

ChemComm

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/chemcomm

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Composite porous membranes with ultrathin selective layer for vanadium flow battery

Yun Li,^{a,b} Xianfeng Li^{*a}, Jingyu Cao,^{a,b} Wanxing Xu,^{a,b} and Huamin Zhang,^{*a}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

An ultrathin Nafion film was introduced on the poly (ether sulfone) (PES) / sulfonated poly (ether ether ketone) (SPEEK) porous membranes for vanadium flow battery (VFB) application. The composite membranes showed very high ions selectivity, good stability and excellent performance (energy efficiency 86.5% at 80 mA cm⁻²) in VFB.

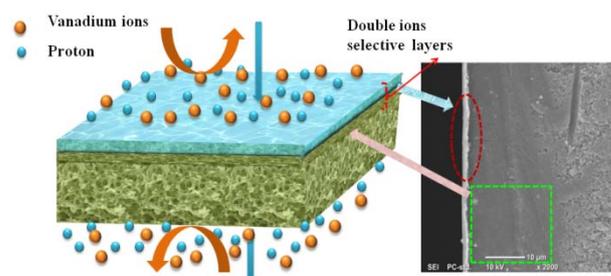
Energy storage is the key technique to ensure the smooth and consistent power output of renewable energy resources. Among a wide range of energy storage techniques, vanadium flow battery (VFB) initiated by M. Skyllas-Kazacos in 1985, becomes one of the most competitive candidates due to its features like flexible design, good operational reliability, high efficiency and high safety.^{1,2} In a VFB, the electricity is stored as chemical energy in flowing electrolytes. As a key part of VFB cell, a membrane is employed to separate electrolytes (vanadium ions), while still transfer protons to complete the energy conversion process.^{3,4} Therefore, the ideal VFB membranes are supposed to possess good chemical stability, high proton conductivity, low vanadium ions permeability and low cost.^{5,6}

However, many types of commercial membranes, e.g. the Asahi Glass, Selemion series (AMV, DMV, CMV) and Daramic membranes,^{7,8} were proved to be unsuitable for VFB application due to their poor chemical stability or ions selectivity. The most commonly used membranes in VFB are perfluorosulfonic polymers such as DuPont Nafion[®] membranes⁹, due to their excellent stability and proton conductivity. However, their extremely high cost and relatively high vanadium crossover^{10,11} have limited VFB commercialization. Therefore, extensive research in VFB is focused on the exploration of membranes with low cost and high performance.^{9,12,13}

Recently, porous membrane separators have attracted wide attention and firstly reported in VFB. They can separate vanadium ions from protons based on pore size exclusion via Stokes radius difference.¹⁴ Besides, their performance can be adjusted via tuning morphology and membrane modification.¹⁵⁻¹⁷

Up to now, different kinds of porous membranes have been explored and investigated in VFB, e.g. poly (ether sulfone), polyvinylidene difluoride (PVDF), polyacrylonitrile (PAN)¹⁴⁻¹⁶. Quite impressive progress was achieved via optimizing the membrane materials and morphology.¹⁶ However, the conflict between ions selectivity and ions conductivity was still not well resolved. Membranes prepared by phase inversion

normally possess an asymmetric structure including a skin layer and a porous support layer. The ions transport resistance and selectivity are mainly determined by the skin layer. Smaller pores of skin layer are preferred in VFBs to keep ions selectivity, however, smaller pores will induce the loss of energy from ohmic polarization. Thus the optimized performance of porous membranes is relatively low. In this paper a composite membrane was designed and fabricated to solve this conflict (Scheme 1). The idea is based on introducing an ultrathin ions selective layer on the porous membrane support. In this design, the pores of skin layer are kept relatively large to ensure membranes conductivity while the ultrathin toplayer will ensure the selectivity and keep ions conductivity. Here we called double ions selective layers (skin layer and toplayer). To realize this idea, porous PES/SPEEK porous membrane was selected as an example, which was prepared by phase inversion, where SPEEK was used to tune membrane pore size and pore size distribution. Considering the excellent stability and proton conductivity of Nafion, an ultrathin selective layer of Nafion was introduced on porous PES/SPEEK membranes to improve the membranes selectivity and keep proton conductivity.



