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Ion Selective Bifunctional Metal–Organic Framework-Based Membrane for Lithium Metal-Based Nonaqueous Redox Flow Battery

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anionic transport channels of Li^+ across the membrane, the resultant Li-based hybrid NARFB delivers a high-capacity retention (99.95% per cycle) over 500 cycles with a well-assembled stable interphase after long time lithium plating/stripping, which decreases the voltage efficiency during the cycling. Calculations reveal that the membrane easily desolvates Li^+ in the unique micropore structure of MOF before Li deposition occurs, which suppresses parasitic reaction and accelerates Li uniform deposition. This work provides a viable method to design bifunctional NARFB membranes which achieve ion sieving and ion exchange functions.

KEYWORDS: Energy storage, Membrane, Nonaqueous redox flow battery, Metal-organic framework, Bifunctional

INTRODUCTION

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With the introduction of Carbon Neutrality goals, the proportion of renewable energy in total energy consumption worldwide has been increasing. Among them, solar photovoltaics accounted for 55% of the renewable capacity additions in 2020, followed by wind power (36%).¹ This development requires large-scale installations of solar and wind power plants, as well as breakthroughs in energy storage.² Redox flow battery (RFB) has been widely considered as one of the most prospective energy storage systems due to its decoupled energy and power units. The development of aqueous RFB is welldeveloped; for example, the all-vanadium system has been commercialized.³ However, the electrochemical window of water is narrow, which limits the voltage and energy density of the battery.³ Nonaqueous RFB (NARFB) can achieve higher output voltage, further reduce the complexity and economic cost of the entire RFB energy storage system, and at the same time broaden the normal working temperature range of the electrolyte, realizing the application of energy storage devices in high- and low-temperature environments.⁴ Although many researchers have researched in the NARFBs field in recent years, the serious crossover effect of the electrolytes still limits their development and application.

Benefiting from the unique micropore structure of MOF and the

Membrane is one of the key components deciding the Coulombic efficiency (CE) and preventing the crossover of the anodic and cathodic active materials, while facilitating the transfer of supporting electrolyte ions.⁶ The commercial ion exchange membranes, such as Neosepta⁷ and Fumasep,⁸ have been widely used in NARFBs. However, the high swelling ratio and poor chemical stability in organic solvents limit their application. And Daramic⁹ and Celgard¹⁰ porous membranes were also used. But the major challenge of porous membrane is the extremely low ionic selectivity, which will cause serious crossover and self-discharge of the battery.^{9,11,12} Correspondingly, various strategies have been proposed; many groups have reported modification of existing membranes for NARFBs recently.^{13–15} Despite significant improvement in cycling performance, modifying functional materials will increase both

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the weight and thickness of the membrane, which leads to the complexity of large-scale production.¹⁶ To support the practical applications of NARFBs. it is crucial to develop freestanding membranes to replace the modified membranes.

Metal-organic frameworks (MOFs) have been widely applied in molecular/ion separation owing to their regular micropores and high porosity.¹⁷ MOF-based materials are used as ionic sieves to mitigate the crossover of active materials due to its inherent ordered pore structure.¹⁸ Some MOF-based membranes were also developed for NARFBs owing to their capability in controlling ion transport, such as copper(II) benzene-1,3,5-tricarboxylate (HKUST-1),19 nickel(II) benzene-1,4-dicarboxylate (Ni-BDC),¹³ and zinc(II) benzene-1,4dicarboxylate (MOF-5).²⁰ However, all of them achieve ion sieving only by size effect, which causes low ionic conductivity. Zirconium(II) 1,4-benzenedicarboxylate (UiO-66), constructed from Zr₆O₄ nodes with 1,4-benzodicarboxylic acid struts between the nodes, has been used in aqueous RFB.²¹ The pore structure of UiO-66 can be easily functionalized, which can further enhance the performance of the ion separation by ion exchange function.²² UiO-66-SO₃H is an isostructural analogue of UiO-66²³ with a micropores of ~6 Å,²⁴ which was selected owing to high electrochemical stability and achieving ionic sieving by size effect. After lithiation, UiO-66-SO₃Li will provide well-defined Li⁺ conduction channels, which accelerate the transfer of supporting electrolyte (Li⁺) and regulate Li⁺ flux by $-SO_3^-$ group. Thus, the membrane based on anionic MOF has potential to obtain high ionic conductivity in NARFB.

