

Supporting Information

Porous Covalent Organic Framework for High Transference Number Polymer-based Electrolyte

Derui Dong,^{1†} Hui Zhang,^{2†} Bin Zhou,¹ Yufei Sun,¹ Hailian Zhang,¹ Min Cao,¹ Jubai Li,¹ Han Zhou,¹ Hao Qian,¹ Zhiyong Lin¹ and Hongwei Chen^{1*}

¹College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, P.R. China

²State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, P.R. China

† These authors contributed equally to this work

*To whom correspondence should be addressed: hwchen@hqu.edu.cn

Experimental

Chemicals and Materials.

All starting materials and solvents, unless otherwise noted, were obtained from the Aldrich Chemical Co. and used without further purification. Acetone and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of H-COF-1@t

As a standard synthesis, H-COF-1@t was prepared using 1 g of 1,4-benzene diboronic acid (BDBA) in 200 mL of a 1:1 v:v solution mixture of mesitylene and 1,4-dioxane. The reaction mixture was introduced to a three-necked, round-bottomed flask (500 ml) provided with a mechanical stirrer, followed with N₂ bubbling for 0.5 h. Then the mixture was heated at 80 °C with strong stirring for 5 and 10 h under N₂ atmosphere, respectively. A light white solid at bottom of the flask was isolated by centrifugation, washed with acetone (500 ml) and dried overnight at 353 K.

Synthesis of S-COF-1

A Pyrex tube (20 ml) was charged with 1,4-benzene diboronic acid (BDBA) (100 mg) and 5 mL of a 1:1 v:v solution mixture of mesitylene and 1,4-dioxane. The tube was flash frozen at

77 K, evacuated to an internal pressure of 150 mtorr and flame sealed. The reaction mixture was heated at 120 °C for 72 h. A white solid at bottom of the tube was isolated by centrifugation, washed with acetone (100 ml) and dried overnight at 353 K.

Preparation of Polymer Composite Electrolytes

PVDF composite electrolytes containing LiClO₄ and COF additives in various compositions were prepared by a solution casting technique. PVDF was dissolved in NMP in a ratio of 1:9 (w/w) and homogeneous solution as obtained. Different amount of synthesized COF additives were added to the solution and stirred at room temperature for 1 day and then additionally dispersed under sonication for 0.5 h before casting process. Viscous slurries with the COFs were spread on a clean glass plate with a doctor blade apparatus with a gap of 300 μm. The polymer membranes were obtained by immersed the glass plate into a flowing-water bath. During the process, the polymer component in the slurry began to solidify, whereas the solvent component was exuded into the flowing water. It was dried under high vacuum at room temperature. Finally, the membranes were peeled from the glass plate and further placed in a high vacuum condition more than 24 h at 60 °C.

Cell Assembly

To prepare the LiFePO₄ cathode, slurries containing LiFePO₄ powders (MTI Inc.), carbon black and binder in ratio of 7:2:1 was thoroughly ground in a mortar, and then dispersed in NMP and stirred overnight. The slurries were then uniformly coated on the carbon coated aluminum foil to produce electrode films. Before cell assembly, the prepared polymer composite electrolytes were immersed in a 1 M LiClO₄ /EC: DMC (1:1) solution for 1 h to form the gel electrolytes used for electrochemical studies. For symmetric Li||SPE||Li cell, coin-type (CR2025) cells were fabricated by sandwiching the polymer composite electrolytes between the lithium metal foils in a high-purity argon-filled glove box. For Li||SPE||LiFePO₄ cell, coin-type (CR2025) cells were fabricated by sandwiching the polymer composite electrolytes between the LiFePO₄ cathode and lithium metal anode in a high-purity argon-filled glove box. For ionic conductivity measurement, symmetric stainless steel||SPE||stainless steel

cells were assembled. For lithium transference number measurement, symmetric Li|SPE|Li cells were assembled.

