



This is an electronic reprint of the original article. This reprint may differ from the original in pagination and typographic detail.

Yuan, Jiashu; Zhang, Cuijuan; Qiu, Qianyuan; Pan, Zhengze; Fan, Lijun; Zhao, Yicheng; Li, Yongdan

Highly selective metal-organic framework-based (MOF-5) separator for non-aqueous redox flow battery

Published in: Chemical Engineering Journal

DOI: 10.1016/j.cej.2021.133564

Published: 01/04/2022

Document Version Publisher's PDF, also known as Version of record

Published under the following license: CC BY

Please cite the original version: Yuan, J., Zhang, C., Qiu, Q., Pan, Z., Fan, L., Zhao, Y., & Li, Y. (2022). Highly selective metal-organic framework-based (MOF-5) separator for non-aqueous redox flow battery. *Chemical Engineering Journal, 433*, Article 133564. https://doi.org/10.1016/j.cej.2021.133564

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



Contents lists available at ScienceDirect

Chemical Engineering Journal



journal homepage: www.elsevier.com/locate/cej

Highly selective metal-organic framework-based (MOF-5) separator for non-aqueous redox flow battery

Jiashu Yuan^{a,b,c}, Cuijuan Zhang^{b,c,*}, Qianyuan Qiu^a, Zheng-Ze Pan^a, Lijun Fan^{a,b,c}, Yicheng Zhao^{b,c}, Yongdan Li^{a,b,c,*}

^a Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland

^b State Key Laboratory of Chemical Engineering (Tianjin University), Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical

Engineering and Technology, Tianjin University, Tianjin 300072, China

^c Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China

ARTICLE INFO

Keywords: Energy storage Membrane Redox flow battery Separator Metal-organic frameworks

ABSTRACT

Non-aqueous redox flow batteries (NARFBs) are promising in the grid-scale energy storage for the harvesting of the intermittent renewable power sources. However, the lack of efficient separator is still impeding their further development. A flexible nanoporous separator is prepared through a "rolling dough" strategy, with zinc metal-organic framework (MOF-5) and polytetrafluoroethylene as the substrate. The prepared separator shows a remarkable ionic selectivity of Li⁺ over N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium ions (Fc1N112⁺) at a high ratio 26.6. A Li-based hybrid NARFB constructed with the separator exhibits substantially high Coulombic efficiency 99.7% and average discharge capacity 2.26 Ah L⁻¹ with capacity retention 99.96% per cycle over 200 cycles at 4 mA cm⁻². The excellent performance is attributed to the MOF nanoparticles and the designed composite structure, which achieves both high ionic selectivity and chemical stability simultaneously. This work provides a facile and efficient strategy to fabricate high-performance separator for NARFBs.

1. Introduction

Redox flow battery (RFB) has been regarded as one of the most promising grid-scale energy storage technology owing to its decoupled power and energy features, flexible modular design, excellent scalability, long cycle life and rapid response [1,2]. Early RFBs are based on aqueous electrolytes and the all-vanadium as well as Zn/Br systems have been commercially demonstrated [3]. However, the aqueous electrolyte limits the output potential, resulting in a limited energy density [4]. In contrast, the non-aqueous RFBs (NARFBs) based on organic solvents potentially have much wider electrochemical window and thus higher energy density [5]. Although a great effort has been devoted to the development of NARFBs, the crossover of the electrolyte, viz. active species diffusion through the membrane, and the low ionic conductivity have been among the major challenges for their practical application [6,7].

The separator, i.e. the membrane, which serves as preventing the crossover of the positive and negative active species whilst facilitating

the transport of the supporting electrolyte ions, is crucial to achieve a high performance and long-term stability [8]. An ideal membrane in a NARFB should have high ionic conductivity and selectivity, low swellability, low-cost, both high mechanical and chemical stability in the organic solvent [7]. The commercially available ion exchange and porous membranes, such as Fumasep [9,10] and Celgard [11,12] products have been used in NARFBs [8], but these ion exchange membranes show high swellability and poor chemical stability in organic solvents [13]. Meanwhile, commercial porous separators often have too large pore size which leads to unacceptable crossover [14,15]. In recent years, many modification strategies have been proposed to alleviate the issues [13,16-20]. Nevertheless, the thickness and mass of the modified membrane increase obviously, making the situation more complex [21]. For the large-scale application of NARFBs, it is important to develop cost-effective as well as easy fabrication membranes since a high ratio of the cost of a RFB comes from the membrane [22]. Furthermore, readily repairability is another plus especially when the membrane is broken during transportation or operation, and easy fabrication into various

https://doi.org/10.1016/j.cej.2021.133564

Received 22 August 2021; Received in revised form 11 October 2021; Accepted 7 November 2021 Available online 14 November 2021 1385-8047/@ 2021 The Authors, Published by Elsevier B.V. This is an open access article under the CC BV license (http://creat

1385-8947/© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding authors at: State Key Laboratory of Chemical Engineering (Tianjin University), Tianjin Key Laboratory of Applied Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China (C. Zhang). Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, FI-00076 Aalto, Finland (Y. Li).