Herein, a flexible freestanding anionic-MOF-based membrane (defined as MPM) is prepared with UiO-66-SO₃H and polyvinylidene fluoride (PVDF) through a solution casting approach. In the proof-of-concept battery, N-(ferrocenylmethyl) - N, N - dimethyl - N - ethylammonium bis-(trifluoromethanesulfonyl)imide (Fc1N112-TFSI) is used as active materials owing to its high reversibility, rapid redox kinetics, high solubility, and stability in organic solvent.²⁵ Lithium bis(tetrafluoromethylsulfonyl)amide (LiTFSI) as the supporting electrolyte due to the cation Li⁺ has a small radius and high ionic conductivity. Li-based hybrid NARFB was used as a model to demonstrate the cell performance of MPM membrane. The membrane shows an impressive ionic selectivity of Li⁺ to Fc1N112⁺ ions and high ionic conductivity. Meanwhile, the nanoporous structure of MOF can remove solvent molecules from its solvation sheath to regulate the energy state of Li⁺ and will lead to the Li⁺ reduced more preferentially than the molecules still in the Li-solvation sheath, which contribute to the uniform deposition of lithium. The battery exhibits both excellent high-rate discharging capability and super-long-term cycling stability over 500 cycles at the current density of 4 mA cm^{-2} .

EXPERIMENTAL DETAILS

Materials. Zirconium oxychloride octahydrate (ZrOCl₂·8H₂O, 98%, Sigma-Aldrich), monosodium 2-sulfoterephthalate (98%, TCI Chemicals), *N*,*N*-dimethylformamide (DMF, 99%, Alfa Aesar), lithium hydroxide (LiOH, 99%, Sigma-Aldrich), acetone (99%, VWR Chemicals), acetic acid (99.7%, Sigma-Aldrich), LiTFSI (99%, Acros Organics), ethylene carbonate (EC, 98%, Sigma-Aldrich), ethyl methyl carbonate (EMC, 98%, Sigma-Aldrich), and propylene carbonate (PC, 98%, TCI Chemicals) were used as received without further purification. Fc1N112-TFSI was prepared from bromoethane (98%, Acros Organics), LiTFSI, and (dimethylaminomethyl) ferrocene (96%, Sigma-Aldrich) by our pervious reported method.⁸

The UiO-66-SO₃H particles were synthesized with the following procedure. 3.0 mmol of monosodium 2-sulfoterephthalate and 3.0 mmol of $ZrOCl_2 \cdot 8H_2O$ were first dissolved by 150 mL of DMF in 30 mL of acetic acid. The mixture was transferred to a 250 mL Duran glass bottle and tightly capped. Then the bottle was heated at 120 °C for 24 h, and the prepared nanoparticles were collected by centrifuging and immersed in ethanol with continuous stirring for 3 days after cooling. Finally, UiO-66-SO₃H was collected with centrifuging and dried under vacuum at 60 °C for 24 h.

Fabrication of MPM Membrane. A 0.6 g amount of UiO-66-SO₃H nanoparticles was dispersed in 10 mL of acetone with ultrasonication, and then adding the required amount of PVDF/ DMF (7.5% in weight) solution. After stirring at 50 °C for overnight, the slurry was cast onto a glass plate. The membrane was prepared by using a scraper with 400 μ m thickness and then heated at 60 °C to remove solvent. Finally, the membrane was detached with immersing in ethanol. The prepared membranes were immersed in 0.1 M LiOH/ ethanol for 3 days. The lithiation method was used to replace H with Li in the intrinsic pores of MOF. Finally, the MPM membrane was naturally dried in the open air. The MPM membranes with different weight ratio of MOF were prepared with a similar procedure (weight ratios of MOF:PVDF = 1:4, 2:3, 3:2, and 4:1 are labeled as MPM-1, MPM-2, MPM-3, and MPM-4, respectively).

Characterization. PANalytical X'Pert X-ray diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å) was used to collect the X-ray diffraction (XRD) data. A JEOL JIB-4700F Multi Beam System equipped with an energy dispersive spectroscopy (EDS) unit was used to examine the scanning electron microscopy (SEM) images. Perkin Elmer FTIR spectrometer was used to record the Fourier transform infrared (FTIR) spectroscopy curves. The porosities of samples degassed at 120 °C for 12 h were measured at 77 K in a relative pressure of 0.01–0.99 by Microtrac BELsorp Mini II. A Theta Flex optical tensiometer was used to measure the solvent contact angle with a 5 μ L solvent droplet. A Tensile and Compression Testing Machine MTS 400 was used to do the tensile strength measurement at room temperature.

Permeability Test. The permeability of the supporting electrolyte and active materials through the membrane was measured by using an H-cell, in which the left half-cell was filled with 0.05 M supporting electrolyte or active materials solution while the right side was filled with pure solvent. Solutions at both sides of the H-cell were kept stirring to reduce the concentration polarization. The solutions were sampled from the right compartment at several time points. An UV–vis spectrometer (Varian Cary 50) was used to measure the concentration of the active materials, and the concentration of the supporting electrolyte was determined by the conductivity. The ratio of the permeability of the supporting electrolyte ion to that of the active materials is defined as the ionic selectivity of the membrane.