Characterization

FTIR spectra were collected using a ThermoScientific Nicolet 6700 spectrometer. XRD patterns were recorded on a Bruker D8-advance X-ray diffractometer with Cu-K α radiation ($\lambda=1.5418 \text{ \AA}$), using an operation voltage and current of 40 kV and 40 mA, respectively. SEM images were obtained with a FEI Quanta 400 FEG equipped with EDX (Apollo 40 SDD) operated at 10 kV. Nitrogen adsorption isotherms were measured using a Quantochrome Autosorb instrument. Ionic conductivity of the SPEs was tested by EIS using an Autolab PGSTAT 302N system at varied temperatures ranging from 0 to 80 °C. The SPEs were sandwiched between two stainless-steel plates and the spectra were recorded in the frequency range from 0.01 Hz to 1 MHz with AC amplitude of 10 mV. For polarization potential measurement, the Li|SPE|Li cells were tested at different current density for 350 s. The transference number was measured and calculated by AC impedance and direct-current (DC) polarization (with a DC voltage of 50 mV) using the Bruce-Vincent-Evans method, in which a DC signal is applied to a symmetric Li|SPE|Li cell.^[1] LSV experiment was performed on a working electrode of stainless steel as a counter and reference electrode of lithium metal, with a sweep rate of 0.5 mV s⁻¹ between 0 and 5.0 V.

RESULT SECTION

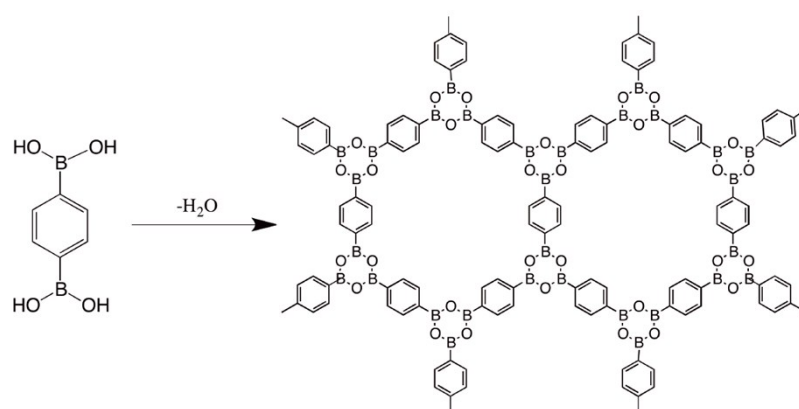


Figure S1. Reaction of boronic acids used to produce the COFs.

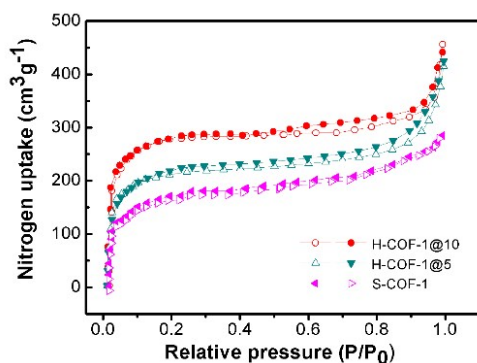


Figure S2. Nitrogen gas adsorption isotherms for different samples

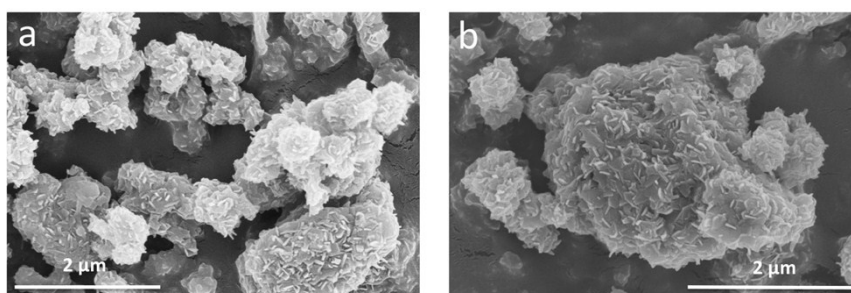


Figure S3. SEM images of the H-COF-1@5 sample.