E-mail addresses: cjzhang@tju.edu.cn (C. Zhang), yongdan.li@aalto.fi (Y. Li).

shapes can meet different needs. Accordingly, development of new methods to prepare composite free-standing membrane can be an alternative solution.

Metal-organic frameworks (MOFs), with central metallic atoms and organic ligands, have regular micropores and high porosity [23], and can serve as molecule and ion sieves and have been applied in gas separation [24] and recently, the application of MOFs has been extended to energy storage [21,25]. Copper (II) benzene-1,3,5-tricarboxylate (HKUST-1) [17], zirconium (II) 1,4-benzenedicarboxylate (UiO-66) [26], and nickel (II) benzene-1,4-dicarboxylate (Ni-BDC) [16] have shown good ion sieving effect and demonstrated potential as a component of a separator in an RFB. The MOF-5 is zinc (II) benzene-1,4-dicarboxylate, which is constructed of Zn₄O nodes with 1,4-benzodicarboxylic acid struts between the nodes. MOF-5 has been applied in gas separation [27], catalysis [28], water treatment [29] and supercapacitor [30]. The micropores stemmed from the MOF-5 crystals (\sim 8 Å [31]) may mitigate the crossover of large-sized active species and provide continuous ion-transfer pathways for small supporting electrolyte ions.

MOF particle cannot self-assembled without binders. Polymer such as polyethylene, polyvinylidene fluoride and polytetrafluoroethylene (PTFE), show good chemical stability, and have been used as binders applied in the separator of lithium batteries [32,33]. PTFE show good stability in RFB application [34,35]. Meanwhile, PTFE is highly stable in organic electrolyte [32]. Furthermore, other components of our in-house designed NARFB device are made from PTFE. To avoid the effects caused by using of other polymers, PTFE is a good choice.

The iron-based metal-ligand complexes are earth abundant and have good electrochemical properties and fast kinetics [36]. The ionicderivatized ferrocene compound, N-(ferrocenylmethyl)-N,N-dimethyl-N-ethylammonium bis (trifluoromethane-sulfonyl) imide (Fc1N112-TFSI), exhibits rapid redox kinetics, high reversibility, stability, and solubility in organic solvent [10,37]. Wei et al [37] reported a Li-based hybrid NARFB using Fc1N112-TFSI and lithium bis(tetrafluoromethylsulfonyl)amide (LiTFSI) as the active species and supporting electrolytes, respectively, and show a good cycling performance.

Herein, we report that a MOF-5-based mixed-matrix (MMM) enables a facile "rolling dough" preparation of a flexible free-standing separator. A similar Li-based hybrid NARFB is assembled according to Ref. [37]. The separator shows a remarkably high ionic selectivity of Li⁺ over Fc1N112⁺ ions and good long-term stability over 200 cycles at 4 mA cm⁻².

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), terephthalic acid (H₂BDC, 98%), ethylene carbonate (EC, 98%), ethyl methyl carbonate (EMC, 98%), and PTFE dispersion (60 wt%) were bought from Sigma-Aldrich. N,N-Dimethylformamide (DMF, 99%) was purchased from Alfa Aesar. Propylene carbonate (PC, 98%), 4-Fluoro-1,3-dioxolan-2-one (FEC, 98%) were purchased from TCI Chemicals. LiTFSI (99%) was supplied by Acros Organics. All chemicals were used as received without further purification. A Celgard PP (Celgard 2500, 25 μ m thickness) separator for comparison was obtained from Celgard LLC. Fc1N112-TFSI was prepared from (dimethylaminomethyl) ferrocene (96%, Sigma-Aldrich), bromoethane (98%, Acros Organics), and LiTFSI according to a reported procedure [37].

The MOF-5 nanoparticles were synthesized according to the reported method [27]. In a 100 mL Teflon-lined autoclave, $Zn(NO_3)_2\cdot 6H_2O$ (1.664 g, 5.60 mmol) and H_2BDC (0.352 g, 2.12 mmol) were dissolved in 80 mL DMF solvent. Then the autoclave was sealed and heated to 403 K for 4 h. After cooling down to room temperature, the colorless MOF-5 powder was collected with centrifugation and washed thoroughly with DMF to remove the unreacted zinc nitrate. The prepared MOF-5 crystals were dispersed in methanol 3 days for solvent exchange and then dried

under vacuum at 433 K overnight.