Electrochemical Test. The battery employed 0.1 M Fc1N112-TFSI/1 M TEATFSI in EC/PC/EMC (4:1:5 by weight) as catholyte and 1 M TEATFSI in EC/PC/EMC (4:1:5 by weight) as anolyte. Meanwhile, lithium metal foil and graphite felt were used as anode and cathode, respectively. The catholyte (5 mL) was circulated between the cathodal cell and storage tank at a flow rate of 20 mL min⁻¹ by peristaltic pump (BT100-1L, Longer Precision Pump Co., Ltd., China); 1 mL of anolyte was added to the anode compartment. Otherwise, a static cell constructed with two Teflon shells separated by a specific membrane, which was utilized to test the conductivity and rate performance of the membranes in the argon-filled glovebox. The battery cycling performance was measured on a cell test system (LAND, China). And the electrochemical impedance spectra (EIS) tests were carried out on the PARSTAT MC 200 Multichannel Potentiostat (AMETEK, USA) at the frequency range of $0.01-10^5$ Hz with a perturbation amplitude of 10 mV.

Theoretical Calculation Method. Crystalline structure of UiO-66 was obtained using single crystallographic data from ChemTube3D. The geometric optimization and formation energy computation of pristine UiO-66 and guest molecules accommopanying UiO-66 (Li(solvent)₄+@UiO-66, Li(solvent)₃+@UiO-66, solvent@UiO-66), Li(solvent)₄, Li(solvent)₃, solvent (solvent = EC/PC/EMC)) were performed using the density functional theory (DFT) method in the

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Figure 1. (a) XRD patterns of synthesized UiO-66-SO₃H powders and MPM membranes. (b) SEM image of the UiO-66-SO₃H powders. (c) FTIR spectra of MPM membranes. (d, e) Photographs of the MPM membranes.



Figure 2. (a) Back surface, (b) front surface, and (c, d) cross-section SEM images of the MPM membrane. (e) Contact angle test of EC/PC/EMC solvent on the surface of MPM and Celgard 2500 membranes.

DMol3 module of Material Studio 2019 with the generalized gradient approximation (GGA) with a Perdew–Burke–Ernzerhof (PBE) function. Grimme dispersion correction was employed in all calculations to describe van der Waals (vdW) interactions. And polarization functions (DNPs) were selected as the basis set. A dielectric constant of 20.7 was adopted in the COSMO solvation model to represent the electrolyte environment.²⁶ The structures were relaxed until the force, energy, and displacement were respectively less than 0.002 Ha Å⁻¹, 1 × 10⁻⁵ Ha, and 0.005 Å, with the *k*-point grid of 1 × 1 × 1 being used. All of the energy was calculated with final optimized crystal models. The dissolution energy (E_{desol}) of Li(solvent)₄ in pores of UiO-66 was defined as

$$\begin{split} E_{\rm desol} &= E_{\rm Li(solvent)_4 \, @ \, UiO-66} \, + \, E_{@ \, UiO-66} \, - \, E_{\rm Li(solvent)_3 \, @ \, UiO-66} \\ &- \, E_{\rm solvent \, @ \, UiO-66} \end{split}$$

and the solvent is EC, PC or EMC, while in the environment without UiO-66, E_{desol} of Li(solvent)₄ was defined as

$$E_{\text{desol}} = E_{\text{Li(solvent)}_4} - E_{\text{Li(solvent)}_3} - E_{\text{solvent}}$$

RESULTS AND DISCUSSION

UiO-66-SO₃H is an isostructural analogue of UiO-66, which has similar pore structure. The XRD results show that the MOF and

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Figure 3. (a) Nitrogen sorption isothermal curves of the UiO-66-SO₃H particles and MPM membrane. (b) Pore size distribution of the MPM membrane.



Figure 4. (a) Permeation tests of Fc1N112-TFSI and LiTFSI in MPM and Celgard 2500 membranes. (b) EIS spectra of the H-cells with different membranes.