Scheme 1 The design of composite membrane. SPEEK polymers were obtained by direct sulfonation of PEEK with sulfuric acid at 70 °C for 2 h and the sulfonation degree was determined as 0.8 by ¹H NMR.¹⁸ The porous PES/SPEEK membranes were obtained by traditional phase inversion method. The polymer solution consisted of 28.0 wt. % PES, 7.0 wt. % SPEEK, which were dissolved in N, N-dimethylacetamide (DMAc). Then, 1.0 wt. % Nafion solution was sprayed uniformly on the prepared PES/SPEEK membrane with an airbrush at a pressure of 0.2 MPa. The solution was prepared by diluting 5.0 wt. % Nafion dispersion (Dupont, D-520) with isopropyl alcohol.

In order to increase the compatibility between membranes and Nafion solution, the membranes were soaked in the isopropyl alcohol for 0.5 h in advance. Finally, the membranes were stored in the deionized water for characterization.

Table 1. Battery performance of PES/SPEEK porous membranes with different proportion of Nafion at a current density of 80 mA cm^{-2} .

Sample	Mass fraction of Nafion (wt.%)	Coulombic efficiency (%)	Energy efficiency (%)	Voltage efficiency (%)
M_0	0	77.1	68.5	88.9
$M_{2.56}$	2.56	98.5	86.5	87.8
$M_{5.44}$	5.44	98.1	83.1	84.8
$M_{7.86}$	7.86	98.6	83.0	84.2
Nafion 115	-	94.6	82.1	86.8

The morphology of the prepared membranes was investigated by SEM shown in Fig. 1. The cross section of PES/SPEEK porous membrane M_0 exhibited a typical sponge-like porous structure (Fig. 1(c), the magnified cross section structure was shown as Figure 1s in supporting information). The membrane showed a relatively rougher surface. It can be seen from Fig. 1(b) that the pores disappeared and a smooth surface was formed after coverage of Nafion layer. Fig. 1(d) showed the cross section of the composite membranes, an ultra thin (around $1 \mu\text{m}$) dense layer of Nafion film was clearly illustrated and successfully introduced on the porous support. It is suggested that this spray method could be used to form a defect free functional layer on the surface of PES/SPEEK membrane and the thickness could be controlled by adjusting the volume of the Nafion solution.

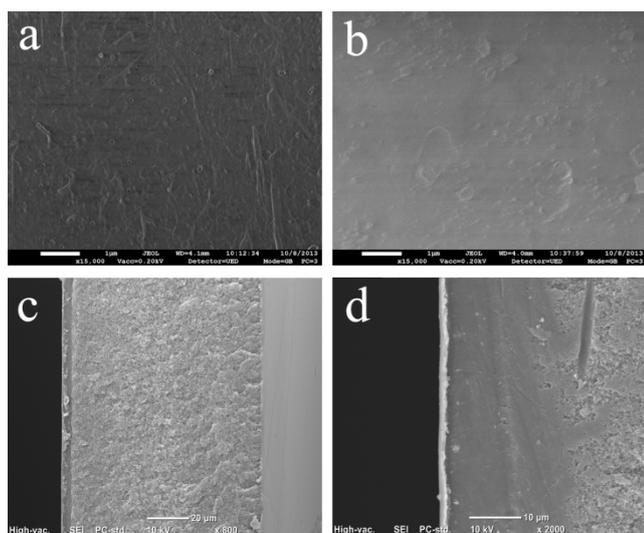


Fig. 1. Surface and cross-section morphology of membranes (a and c: M_0 , b and d: $M_{2.56}$)

Fig. 2(a) shows a linear plot of vanadium concentration versus time, the slope of the line corresponding to M_0 is much higher than that of modified membranes. It suggests that the initial PES/SPEEK porous membrane owns certain ability to exclude the vanadium ions, however, the ultra thin layer plays the most important role in improving ions selectivity. Compare with pristine Nafion membranes (vanadium permeability $11.9 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$)¹⁵, the composite membrane $M_{2.56}$ showed a lower value $5.39 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ or much higher selectivity. As for traditional Nafion membrane, the vanadium permeability is related to the thickness and swelling property of the membrane.

Considering that the modified layer is very thin, it could be attributed to the fact that the interface of PES/SPEEK polymer matrix hinders the swelling of Nafion effectively. Besides, part of Nafion polymers could possibly diffuse into and block the pores of PES/SPEEK substrate, thus the pore size became smaller, so the ions selectivity of the PES/SPEEK substrate was enhanced. The pore size and porosity of membranes determined by water permeability method¹⁹ confirmed the above assumption (Figure S2, S3 in supporting information). After introducing the very thin layer of Nafion on membranes support, the average pore size decreased from 3.6 nm to 0.7 nm and the porosity of the membranes slightly decreased as well. Still, the pores of PES/SPEEK could confine the swelling of Nafion and increase the selectivity as well. With the proportion of Nafion increasing, the vanadium permeability of different membranes varied only in a very narrow range and kept at a very low level, indicating that the modified layer could inhibit the vanadium ions crossing through the membranes dramatically.