2.2. Fabrication of MMM separator

Specific amount of MOF-5 powder was ground in a mortar, after which the PTFE dispersion was added, finally making a weight ratio of MOF:PTFE = 4:1. After uniform mixing, the material was dried and kneaded until a dough-like mass formed, followed by repeated rolling to obtain a smooth and thin separator. After peeling-off, the separator was cut into required size and immersed in the EMC/EC/PC (5:4:1 by weight) solvent to achieve phase conversion. After drying at 373 K in vacuum, the separator was stored in the glove box. The remained material after cutting the used part was remixed into a dough-like mass, kneaded and rolled flat to obtain a new separator following the same procedure described.

2.3. Characterization

The X-ray diffraction (XRD) data were collected at room temperature on a PANalytical X'Pert X-ray diffractometer at 45 kV, 40 mA for Cu Ka radiation ($\lambda = 1.54056$ Å). Scanning electron microscopy (SEM) images were recorded using a JEOL JIB-4700F Multi Beam System equipped with an Energy dispersive spectroscopy (EDS) unit. Fourier transform infrared spectroscopy (FTIR) curves were acquired with a PerKin Elmer Fourier transform infrared spectrometer. Solvent contact angle was measured on a Theta Flex optical tensiometer with 5 µL solvent droplet. Nitrogen adsorption/desorption isotherms were measured with Microtrac BELsorp Mini II. The samples were degassed at 393 K for 24 h under vacuum before the nitrogen sorption analysis were performed at 77 K in a relative pressure range 0.01-0.99. The tensile strength measurement was done with Tensile and Compression Testing Machine MTS 400 at room temperature. Thermal gravimetric analysis (TGA) was studied using TA Instruments TGA Q500 at a heating rate of 10 °C min⁻¹ in N₂ atmosphere.

2.4. Permeation test

The permeability of the active species and supporting electrolyte through the separator was measured using an H-cell, in which the right half-cell was filled with 10 mL 0.05 M redox species solution or supporting electrolyte solution while the left side with the 10 mL solvent. The effective area of the membrane is ca. 1 cm². Solutions at both sides were stirred to minimize the concentration polarization. The samples were taken from the left compartment from time to time. The concentration of the active species was monitored with an UV-Vis spectrometer (Varian Cary 50) and that of the supporting electrolyte was determined with measuring the conductivity. The solution samples were poured back to the cell immediately after the measurement. The permeability is calculated according to the equation [7]:

$$V\frac{dC_t}{dt} = A\frac{P}{L}(C_0 - C_t) \tag{1}$$

where *V* is the volume of the solution in the active species compartment, C_t the concentration of the active species in the same side as a function of time, *A* the effective area, *L* the thickness of the separator, *P* the permeability of the membrane and C_0 the concentration of active species in the other half-cell. The ionic selectivity is defined as the ratio of the permeability of the supporting electrolyte ion to that of the active species:

Ionic selectivity
$$= \frac{P_s}{P_a}$$
 (2)

where P_s and P_a are the permeability of the supporting electrolyte ion and the active species, respectively.



Fig. 1. a) XRD patterns of the synthesized MOF-5 powder and MMM separator. b) SEM image of the MOF-5 powder. c) Scheme of the separator fabrication steps. d) Photographs of the flexible separator.

2.5. Electrochemical test

Graphite felt, lithium metal foil and stainless steel were used as cathode, anode and current collector, respectively. A single cell was constructed with a specific membrane sandwiched by two Teflon shells. The electrolyte containing 0.1 M Fc1N112-TFSI, 1 M LiTFSI and 5 wt% FEC in EMC/EC/PC (5:4:1 by weight) was employed as catholyte, while the same electrolyte without Fc1N112-TFSI as anolyte. Before test, the separator was cut into pieces of 28 mm in diameter and immersed in the anolyte for 24 h. In the flow cell mode, static anolyte (1 mL) was added to the anode compartment, the catholyte (5 mL, theoretical volume specific capacity 2.68 Ah L^{-1}) was circulated between cell and storage tank with a peristaltic pump (BT100-1L, Longer Precision Pump Co., Ltd., China) at a flow rate of 20 mL min $^{-1}$. Galvanostatic charge and discharge cycling was carried out on a cell test system (LAND, China). The electrochemical impedance spectra of the cell were measured in the frequency range of $0.01-10^5$ Hz with a perturbation amplitude of 10 mV with the PARSTAT MC 200 Multichannel Potentiostat (AMETEK, USA).