MPM membranes were successfully synthesized (Figure 1a). UiO-66-SO₃H particles are well-consistent with the simulated pattern of UiO-66, which is obtained by Material Studio; as shown in the SEM image (Figure 1b), the synthesized UiO-66-SO₃H particles are nanoscale, which contributes to the preparation of homogeneous membranes. The significant MOF peaks in the XRD pattern of the MPM membranes demonstrate the structural stability of MOF particles during the membrane fabrication, and the diffraction peak at ca. 20° is assigned to the PVDF. The peak of PVDF decreases with the decrease of PVDF content. As shown in the FTIR spectra (Figure 1c), the characteristic peaks of PVDF polymer and MOF particles further demonstrate their coexistence. The peaks found at 1588 and 1404 cm⁻¹ were contributed to by the asymmetric stretch and symmetric stretch of the carboxyl groups of UiO-66-SO₃H. The peak at 1173 cm⁻¹ was caused by sulfonyl groups, and the peak at 649 cm⁻¹ represented the Zr-O bond. The appearance of the C-F bond at 876 and 837 cm⁻¹ confirms the existence of PVDF. The MPM membrane is semitransparent and flexible, and the transparency of the MPM membrane decreases with the increase of MOF content (Figure 1d,e).

The conductivity of the MPM membranes obtained by EIS measurements (Supporting Information Figure S1) was tested to determine the optimal weight ratio of MOF and PVDF components in the MPM membrane. A static cell constructed with two Teflon shells separated by a specific membrane was utilized to test the conductivity of the MPM membranes in the argon-filled glovebox, and 1 mL of electrolyte was added in both

of the two Teflon shells. By comparison, the MPM membrane with 60 wt % MOF was used in the following works. The back surface of the MPM membrane, which contacts the glass plate during the casting process, is smoother than the front surface (Figure 2a,b). Both of them are flat without cracks, as evidenced by the SEM results. Inside the membrane, MOF crystals are tightly packed by PVDF polymer to form a quite dense morphology with the thickness of ~25 μ m (Figure 2c,d). The corresponding EDS elemental mapping demonstrates the uniform distribution of MOF and PVDF throughout the cross-section of the membrane (Figure S2). The front and back surfaces of MPM membrane exhibit good affinity to electrolyte with small contact angles of $\sim 4.3^{\circ}$ and $\sim 8.1^{\circ}$, respectively, which are much smaller than that of a Celgard 2500 membrane (\sim 41.6°) (Figure 2e). We measured the mechanical stability of the MPM separator, and the flexible MPM separator demonstrates a maximum tensile stress of 29.0 MPa (Figure S3).

To explore the porosity of the membrane, nitrogen isotherms at 77 K were measured (Figure 3a). Combination of type-I and type-IV isotherm curves with an obvious H3 hysteresis loop is observed in the MPM membrane, indicating a large amount of micropores coexisted with a small amount of mesopores in the MPM membrane. The pore size distribution of the MPM membrane is calculated according to the nonlocal DFT model. The pore size is mainly concentrated at around 0.6 nm, which indicates its microporous nature and matches quite well with the crystal structure of MOF.²⁴ Such smaller pores compared with those in Celgard 2500 membrane (63 nm²⁷) are expected to

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Figure 5. (a) Electrochemical performance of the NARFB with MPM membrane at current densities of 2-12 mA cm⁻². (c) Voltage and Coulombic efficiencies of the batteries assembled with MPM and Celgard 2500 membranes.



Figure 6. (a) Battery performance of the NARFB assembled with MPM membrane at the current density of 4 mA cm⁻² over 500 cycles. (b) EIS of the battery before and after cycling. (c) Charge/discharge voltage profiles.

limit the transportation of active materials of Fc1N112-TFSI ($\sim 1 \text{ nm for Fc1N112}^{+28}$).

As a membrane in a NARFB, the permeability of the MPM membrane toward supporting electrolyte and active materials is an important factor. The undesirable diffusion of the active species across the membrane will cause the self-discharge of the cell. The permeation experiments were conducted using an Htype diffusion cell. The concentrations of supporting electrolyte (LiTFSI) and active materials (Fc1N112-TFSI) were obtained based on the calibration curves (Figure S4), which were measured by conductivity test or UV-vis spectrometer. Both of the MPM and Celgard 2500 membranes exhibit higher permeation rates of the supporting electrolyte than that of the active species (Figure 4). Compared with the case of the LiTFSI, the permeation rate of the Fc1N112-TFSI is reduced more seriously when using the MPM membrane. As an ionic sieve, the MPM membrane demonstrates obvious blocking effects toward active species. If the LiTFSI/Fc1N112-TFSI selectivity is defined as the ratio of the slope for LiTFSI to that for Fc1N112-TFSI, the MPM membrane shows higher LiTFSI/

Fc1N112-TFSI selectivity (37.6), six times that of a Celgard 2500 separator (6.0). Compared to our recent work, the MPM membrane exhibits higher ion selectivity than that of the membrane based on MOF-5 without ion exchange groups (26.6).²⁰ The size-sieving effect and ion exchange function of UiO-66-SO₃Li inside the MPM membrane contribute to such high ion selectivity. The structural pore size of UiO-66-SO₃H is 0.6 nm,²⁴ which is larger than the size of Li⁺ (0.15 nm in diameter²⁹) but smaller than that of Fc1N112⁺ (~1 nm²⁸). Furthermore, the $-SO_3^-$ groups in the pore structure of the MOF provide fast nanochannels for Li⁺ conduction after lithiation.