As demonstrated in Fig. 2(b), with the proportion of Nafion increasing, the area resistance showed an increasing trend. The area resistance of $M_{2.56}$ was $0.254 \Omega \text{ cm}^2$, which was comparable to the original membrane M_0 ($0.21 \Omega \text{ cm}^2$). However, as for membranes $M_{5.44}$ and $M_{7.86}$, the area resistance increased clearly,

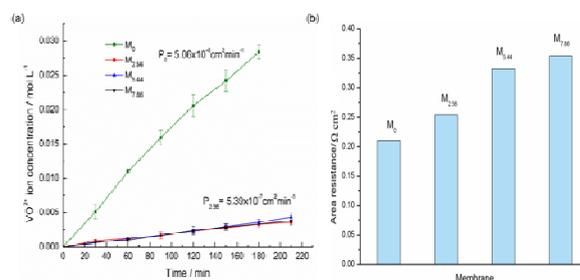


Fig. 2. a) VO_2^+ concentrations in the deficiency side of the permeation measuring device; and b) The area resistance of membranes.

suggesting that too much Nafion is not beneficial to the ions conductivity, which could be attributed to the increased ions transport resistance induced by pores blockage. This is well in agreement with the results of vanadium ions permeability described above.

The VFB performance of modified porous membranes with different proportion of Nafion resin was shown in Table 1. VFBs assembled with modified membranes exhibited coulombic efficiency (CE) of around 98%, which was much higher than that of initial porous membrane (77.1%). CE represents the capacity loss in VFB and mainly relates to the rate of vanadium ions cross-mixing during charge-discharge cycles. Thus, the composite PES/SPEEK porous membranes with extremely low vanadium permeability had much higher CE than original membranes. With proportion of Nafion increasing, the voltage efficiency (VE) declined gradually from 87.8 % to 84.2 %, due to larger ohmic polarization. As expected, the energy efficiency (EE) also showed a downtrend, and $M_{2.56}$ with 2.56 wt. % Nafion showed the best performance of EE 86.5 %, indicating that moderate Nafion polymer plays a key role in determining the performance of VFB. Compare with commercialized Nafion 115, the composite membranes showed much higher CE and EE, therefore much better overall performance (Table 1). Further decreasing the mass

fraction of Nafion, the toplayer becomes thinner and the selectivity decreases, further leading to lower CE. For example, when the mass fraction decreased to 1.08%, the CE of the VFB single cell declined to 92% and EE decreased to 77% (Figure S4 in supporting information). Fig. 3 demonstrates the efficiency of the batteries assembled with M_0 and $M_{2.56}$ at the range of current densities from 40 mA cm⁻² to 120 mA cm⁻². Much higher coulombic efficiencies (CE) of $M_{2.56}$ than that of M_0 were realized under comparable operating conditions. Although the voltage efficiencies (VE) of $M_{2.56}$ decreased marginally due to higher area resistance, the cell assembled with $M_{2.56}$ shows excellent EEs (90.4, 87.3 and 86.5% at 40, 60 and 80 mA cm⁻², respectively) that are much higher than that of M_0 at responding current density. Although the tendency becomes less distinct at higher current densities, the EE of $M_{2.56}$ still exceeds that of M_0 by 7.4 % at 120 mA cm⁻². Moreover, the single cell assembled with $M_{2.56}$ continuously ran more than 100 cycles at a current density of 80 mA cm⁻² and no efficiency decay was found. And there is no remarkable decay on the charge capacity after running

for 10, 30 and 50 cycles, showing good storage stability (Figure S5 in supporting information). It could be seen that the modified layer still exist on the porous membrane surface after test, suggesting good chemical stability. Further accelerating ex-situ oxidation stability was carried out on $M_{2.56}$ by immersing the membranes in VO₂⁺ for more than 200 hours (Figure S6 in supporting information), the concentration of VO₂⁺ barely changed comparing with the blank solution, indicating the high chemical stability of prepared membranes as well²⁰. All results suggest that porous PES/SPEEK porous membranes with ultrathin Nafion layer could serve as a competitive high-performance membrane material for VFBs. Apart from PES/SPEEK membranes, this concept can surely extend to other porous membranes like polyvinylidene difluoride (PVDF), polyacrylonitrile (PAN) etc, thus providing an effective way to fabricate composite membranes with high potential in the application of VFB.