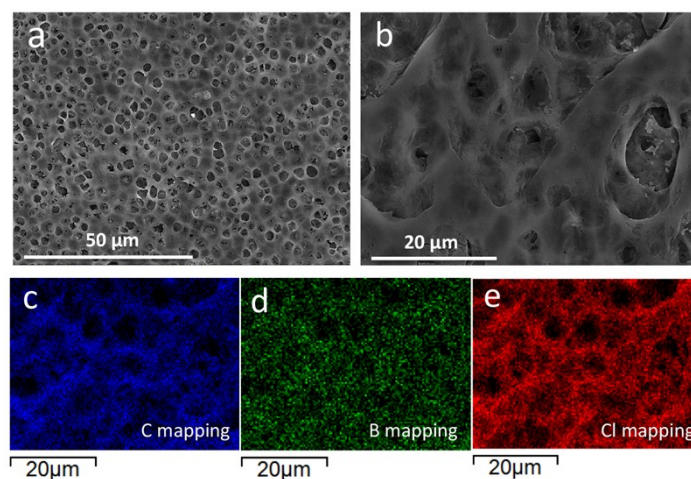


Figure S4. SEM and EDX of the prepared polymer electrolyte film.

The SEM images show the uniform distribution of micrometre-sized pores in the PVDF/COF composite films. EDX analysis indicated that the major chemical components of COF (C, B) and corresponding LiClO_4 (Cl) are evenly distributed across the resulted film.

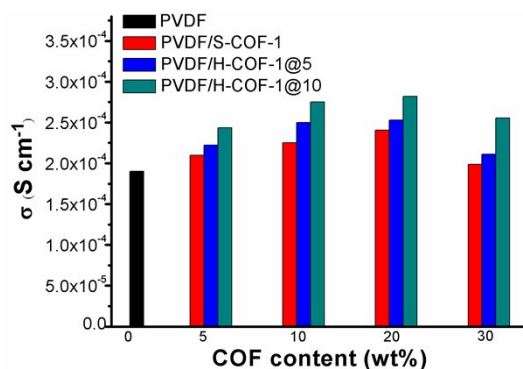


Figure S5. Ionic conductivity of the electrolytes with different COF contents.

Table S1. Textural properties of samples obtained under different synthesis conditions

Sample	Time (h)	S _{BET} (m ² g ⁻¹)	V _{total} (cm ³ g ⁻¹)
S-COF-1	72	690	0.47
H-COF-1@5	5	717	0.46
H-COF-1@10	10	812	0.48

Table S2. t_{Li^+} of different electrolytes

Sample	5% COF	10% COF	20% COF	30% COF
PVDF/S-COF-1	0.39	0.45	0.46	0.46
PVDF/H-COF-1@5	0.42	0.51	0.61	0.61
PVDF/H-COF-1@10	0.50	0.63	0.71	0.65

