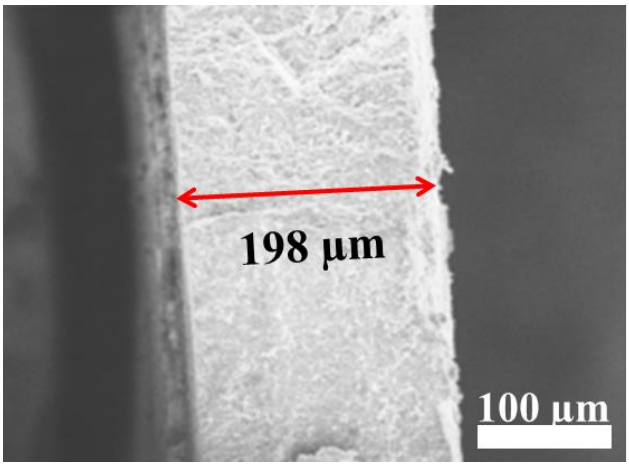

Figure S4. Thickness of UiO-66-LiSS pellet.

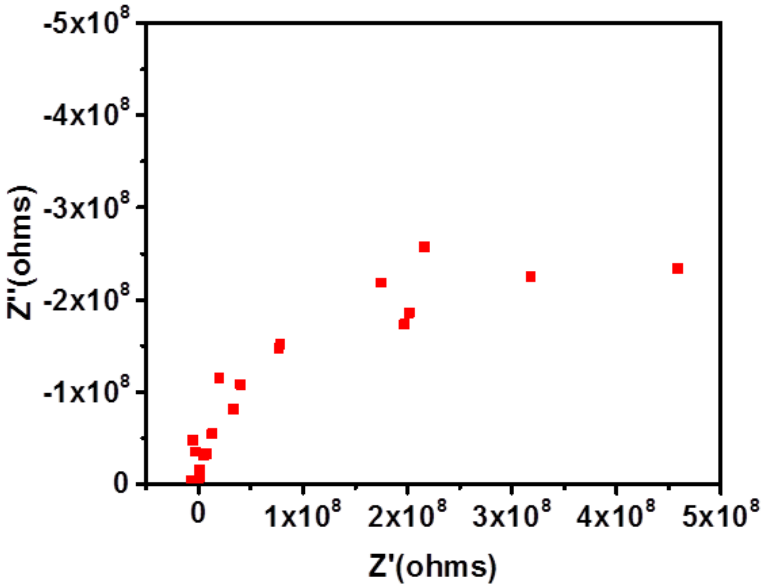

Figure S5. EIS plot of UiO-66-Br measured at room temperature.

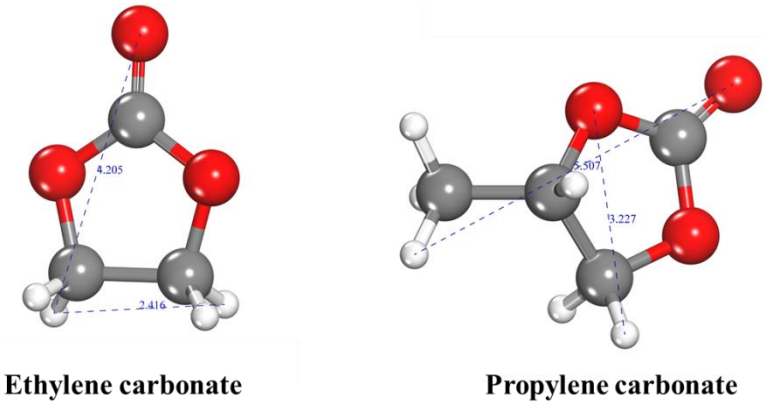

Figure S6. Molecular size (Å) of ethylene carbonate and propylene carbonate.

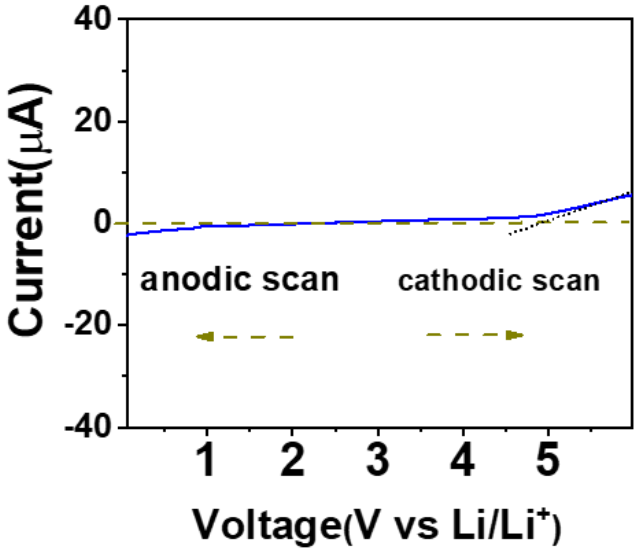

Figure S7. Linear sweep voltammetry (LSV) curve of the UiO-66-LiSS incorporated with 50 wt. % EC/PC.

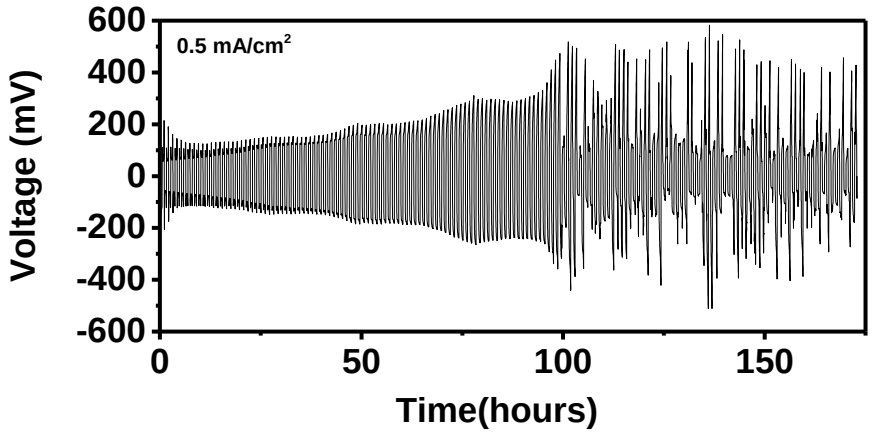

Figure S8. Galvanostatic Li plating/stripping voltage profile of Li|LiPF6 |Li at current density of 0.5 mA/cm^2.