3. Results

The XRD measurement results show that the MOF-5 material was successfully synthesized (Fig. 1a). The crystals are nano cubes (Fig. 1b). As schematically illustrated in Fig. 1c, flexible MMM separator was prepared with 100% utilization of material with the "rolling dough" approach. A broken separator was reused by redo the rolling dough practice to make a new one with the material. The XRD pattern of MMM separator is flexible (Fig. 1d). The FTIR results further confirm the existence of the MOF and the PTFE components (Fig. 2a). The MOF nanoparticles are

closely packed in the PTFE bulk phase without cracks at the surface (Fig. 2c). The separator is dense, with a thickness close to 85 μ m (Fig. 2d and e). In addition, the MMM separator exhibits a much smaller contact angle (~9.5°) than that of the commercial Celgard PP separator (~41.6°) (Fig. 2b) with the solvent. The MMM separator has a tensile strength of 3.8 MPa (Fig. 2f). A good thermal stability is further proved with the high decomposition temperature of ~400 °C, as shown in the TGA curve in Fig. 2g.

The nitrogen adsorption/desorption isotherms at 77 K were measured (Fig. 3a). Combination of type-I and type-IV isotherm curves are identified for the MMM separator i.e. has strong gas adsorption in low relative pressure range and a hysteresis loop in medium relative pressure > 0.45 range, indicating the coexistence of micropores with a large volume (0.199 cm³ g⁻¹) and mesopores with a smaller volume (0.048 cm³ g⁻¹). The pore size distribution calculated with the non-linear density functional theory (NLDFT) model shows that the pores are mainly concentrated at ~0.8 nm which is the structural nanopore of MOF-5 [31] (Fig. 3b and c). The pore size of the MMM separator is much smaller than that of Celgard PP (64 nm [7]). Such small pores are expected to impede the transport of active species of Fc1N112-TFSI (~1 nm for Fc1N112⁺ [38]).

The permeation experiments were done with using an H-type diffusion-cell. The concentrations of the active species (Fc1N112-TFSI) and supporting electrolyte (LiTFSI) were derived from the calibration curves, obtained with the UV-Vis and conductivity measurements, respectively. Both the MMM and PP separators exhibit higher permeation rate of the supporting electrolyte than that of the active species (Fig. 3d). The permeabilities of Fc1N112-TFSI in MMM and PP separators are measured as 2.95×10^{-8} and 6.47×10^{-8} m² s⁻¹, respectively. The MMM separator shows four times higher selectivity for Li⁺ over



Fig. 2. a) FTIR spectra of the MMM separator and MOF-5 particles. b) Contact angle test of EMC/EC/PC (5:4:1 by weight) solvent on MMM and Celgard PP separators. Surface (c) and cross-section (d, e) SEM micrographs of the separator. f) Stress-strain curve of the MMM separator. g) TGA curve of MMM separator under N_2 atmosphere.

 $Fc1N112^+$ (26.6) than that of the PP separator (6.0).

A single static cell was assembled (Fig. 4a) with a separator size of 28 mm in diameter. Good rate capability of battery is an important merit for fast charge/discharge in storing/releasing the energy. Before testing cell performance, Cyclic voltammetry (CV) measurement of active species was conducted (Fig. 4b). The redox peak current ratio of the Fc1N112-TFSI is roughly 1.0, which indicate the redox reaction is quasireversible. The cell assembled with the MMM separator exhibits excellent rate capability at *j* of 2–12 mA cm⁻² (Fig. 4c). CE of the MMM separator-based battery increases gradually with *j* which is higher than 97%, and almost close to 100% at high *j*, and is much better than that of the battery using a PP separator in all the current density range examined (Fig. 4d and e). The voltage efficiency (VE) decreases rather quickly with the increase of *j*. Energy efficiency (EE) of the MMM based cell is higher than that of the cell assembled with the PP separator (87.4% vs. 83.7% at $i = 2 \text{ mA cm}^{-2}$). The capacity decay always happens during the test; thus, the capacity value does not recover when the current density condition goes back to 2 mA cm⁻². The EIS curves of the cells with both MMM and PP separators are plotted in Fig. 4f. The intercept of EIS with

the X-axis at the highest frequency is dominated by the separator resistance (R_m). The semicircles at the medium frequency are related to the charge transfer process (R_{ct}) at the interface between the electrodes, electrolyte and separator. W₁ is the Warburg diffusion element related to active species diffusion capacitance. Q₁ is the constant phase element which is related to the electric double layer capacitor [39]. The MMM separator is thicker than PP (85 vs. 25 µm), which causes larger R_m than that of PP (12.9 vs. 4.6 Ω cm²), leading to low VE. However, the MMM separator has smaller R_{ct} than that of with PP (16.4 vs. 25.6 Ω cm²), which indicates that the interfacial resistances in the cell with MMM membrane are lower than those in the cell with PP membrane, meaning faster pathways for Li⁺ transport in the cell with MMM membrane as the separator.