The conductivities of the MPM membranes before and after lithiation were obtained by EIS tests (Figure 4b). The UiO-66-SO₃Li-based membrane exhibits a resistance of 3.8 Ω cm², which is smaller than that of the UiO-66-SO₃H-based membrane (4.7 Ω cm²). The corresponding ionic conductivities of UiO-66-SO₃H-based and UiO-66-SO₃Li-based membranes are 0.53 and 0.65 mS cm⁻¹, which shows that the UiO-66-SO₃Li-based membrane, i.e., MPM membrane, possesses higher Li⁺



Figure 7. (a, b) Desolvation energy of $\text{Li}(\text{EC})_4^+$ to $\text{Li}(\text{EC})_3^+$ and EC molecule in bulk electrolyte and UiO-66, respectively. (c, d) Desolvation energy of $\text{Li}(\text{PC})_4^+$ to $\text{Li}(\text{PC})_3^+$ and PC molecule in bulk electrolyte and UiO-66, respectively. (e, f) Desolvation energy of $\text{Li}(\text{EMC})_4^+$ to $\text{Li}(\text{EMC})_3^+$ and EMC molecule in bulk electrolyte and UiO-66, respectively.

conductivity. The rate capability of the cell shows fast charge/ discharge ability which is an important merit in storing/releasing the intermittent energy. The cell assembled with MPM membrane exhibits an excellent high-rate performance at the tested current range of 2-12 mA cm⁻² (Figures 5 and S5). CE of the cell assembled with MPM membrane reached 97.7%, which is superior to that of the cell with a Celgard 2500 membrane (88.4%) at current density of 2 mA cm⁻². Compared with the CE of Celgard 2500 membrane, the MPM membrane exhibits a higher CE value (>97%) under different current densities. And the voltage efficiencies (VEs) of the batteries decrease rather quickly with the rise of current density.

The NARFB assembled with the MPM membrane shows stable cycling performance and high-capacity retention (Figure 6a). The impressive ionic selectivity of the MPM membrane contributed to high CEs among the cycling, which stabilizes at ~99.0%. The NARFB exhibits an average discharge capacity of 1.95 Ah L^{-1} over 500 cycles with 99.95% capacity retention per cycle, which indicates the high utilization rate of active materials and good cycling stability. The charge-discharge curve further confirms the stability of MPM membrane in long-term cycling (Figure 6c). VE is mainly determined by the polarization resistance and ohmic resistance of the battery, which generally decreases with cycling.³⁰ However, VE of the battery assembled with the MPM membrane increases during the long-term cycling, which stabilizes at ~89.1%. It can be obviously found that the charge-discharge potential difference of the last ten cycles is smaller than that of the first ten cycles (Figure 6c). The membrane resistance (R_m) and charge transfer resistance (R_{ct}) of the cells are also compared before and after cycling (Figure 6b). Although the $R_{\rm m}$ increases slightly from ~16 to ~24 Ω cm² after cycling, the R_{ct} decreases from ~80 to ~20 Ω cm². The total resistance was increased, which contributes to the increase in polarization and overpotential of the battery. The NARFB assembled with the MOF-5-based membrane under the same electrolyte and current density in our recent work exhibits an average VE of 81.1% and the ohmic resistance and polarization resistance increase during the cycling of the MOF-5-based battery, leading to the slow decline of VE.²⁰ By comparison, the

NARFB assembled with the MPM membrane shows a high average VE (85.1%) and the $-SO_3^-$ groups in the pores of the MOF decrease the polarization while VE and energy efficiency (EE) increase during the cycling. The cycling performance of the NARFB is remarkably good, which is better than that of recently reported membranes for NARFBs (Table S1).

The 500-cycled membrane was washed with the solvent (EC/ PC/EMC), then dried, and tested by SEM. The front surface contacts the anode while the back surface faces the cathode during the cycling. It remains integrated; no obvious crack on the two surfaces of the membrane is found (Figures S6 and S7). The composition of the MPM membrane maintains constant only a little deposition of Fe-related species on the two surfaces of the MPM membrane, which are detected by EDS. Confirmed by the XRD and FTIR characterizations, the peaks in the XRD and FTIR of the MPM membrane after long-term cycling are nearly identical to the pristine ones (Figure S8). No other new peaks observed in the FTIR spectrum and XRD pattern. All those results infer the MPM membrane maintains its pristine morphology and chemical composition, proving its high stability in long-term battery operation.