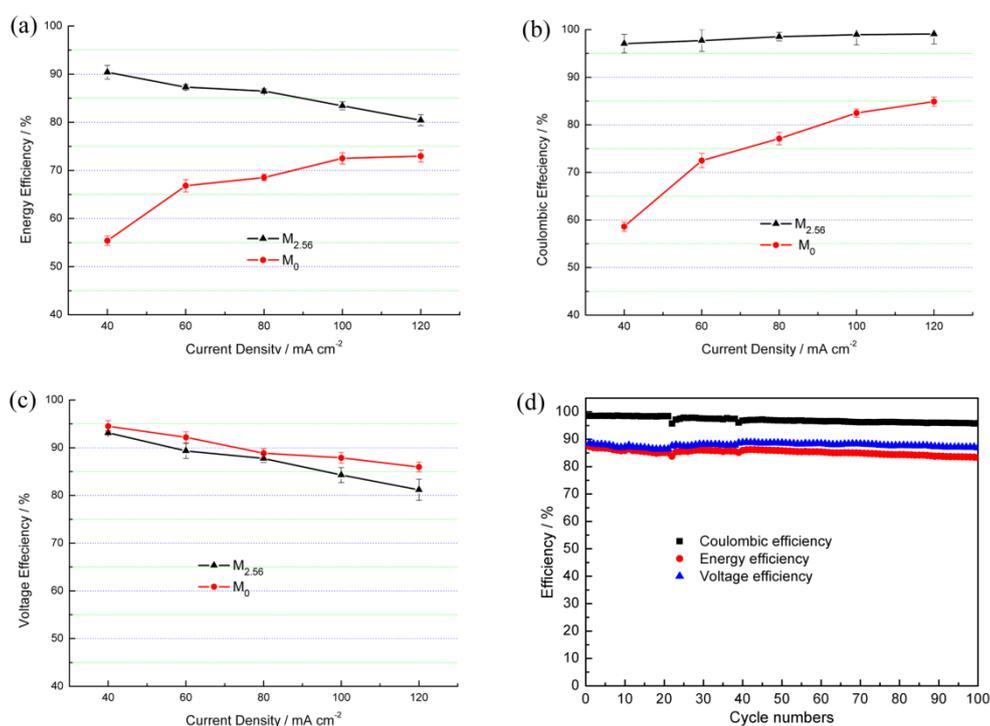


Fig. 3. a) VFB coulombic efficiencies at different current densities; b) VFB voltage efficiencies at different current densities; c) VFB energy efficiencies at different current densities; and d) The charge-discharge cycling performance of VFB assembled with $M_{2.56}$ at 80 mA cm⁻²

Conclusions

In this work, composite PES/SPEEK porous membranes with ultrathin Nafion layer were prepared and introduced into VFB. The low-cost membrane was proved to be very suitable for VFB. The single cell assembled with them exhibited much better performance than commercialized Nafion 115 (energy efficiency 86.5% Vs 82.1%, 80 mA cm⁻²) and a stable performance after 100 cycles in a charge-discharge test. This study provides a simple method to fabricate composite membranes, combining excellent performance and low cost for VFB application.

Acknowledgement:

The authors acknowledge the financial support from China Natural Science Foundation (No. 21206158) and National Basic Research Program of China (973 program No. 2010CB227202).

Notes and references

- ^a Division of energy storage, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Zhongshan Road 457, Dalian 116023, China Email: zhanghm@dicp.ac.cn; lixianfeng@dicp.ac.cn
^b University of Chinese Academy of Sciences, Beijing 100039, China
 † Electronic Supplementary Information (ESI) available:

Experimental

65

The cross-section and surface morphologies of the membranes were investigated by SEM (JEOL JCM-6000, Japan). The membrane samples were obtained by breaking the membranes in liquid nitrogen and coating them with gold before measurement.