A large-size MMM separator can be easily obtained. An in-house designed standard NARFB device with an effective area of 2 cm \times 2 cm was assembled. High average CE of 99.7% and EE of 80.9% are achieved (Fig. 5a) for 200 cycle at *j* = 4 mA cm⁻². VE is determined by the ohmic resistance and polarization resistance which generally increases with cycling [40], leading to the slow decline of VE. The flow



Fig. 3. a) Nitrogen sorption isothermal curve of the MOF-5 powder and MMM separator. Pore size distribution of the (b) MOF-5 particles and (c) MMM separator. d) Permeation rates of LiTFSI and Fc1N112-TFSI in Celgard PP and MMM separators.



Fig. 4. a) Cell design and configuration. b) CV curve of 0.01 M Fc1N112-TFSI in the electrolyte at scan rate of 100 mV s⁻¹. Electrochemical performance of the cells with (c) MMM and (d) PP as separator at different current densities (2–12 mA cm⁻²). e) Coulombic and voltage efficiencies of the cells made with MMM and PP separators at the current density range of 2–12 mA cm⁻². f) EIS curves of the cells with the two separators, respectively.

battery exhibits an average discharge capacity of 2.26 Ah L^{-1} over 200 cycles (99.96% capacity retention per cycle). The representative charge/discharge profiles of the flow battery are shown in Fig. 5b. The performance of the flow battery is remarkably good.

The separator after long term cycling test was washed with EMC/EC/ PC solvent, dried and then subjected to SEM observation. The SEM morphology and corresponding EDS elemental mappings are shown in Fig. 6. The XRD and FTIR patterns of the MOF and PTFE components in



Fig. 5. (a) Cycling performance of the NARFB over 200 cycles assembled with large-size MMM separator at j = 4 mA cm⁻². (b) Representative charge/discharge profiles of the flow battery.



Fig. 6. SEM micrographs and the corresponding EDS elemental mappings of the cycled MMM separator.



Fig. 7. (a) XRD patterns and (b) FTIR spectra and of the MMM separator before and after the cycling test.

the separator after cycle test are similar with those of pristine ones (Fig. 7).

4. Discussion

The XRD results show that the MOF-5 material was successfully synthesized with the solvothermal method with high purity and crystallinity (Fig. 1a). Comparing the separator XRD with the powder XRD, the XRD pattern of MMM separator clearly shows the MOF diffraction peaks at same locations with similar relative intensities, which confirms the structural stability of the MOF during separator preparation. The diffraction peak (200) represents the porous structure of MOF-5. The peak intensity decreases after separator fabrication partly due to the pore filling with solvent. The FTIR result (Fig. 2a) further confirm the existence of the MOF and the PTFE components. The peaks at 1600 cm⁻¹

and 1390 cm⁻¹ represented the asymmetric stretch and symmetric stretch of the carboxyl groups of MOF-5. The peaks caused by C–H stretch can be seen at 746 and 824 cm⁻¹. The peak at 1660 cm⁻¹ was contributed by the carbonyl bond from the entrapped DMF solvent. In addition, two characteristic peaks at 1155 and 1220 cm⁻¹ indicated the presence of C-F stretch from PTFE. The MOF nanoparticles are closely packed in the PTFE bulk phase without cracks at the surface (Fig. 2c). In addition, the MMM separator exhibits a much smaller contact angle (~9.5°) than that of the commercial Celgard PP separator (~41.6°) (Fig. 2b), which means better affinity to the electrolyte.

The cell assembled with the MMM separator exhibits excellent rate capability. CE increases gradually with j due to the reduced crossover effect. The CE of MMM separator-based battery is higher than 97%, and almost close to 100% at high j, and is much better than that of the battery using a PP separator in all the current density range examined



Fig. 8. Schematic permeation of $\rm Li^+,~\rm TFSI^-,$ and $\rm Fc1N112^+$ through the MMM separator.

(Fig. 4c). The VE decreases rather quickly with the increase of *j* due to the increased concentration polarization loss. The EIS curves of the cells with both MMM and PP separators are given in Fig. 4d. The MMM separator has larger R_m than that of PP (12.9 vs. 4.6 Ω cm²), leading to lowered VE, while the MMM separator has small R_{ct} (16.5 Ω cm²), indicating that the interfacial resistances in the cell with MMM membrane are low, meaning faster pathways for Li⁺ transport in the cell with MMM membrane as the separator.

Wei et al. [37] used commercial Celgard 3501 separator with the same electrolyte as in this work, and their cell exhibited excellent 99.0% CE and 99.95% capacity retention per cycle over 100 cycles at j = 3.5 mA cm⁻². For comparison, the NARFB in this work with MMM separator shows 99.7% CE and 99.96% capacity retention per cycle over 200 cycles at j = 4 mA cm⁻². Such high CE and capacity retention is attributed primarily to the high ion selectivity of the MMM separator which effectively suppresses the cross-over of the active species, and the chemical stability of the separator.