The underneath mechanism of the uniform deposition of Li contributed by UiO-SO₃Li was further understood by using DFT calculation. Using current computational chemistry tools to study the complex structure of the UiO-SO₃Li is quite difficult. To simplify the crystal structure of UiO-SO₃Li, UiO-66 was chosen as the host material for modeling. According to components of the solvent (EC/PC/EMC), the dissociation energies of Li⁺ with different solvent molecules were discussed. In the UiO-66 substrate, the dissociation energy of $Li(EC)_4^+$ to Li(EC)₃⁺ was ca. 28.6 kJ mol⁻¹, which was lower than the dissociation energy of Li(EC)₄⁺ to Li(EC)₃⁺ in the bulk electrolyte environment (43.9 kJ mol⁻¹, Figure 7a,b), and about 31.1 kJ mol⁻¹ of the dissociation energy of $Li(PC)_4^+$ to $Li(PC)_3^+$ and one PC molecule in the UiO-66 substrate was calculated, which was also lower than that in the bulk electrolyte (48.5 kJ mol⁻¹, Figure 7c,d), while the dissociation energies of $Li(PC)_4^+$ to $Li(PC)_3^+$ in the UiO-66 substrate and bulk electrolyte were about 32.0 kJ mol⁻¹ and 54.1 kJ mol⁻¹,

respectively (Figure 7e,f). Each dissociation energy of Li-(solvent)₄⁺ to Li(solvent)₃⁺ in the UiO-66 substrate was lower than that in the bulk electrolyte environment. The common carbonate-based electrolyte will appear as the primary parasitic reaction, i.e., the reduction of solvent in the primary Li⁺solvation sheath, which will prevent Li uniform deposition.²⁶ The calculations results indicated that the Li⁺-solvent complexes are partially dissociated in the UiO-66 structure, which contribute to forming a well-assembled stable interphase after long-time lithium plating/stripping, as illustrated by the SEM image (Figure S9). Owing to the good properties of MPM separator, the regular dendrites show uniform growth on the Li anode after cycling.

According to the electrochemical experiments results, the remarkable cycling performance of the MPM membrane is attributed to the ion size-sieving effect of the MOF structure and ion exchange function of the $-SO_3^-$ group in the MOF pore structure. The pores of MOF (0.6 nm) limit the diffusion of Fc1N112⁺ (~1 nm²⁸) and TFSI⁻ (0.65 nm²⁹), which allow the transfer of Li⁺ (0.15 nm²⁹). The $-SO_3^-$ group in the MOF pore structure form the well-defined anionic channels further impedes TFSI⁻ migration and facilitates Li⁺ conduction. Such mechanism of the MPM membrane in NARFB is illustrated in Figure 8. Thus, combined with calculations results, it is inferred



Figure 8. Schematic illustration of Fc1N112⁺, Li⁺, and TFSI⁻ through the MPM membrane.

that the $-SO_3^-$ group on the anionic MOF further plays a role in defining the Li⁺ conduction channels, which not only facilitates a high Li⁺ transfer number but also uniformly regulates the Li⁺ flux and desolvates Li⁺ before Li deposition occurs, forming a stable interphase after long-time lithium plating/stripping

CONCLUSIONS

In summary, we developed a flexible freestanding anionic-MOFbased bifunctional membrane to effectively impede the crossover of the active materials and thus enhance the performance of NARFB. UiO-SO₃Li can not only provide obvious blocking effects toward active species but also form definite Li⁺ conduction channels which accelerate the Li⁺ transfer. The MPM membrane exhibits a high ionic selectivity of Li⁺ over Fc1N112⁺ ion at a ratio of 37.6 and high ionic conductivity of 0.65 mS cm⁻¹. The NARFB assembled with MPM membrane exhibits high CE (99.0%) and capacity retention (99.95% per cycle) over 500 cycles. Such superior performance of the NARFB is attributed to the synergy of ion sieving and ion exchange functions of bifunctional MPM membrane. Furthermore, the nanostructure of MOF can regulate the energy state of Li⁺ effectively and contribute to the Li⁺ being reduced more preferentially than the molecules still

in the Li-solvation sheath, which contribute to the uniform deposition of Li.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.2c03324.