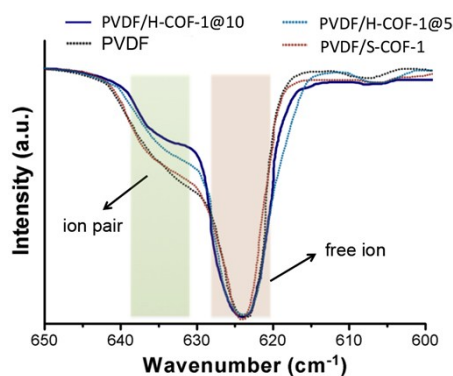


Figure S6. FTIR spectra (for ClO₄⁻) of different electrolytes at 600-650 cm⁻¹

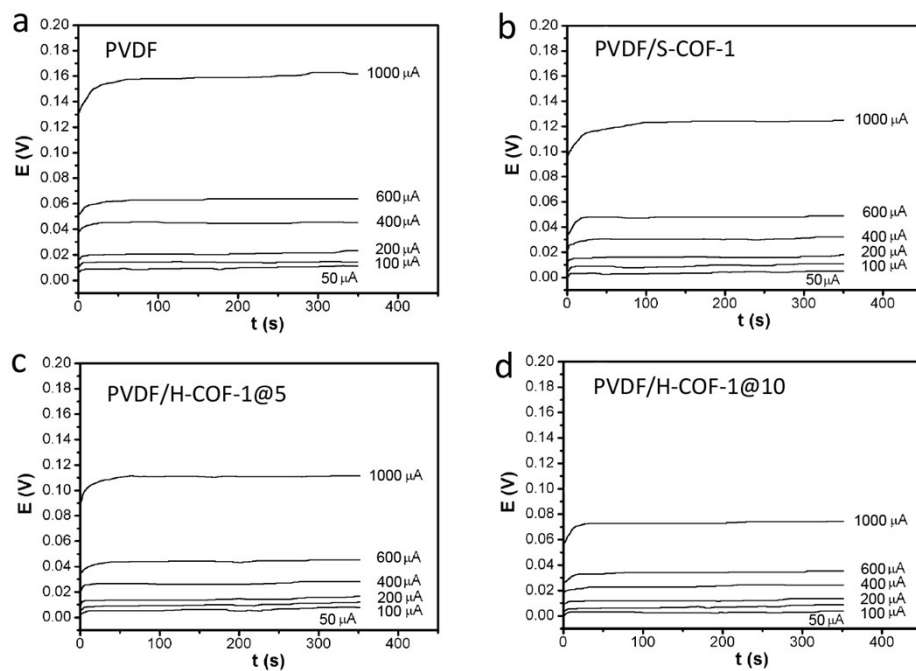


Figure S7. Polarization potential as a function of time for PVDF, PVDF/S-COF-1, PVDF/H-COF-1@5 and PVDF/H-COF-1@10 electrolyte.

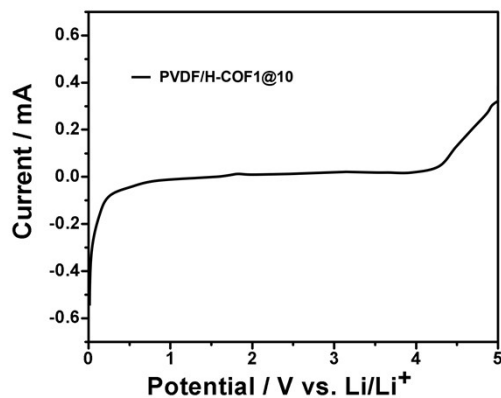


Figure S8. LSV results of PVDF/COFs film (with a sweep rate of 0.5 mV s^{-1}).

The linear sweep voltammetry (LSV) result shows that the electrochemical window of the PVDF/COFs can be larger than $\sim 4.3 \text{ V}$, which means that the COFs-containing polymer electrolytes can be employed in conventional lithium ion battery systems.

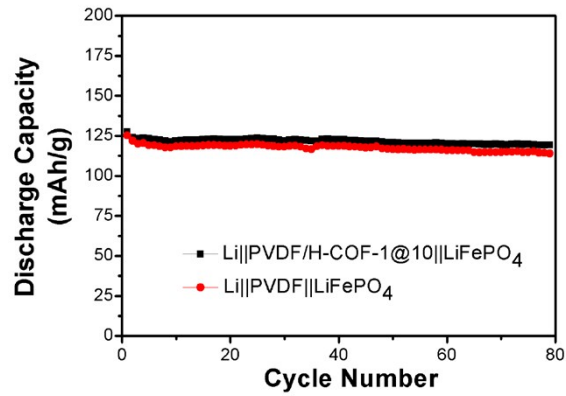


Figure S9. Cycling stability of Li||PVDF/H-COF-1@10||LiFePO₄ (1 C)

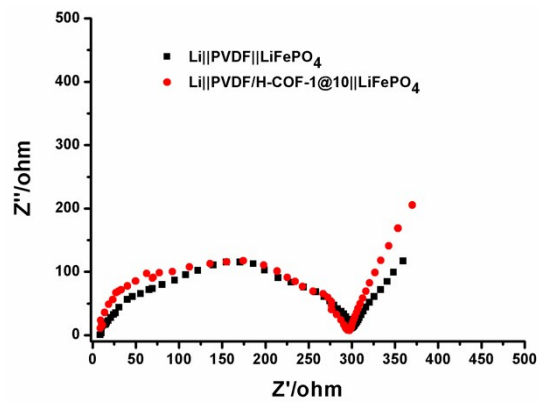


Figure S10. EIS results of Li||PVDF||LiFePO₄ and Li||PVDF/H-COF-1@10||LiFePO₄ cells

References

- [1] a) P. G. Bruce, J. Evans, C. A. Vincent, *Solid State Ionics* **1988**, 28, 918; b) Y. Y. Lu, M. Tikekar, R. Mohanty, K. Hendrickson, L. Ma, L. A. Archer, *Adv. Energy Mater.* **2015**, 5, 1402073.