According to the electrochemical experiment results, the remarkable selectivity is attributed to the ion-size sieving effect of MOF-5 and the dense combination of the two components in the composite membrane. Crossover of active species causes capacity decay and decreases the capacity retention. Low permeability contributes to obtain high capacity retention. The size of the pores of MOF-5 is 0.8 nm, much bigger than the diameter of Li⁺ (0.15 nm [41]) and TFSI⁻ (0.65 nm [41]), but smaller than that of Fc1N112⁺ (~1 nm [38]). Therefore, MOF nanoparticles in the composite membrane effectively limits the diffusion of Fc1N112⁺ ion, while facilitates the diffusion of Li⁺ and TFSI⁻. The ion transfer mechanism through the MMM separator is illustrated in Fig. 8. MMM separator serves as a sieve to mitigate the active species crossover and allows the supporting electrolyte ions transport. Most active species are blocked by the MOF whereas the supporting electrolyte ions (Li⁺ and TFSI⁻) can pass through the intracrystalline MOF pores.

The separator after long term cycling test was washed with EMC/EC/ PC solvent, dried and then subjected to SEM observation. It remains integrated with no obvious cracks on the surface. A little deposition of Fe-related species is found on its surface (Fig. 6). The XRD and FTIR patterns of the MOF and PTFE components in the separator after cycle test are similar with those of pristine ones. The C = O stretch peak coming from DMF during the MOF synthesis disappeared after cycling test. Meanwhile, no other new peaks in XRD pattern and FTIR spectrum are observed in Fig. 8 after the cycling test, which demonstrates that the MMM separator maintains its original chemical structure, proving its high stability in long-term battery operation.

5. Conclusions

In summary, we reported a facile "rolling dough" preparation to synthesize the MMM separator to moderate the cross-over effect and thus improve the performance of NARFBs. The MOF-5 crystals inside the MMM separator cannot only block the active species, but also provide an efficient Li^+ ion pathway through the structural nanopores. The separator shows a remarkable ionic selectivity of Li^+ over Fc1N112⁺ ion at a high ratio 26.6. The flow cell assembled with MMM separator delivers high CE (99.7%) and capacity retention (99.96% per cycle) over 200 cycles at 4 mA cm⁻². The superior performance of this NARFBs is attributed to the deliberately designed MMM separator, which shows high ionic selectivity, cycling performance and chemical stability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21636007) and the Start-up Package of T10108 Professorship offered by Aalto University to Y. Li. J. Yuan, Q. Qiu, and L. Fan acknowledge the financial support from the China Scholarship Council (Grant No. 201906250030, 201906150314, and 201806250102). Z.-Z. Pan acknowledges the financial support of the Academy of Finland (Grant No. 324414).