More SEM images, EDS elemental mappings, XRD patterns, FTIR spectra, UV-vis calibration curves, stress-strain curve, EIS spectra, and cycling performance of the NARFB (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CE, Coulombic efficiency; EE, energy efficiency; Fc1N112-TFSI, *N*-(ferrocenylmethyl)-*N*,*N*-dimethyl-*N*-ethylammonium bis(trifluoromethanesulfonyl)imide; LiTFSI, lithium bis-(tetrafluoromethylsulfonyl)amide; MOF, metal—organic framework; MPM, flexible freestanding anionic-MOF-based membrane; NARFB, nonaqueous RFB; RFB, redox flow battery; UiO-66, zirconium(II) 1,4-benzenedicarboxylate; VE, voltage efficiency

REFERENCES

(1) Murdock, H. E.; Gibb, D.; Andre, T.*Renewables 2021 global status report;* Renewable Energy Policy Network for the 21st Century: Paris, 2021.

(2) Yang, Z.; Zhang, J.; Kintner-Meyer, M. C. W.; Lu, X.; Choi, D.; Lemmon, J. P.; Liu, J. Electrochemical energy storage for green grid. *Chem. Rev.* **2011**, *111* (5), 3577–3613.

(3) Soloveichik, G. L. Flow batteries: current status and trends. *Chem. Rev.* **2015**, *115* (20), 11533–11558.

(4) Leung, P.; Shah, A. A.; Sanz, L.; Flox, C.; Morante, J. R.; Xu, Q.; Mohamed, M. R.; Ponce de León, C.; Walsh, F. C. Recent developments in organic redox flow batteries: a critical review. *J. Power Sources* **2017**, *360*, 243–283.

(5) Shin, S.-H.; Yun, S.-H.; Moon, S.-H. A review of current developments in non-aqueous redox flow batteries: characterization of their membranes for design perspective. *RSC Adv.* **2013**, *3*, 9095–9116.

(6) Yuan, J.; Pan, Z.-Z.; Jin, Y.; Qiu, Q.; Zhang, C.; Zhao, Y.; Li, Y. Membranes in non-aqueous redox flow battery: a review. *J. Power Sources* **2021**, *500*, 229983.

(7) Stauber, J. M.; Zhang, S.; Gvozdik, N.; Jiang, Y.; Avena, L.; Stevenson, K. J.; Cummins, C. C. Cobalt and vanadium trimetaphosphate polyanions: synthesis, characterization, and electrochemical evaluation for non-aqueous redox-flow battery applications. *J. Am. Chem. Soc.* **2018**, *140* (2), 538–541.

(8) Zhen, Y.; Zhang, C.; Yuan, J.; Zhao, Y.; Li, Y. A high-performance all-iron non-aqueous redox flow battery. *J. Power Sources* **2020**, 445, 227331.

(9) Yuan, J.; Zhang, C.; Zhen, Y.; Zhao, Y.; Li, Y. Enhancing the performance of an all-organic non-aqueous redox flow battery. *J. Power Sources* **2019**, *443*, 227283.

(10) Kwon, G.; Lee, K.; Lee, M. H.; Lee, B.; Lee, S.; Jung, S.-K.; Ku, K.; Kim, J.; Park, S. Y.; Kwon, J. E.; Kang, K. Bio-inspired molecular redesign of a multi-redox catholyte for high-energy non-aqueous organic redox flow batteries. *Chem.* **2019**, *5* (10), 2642–2656.

(11) Kim, D.; Song, J.; Won, J. Structural effects of anion exchange composite membranes in non-aqueous redox flow batteries. *J. Membr. Sci.* **2018**, *564*, 523–531.

(12) Doris, S. E.; Ward, A. L.; Baskin, A.; Frischmann, P. D.; Gavvalapalli, N.; Chenard, E.; Sevov, C. S.; Prendergast, D.; Moore, J. S.; Helms, B. A. Macromolecular design strategies for preventing activematerial crossover in non-aqueous all-organic redox-flow batteries. *Angew. Chem., Int. Ed.* **2017**, *56* (6), 1595–1599.

(13) Yuan, J.; Zhang, C.; Liu, T.; Zhen, Y.; Pan, Z.-Z.; Li, Y. Twodimensional metal-organic framework nanosheets-modified porous separator for non-aqueous redox flow batteries. *J. Membr. Sci.* 2020, *612*, 118463.

(14) Ma, T.; Pan, Z.; Miao, L.; Chen, C.; Han, M.; Shang, Z.; Chen, J. Porphyrin-based symmetric redox-flow batteries towards cold-climate energy storage. *Angew. Chem., Int. Ed.* **2018**, *57* (12), 3158–3162.

(15) Bang, H. S.; Kim, D.; Hwang, S. S.; Won, J. Surface-modified porous membranes with electrospun Nafion/PVA fibres for non-aqueous redox flow battery. J. Membr. Sci. 2016, 514, 186–194.