The area resistance of the membranes was measured with the method described as follows¹⁴. Conductivity cell was separated by the membrane into two compartments, which were filled with 0.5M H₂SO₄. The effective area of the cell was designed as 1 cm². Area electric resistances were determined by electrochemical impedance spectroscopy (EIS) over a frequency range from 1 kHz to 1 MHz, the area resistance was calculated by including the equivalent circuit. (Fig S7-S8 in supporting information)

The vanadium permeability (P_v) through the membranes was calculated with the method according to the Fick diffusion law.¹⁵ The membrane was sandwiched with two half diffusion cells (effective area 9 cm², capacity 75 mL), which were filled with 1.5M VO²⁺ in 3 M H₂SO₄ and 1.5M Mg²⁺ in 3 M H₂SO₄, respectively. Samples from the insufficient VO²⁺ side were collected at regular time interval, and the VO²⁺ concentration was determined by UV-vis spectrometer.

The VFB single cell fabrication and performance evaluation system have been reported previously by our group.¹⁶ The membrane sandwiched with two carbon felt electrodes was clamped by two graphite polar plates, which served as current collector. All these components were fixed between two stainless plates. 30 mL 1.5 M V²⁺/V³⁺ in 3.0 M H₂SO₄ and 30 mL 1.5M VO²⁺/VO₂⁺ in 3.0 M H₂SO₄ solutions were used as negative and positive electrolytes respectively. The electrolyte was cyclically pumped through the corresponding electrodes in airtight pipe lines. Charge-discharge cycling tests were conducted by Arbin BT 2000 with a constant current density. The cut-off voltage for charge and discharge was set at 1.65V and 0.8V respectively to avoid the corrosion of carbon felt and graphite polar plates.

1. M. Skyllas-Kazacos, M. H. Chakrabarti, S. A. Hajimolana, F. S. Mjalli and M. Saleem, *J. Electrochem.Soc.*, 2011, 158, R55.
2. B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, 334, 928-935.
3. M. Skyllas-Kazacos and M. Kazacos, *J. Power Sources*, 2011, 196, 8822-8827.
4. M. Skyllas-Kazacos and L. Goh, *J. Membr. Sci.*, 2012, 399, 43-48.
5. D. Chen, M. A. Hickner, E. Agar and E. C. Kumbur, *ACS Appl. Mater. Interfaces*, 2013, 5, 7559-7566.
6. X. Teng, J. Dai, J. Su, Y. Zhu, H. Liu and Z. Song, *J. Power Sources*, 2013, 240, 131-139.
7. T. Mohammadi and M. Skyllas-Kazacos, *J. Membr. Sci.*, 1995, 98, 77-87.
8. T. Mohammadi and M. S. Kazacos, *J. Appl. Electrochem.*, 1997, 27, 153-160.
9. B. Schwenzer, J. Zhang, S. Kim, L. Li, J. Liu and Z. Yang, *ChemSusChem*, 2011, 4, 1388-1406.
10. C. Ding, H. Zhang, X. Li, H. Zhang, C. Yao and D. Shi, *ChemSusChem*, 2013, 6, 1262-1269.
11. M. Vijayakumar, M. S. Bhuvaneshwari, P. Nachimuthu, B. Schwenzer, S. Kim, Z. Yang, J. Liu, G. L. Graff, S. Thevuthasan and J. Hu, *J. Membr. Sci.*, 2011, 366, 325-334.
12. X. Li, H. Zhang, Z. Mai, H. Zhang and I. Vankelecom, *Energy. Environ. Sci.*, 2011, 4, 1147.
13. A. Parasuraman, T. M. Lim, C. Menictas and M. Skyllas-Kazacos, *Electrochim. Acta*, 2013, 101, 27-40.
14. H. Zhang, H. Zhang, X. Li, Z. Mai and J. Zhang, *Energy. Environ. Sci.*, 2011, 4, 1676.
15. W. Wei, H. Zhang, X. Li, H. Zhang, Y. Li and I. Vankelecom, *Phys. Chem. Chem. Phys.*, 2013, 15, 1766-1771.
16. Y. Li, H. Zhang, X. Li, H. Zhang and W. Wei, *J. Power Sources*, 2013, 233, 202-208.
17. H. Zhang, H. Zhang, X. Li, Z. Mai and W. Wei, *Energy. Environ. Sci.*, 2012, 5, 6299-6303.
18. P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhailenko, K. Wang and S. Kaliaguine, *J. Membr. Sci.*, 2004, 229, 95-106.
19. F.P. Cuperus, C.A. Smolders, *Adv. Colloid Interface Sci.*, 1991, 34, 135-173.
20. S. Kim, T. B. Tighe, B. Schwenzer, J. Yan, J. Zhang, J. Liu, Z. Yang, M. A. Hickner, *J. Appl. Electrochem.* 2011, 41, 1201-1213.