References

- M. Park, J. Ryu, W. Wang, J. Cho, Material design and engineering of nextgeneration flow-battery technologies, Nat. Rev. Mater. 2 (2017) 16080.
- [2] Y. Ding, C. Zhang, L. Zhang, Y. Zhou, G. Yu, Molecular engineering of organic electroactive materials for redox flow batteries, Chem. Soc. Rev. 47 (2018) 69–103.
 [3] G.L. Soloveichik, Flow batteries: current status and trends, Chem. Rev. 115 (2015)
- [3] G.L. Soloveicnik, Flow batteries: current status and trends, Chem. Rev. 115 (2015) 11533–11558.
- [4] C.G. Armstrong, K.E. Toghill, Stability of molecular radicals in organic nonaqueous redox flow batteries: a mini review, Electrochem. Commun. 91 (2018) 19–24.
- [5] P. Leung, A.A. Shah, L. Sanz, C. Flox, J.R. Morante, Q. Xu, M.R. Mohamed, C. Ponce de León, F.C. Walsh, Recent developments in organic redox flow batteries: a critical review, J. Power Sources 360 (2017) 243–283.
- [6] S.-H. Shin, S.-H. Yun, S.-H. Moon, A review of current developments in nonaqueous redox flow batteries: characterization of their membranes for design perspective, RSC Adv. 3 (2013) 9095–9116.
- [7] J. Yuan, Z.-Z. Pan, Y. Jin, Q. Qiu, C. Zhang, Y. Zhao, Y. Li, Membranes in nonaqueous redox flow battery: a review, J. Power Sources 500 (2021) 229983, https://doi.org/10.1016/j.jpowsour.2021.229983.
- [8] H. Chen, G. Cong, Y.-C. Lu, Recent progress in organic redox flow batteries: Active materials, electrolytes and membranes, J. Energy Chem. 27 (2018) 1304–1325.
- [9] C.G. Armstrong, K.E. Toghill, Cobalt(II) complexes with azole-pyridine type ligands for non-aqueous redox-flow batteries: Tunable electrochemistry via structural modification, J. Power Sources 349 (2017) 121–129.
- [10] Y. Zhen, C. Zhang, J. Yuan, Y. Zhao, Y. Li, A high-performance all-iron nonaqueous redox flow battery, J. Power Sources 445 (2020), 227331.
- [11] W. Duan, J. Huang, J.A. Kowalski, I.A. Shkrob, M. Vijayakumar, E. Walter, B. Pan, Z. Yang, J.D. Milshtein, B. Li, C. Liao, Z. Zhang, W. Wang, J. Liu, J.S. Moore, F. R. Brushett, L.u. Zhang, X. Wei, "Wine-Dark sea" in an organic flow battery: storing negative charge in 2,1,3-benzothiadiazole radicals leads to improved cyclability, ACS Energy Lett. 2 (5) (2017) 1156–1161.
- [12] X. Wei, W. Duan, J. Huang, L.u. Zhang, B. Li, D. Reed, W.u. Xu, V. Sprenkle, W. Wang, A high-current, stable nonaqueous organic redox flow battery, ACS Energy Lett. 1 (4) (2016) 705–711.
- [13] D. Kim, J. Song, J. Won, Structural effects of anion exchange composite membranes in non-aqueous redox flow batteries, J. Membr. Sci. 564 (2018) 523–531.
- [14] S.E. Doris, A.L. Ward, A. Baskin, P.D. Frischmann, N. Gavvalapalli, E. Chénard, C. S. Sevov, D. Prendergast, J.S. Moore, B.A. Helms, Macromolecular design strategies for preventing active-material crossover in non-aqueous all-organic redox-flow batteries, Angew. Chem. Int. Ed. 56 (6) (2017) 1595–1599.
- [15] J. Yuan, C. Zhang, Y. Zhen, Y. Zhao, Y. Li, Enhancing the performance of an allorganic non-aqueous redox flow battery, J. Power Sources 443 (2019) 227283, https://doi.org/10.1016/j.jpowsour.2019.227283.
- [16] J. Yuan, C. Zhang, T. Liu, Y. Zhen, Z.-Z. Pan, Y. Li, Two-Dimensional metal-organic framework nanosheets-modified porous separator for non-aqueous redox flow batteries, J. Membr. Sci. 612 (2020), 118463.
- [17] S. Peng, L. Zhang, C. Zhang, Y. Ding, X. Guo, G. He, G. Yu, Gradient-Distributed metal-organic framework-based porous membranes for nonaqueous redox flow batteries, Adv. Energy Mater. 8 (2018) 1802533.
- [18] T. Ma, Z. Pan, L. Miao, C. Chen, M. Han, Z. Shang, J. Chen, Porphyrin-Based symmetric redox-flow batteries towards cold-climate energy storage, Angew. Chem. Int. Ed. 57 (2018) 3158–3162.

J. Yuan et al.

- [19] J. Jung, J. Won, S.S. Hwang, Highly selective composite membranes using ladderlike structured polysilsesquioxane for a non-aqueous redox flow battery, J. Membr. Sci. 595 (2020), 117520.
- [20] J.-H. Kim, S. Ryu, S. Maurya, J.-Y. Lee, K.-W. Sung, J.-S. Lee, S.-H. Moon, Fabrication of a composite anion exchange membrane with aligned ion channels for a high-performance non-aqueous vanadium redox flow battery, RSC Adv. 10 (2020) 5010–5025.
- [21] Y. He, Y. Qiao, Z. Chang, H. Zhou, The potential of electrolyte filled MOF membranes as ionic sieves in rechargeable batteries, Energy Environ. Sci. 12 (2019) 2327–2344.
- [22] V. Viswanathan, A. Crawford, D. Stephenson, S. Kim, W. Wang, B. Li, G. Coffey, E. Thomsen, G. Graff, P. Balducci, M. Kintner-Meyer, V. Sprenkle, Cost and performance model for redox flow batteries, J. Power Sources 247 (2014) 1040–1051.
- [23] M. Zhao, Y. Wang, Q. Ma, Y. Huang, X. Zhang, J. Ping, Z. Zhang, Q. Lu, Y. Yu, H. Xu, Y. Zhao, H. Zhang, Ultrathin 2D metal-organic framework nanosheets, Adv. Mater. 27 (2015) 7372–7378.
- [24] S. Castarlenas, C. Tellez, J. Coronas, Gas separation with mixed matrix membranes obtained from MOF UiO-66-graphite oxide hybrids, J. Membr. Sci. 526 (2017) 205–211.
- [25] L.u. Wang, Y. Han, X. Feng, J. Zhou, P. Qi, B.o. Wang, Metal-Organic frameworks for energy storage: batteries and supercapacitors, Coord. Chem. Rev. 307 (2016) 361–381.
- [26] S. Liu, X. Sang, L. Wang, J. Zhang, J. Song, B. Han, Incorporation of metal-organic framework in polymer membrane enhances vanadium flow battery performance, Electrochim. Acta 257 (2017) 243–249.
- [27] Z. Zhao, X. Ma, Z. Li, Y.S. Lin, Synthesis, characterization and gas transport properties of MOF-5 membranes, J. Membr. Sci. 382 (2011) 82–90.
- [28] N.T.S. Phan, K.K.A. Le, T.D. Phan, MOF-5 as an efficient heterogeneous catalyst for Friedel-Crafts alkylation reactions, Applied Catalysis A: General 382 (2) (2010) 246–253.
- [29] R.M. Rego, G. Kuriya, M.D. Kurkuri, M. Kigga, MOF based engineered materials in water remediation: Recent trends, J. Hazard. Mater. 403 (2021) 123605, https:// doi.org/10.1016/j.jhazmat.2020.123605.
- [30] K. Cendrowski, W. Kukulka, T. Kedzierski, S. Zhang, E. Mijowska, Poly(vinylidene fluoride) and carbon derivative structures from eco-friendly MOF-5 for supercapacitor electrode preparation with improved electrochemical performance, Nanomaterials 8 (2018) 890.