(16) He, Y.; Qiao, Y.; Chang, Z.; Zhou, H. The potential of electrolyte filled MOF membranes as ionic sieves in rechargeable batteries. *Energy Environ. Sci.* **2019**, *12* (8), 2327–2344.

(17) Zhao, M.; Wang, Y.; Ma, Q.; Huang, Y.; Zhang, X.; Ping, J.; Zhang, Z.; Lu, Q.; Yu, Y.; Xu, H.; Zhao, Y.; Zhang, H. Ultrathin 2D metal-organic framework nanosheets. *Adv. Mater.* **2015**, *27* (45), 7372–7378.

(18) Bai, S.; Liu, X.; Zhu, K.; Wu, S.; Zhou, H. Metal-organic framework-based separator for lithium-sulfur batteries. *Nat. Energy* **2016**, *1* (7), 16094.

(19) Peng, S.; Zhang, L.; Zhang, C.; Ding, Y.; Guo, X.; He, G.; Yu, G. Gradient-distributed metal-organic framework-based porous membranes for nonaqueous redox flow batteries. *Adv. Energy Mater.* **2018**, 8 (33), 1802533.

(20) Yuan, J.; Zhang, C.; Qiu, Q.; Pan, Z.-Z.; Fan, L.; Zhao, Y.; Li, Y. Highly selective metal-organic framework-based (MOF-5) separator for non-aqueous redox flow battery. *Chem. Eng. J.* **2022**, 433, 133564.

(21) Liu, S.; Sang, X.; Wang, L.; Zhang, J.; Song, J.; Han, B. Incorporation of metal-organic framework in polymer membrane enhances vanadium flow battery performance. *Electrochim. Acta* 2017, 257, 243–249.

(22) Xu, T.; Shehzad, M. A.; Wang, X.; Wu, B.; Ge, L.; Xu, T. Engineering leaf-like UiO-66-SO3H membranes for selective transport of cations. *Nano-Micro Lett.* **2020**, *12*, 51.

(23) Wang, Z.; Huang, W.; Hua, J.; Wang, Y.; Yi, H.; Zhao, W.; Zhao, Q.; Jia, H.; Fei, B.; Pan, F. An anionic-MOF-based bifunctional separator for regulating lithium deposition and suppressing polysulfides shuttle in Li-S batteries. *Small Methods* **2020**, *4* (7), 2000082.

(24) Yang, Q.; Wiersum, A. D.; Llewellyn, P. L.; Guillerm, V.; Serre, C.; Maurin, G. Functionalizing porous zirconium terephthalate UiO-66(Zr) for natural gas upgrading: a computational exploration. *Chem. Commun.* **2011**, 47 (34), 9603–9605.

(25) Wei, X.; Cosimbescu, L.; Xu, W.; Hu, J. Z.; Vijayakumar, M.; Feng, J.; Hu, M. Y.; Deng, X.; Xiao, J.; Liu, J.; Sprenkle, V.; Wang, W. Towards high-performance nonaqueous redox flow electrolyte via ionic modification of active species. *Adv. Energy Mater.* **2015**, *5* (1), 1400678.

(26) Sheng, L.; Wang, Q.; Liu, X.; Cui, H.; Wang, X.; Xu, Y.; Li, Z.; Wang, L.; Chen, Z.; Xu, G. L.; Wang, J.; Tang, Y.; Amine, K.; Xu, H.; He, X. Suppressing electrolyte-lithium metal reactivity via Li(+)-desolvation in uniform nano-porous separator. *Nat. Commun.* 2022, 13 (1), 172.

(27) Hudak, N. S.; Small, L. J.; Pratt, H. D.; Anderson, T. M. Throughplane conductivities of membranes for nonaqueous redox flow batteries. *J. Electrochem. Soc.* **2015**, *162* (10), A2188–A2194.

(28) Han, K. S.; Rajput, N. N.; Wei, X.; Wang, W.; Hu, J. Z.; Persson, K. A.; Mueller, K. T. Diffusional motion of redox centers in carbonate electrolytes. *J. Chem. Phys.* **2014**, *141* (10), 104509.

(29) Gong, K.; Fang, Q.; Gu, S.; Li, S. F. Y.; Yan, Y. Nonaqueous redox-flow batteries: organic solvents, supporting electrolytes, and redox pairs. *Energy Environ. Sci.* **2015**, *8* (12), 3515–3530.

(30) Escalante-Garcia, I. L.; Wainright, J. S.; Thompson, L. T.; Savinell, R. F. Performance of a non-aqueous vanadium acetylacetonate prototype redox flow battery: examination of separators and capacity decay. *J. Electrochem. Soc.* **2015**, *162* (3), A363–A372.