- [31] Z. Zhao, X. Ma, A. Kasik, Z. Li, Y.S. Lin, Gas separation properties of metal organic framework (MOF-5) membranes, Ind. Eng. Chem. Res. 52 (2012) 1102–1108.
- [32] J. Li, Q. Zhong, Y. Yao, S. Bi, T. Zhou, X. Guo, M. Wu, T. Feng, R. Xiang, Electrochemical performance and thermal stability of the electrospun PTFE nanofiber separator for lithium-ion batteries, J. Appl. Polym. Sci. 135 (2018) 46508.
- [33] Z. Wang, W. Huang, J. Hua, Y. Wang, H. Yi, W. Zhao, Q. Zhao, H. Jia, B. Fei, F. Pan, An anionic-MOF-based bifunctional separator for regulating lithium deposition and suppressing polysulfides shuttle in Li–S batteries, Small Methods 4 (2020) 2000082.
- [34] X. Teng, C. Sun, J. Dai, H. Liu, J. Su, F. Li, Solution casting Nafion/ polytetrafluoroethylene membrane for vanadium redox flow battery application, Electrochim. Acta 88 (2013) 725–734.
- [35] X. Teng, C. Yu, X. Wu, Y. Dong, P. Gao, H. Hu, Y. Zhu, J. Dai, PTFE/SPEEK/PDDA/ PSS composite membrane for vanadium redox flow battery application, J. Membr. Sci. 53 (2017) 5204–5215.
- [36] A. Dinesh, S. Olivera, K. Venkatesh, M.S. Santosh, M.G. Priya, A.M. Inamuddin, H. B.M. Asiri, Iron-Based flow batteries to store renewable energies, Environ. Chem. Lett. 16 (2018) 683–694.
- [37] X. Wei, L. Cosimbescu, W. Xu, J.Z. Hu, M. Vijayakumar, J. Feng, M.Y. Hu, X. Deng, J. Xiao, J. Liu, V. Sprenkle, W. Wang, Towards high-performance nonaqueous redox flow electrolyte via ionic modification of active species, Adv. Energy Mater. 5 (2015) 1400678.
- [38] K.S. Han, N.N. Rajput, X. Wei, W. Wang, J.Z. Hu, K.A. Persson, K.T. Mueller, Diffusional motion of redox centers in carbonate electrolytes, J. Chem. Phys. 141 (2014), 104509.
- [39] H. Yang, C. Fan, Q. Zhu, Sucrose pyrolysis assembling carbon nanotubes on graphite felt using for vanadium redox flow battery positive electrode, J. Energy Chem. 27 (2018) 451–454.
- [40] I.L. Escalante-García, J.S. Wainright, L.T. Thompson, R.F. Savinell, Performance of a non-aqueous vanadium acetylacetonate prototype redox flow battery: examination of separators and capacity decay, J. Electrochem. Soc. 162 (3) (2015) A363–A372.
- [41] K. Gong, Q. Fang, S. Gu, S.F.Y. Li, Y. Yan, Nonaqueous redox-flow batteries: organic solvents, supporting electrolytes, and redox pairs, Energy Environ. Sci. 8 (2015) 3515–3530.