Electronic Supplementary Material (ESI) for Materials Advances.


***Supplementary Information For***

# Suppressing Vanadium Crossover Using Sulfonated Aromatic Ion Exchange Membranes for High Performance Flow Batteries

Tongshuai Wang, Junyoung Han, Kihyun Kim, Andreas Munchinger, Yuechen Gao, Alain Farchi, Yoong-Kee Choe, Klaus-Dieter Kreuer*, Chulsung Bae*, and Sangil Kim*

## Supplementary Information Contents



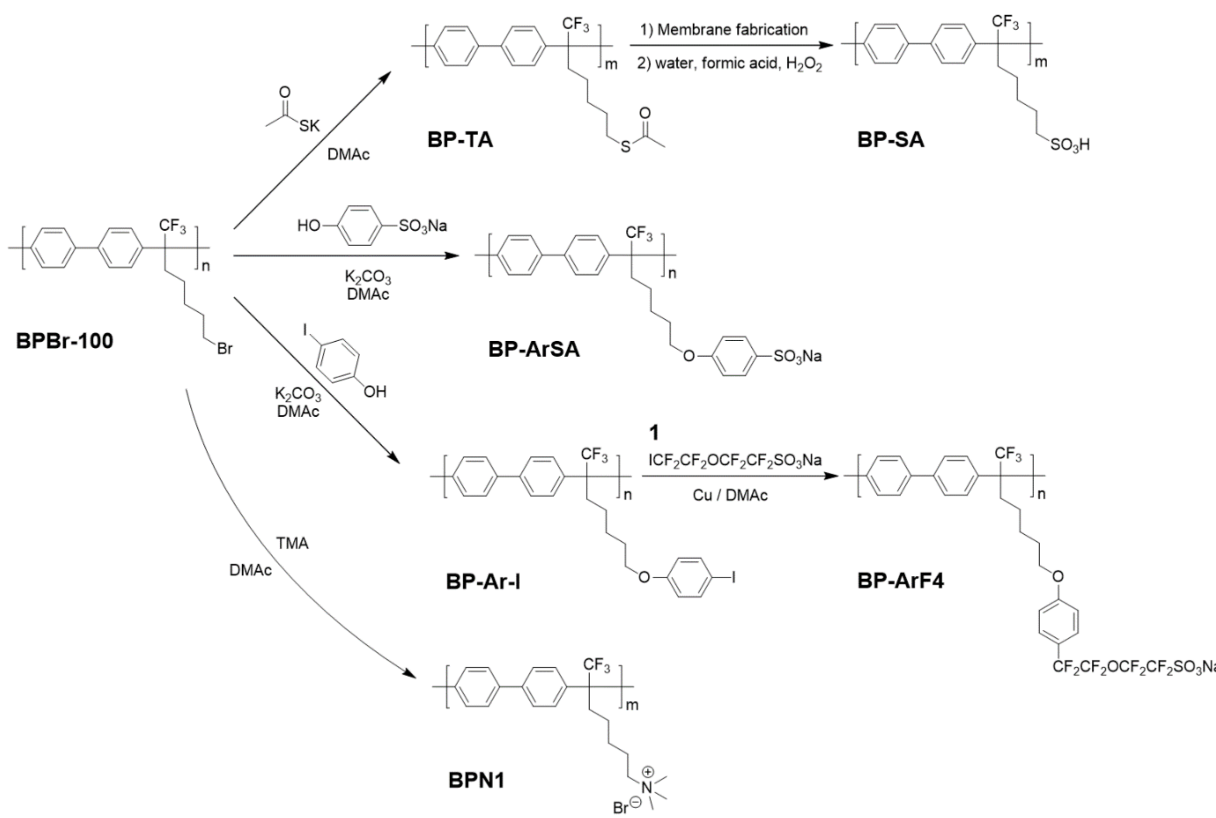



**Figure S1.** Synthesis of functionalized polymer electrolytes with different side chain structures. Compound **1**: $ICF_2CF_2OCF_2CF_2SO_3Na$. Related to the polymer Synthesis and characterization section in the main test.

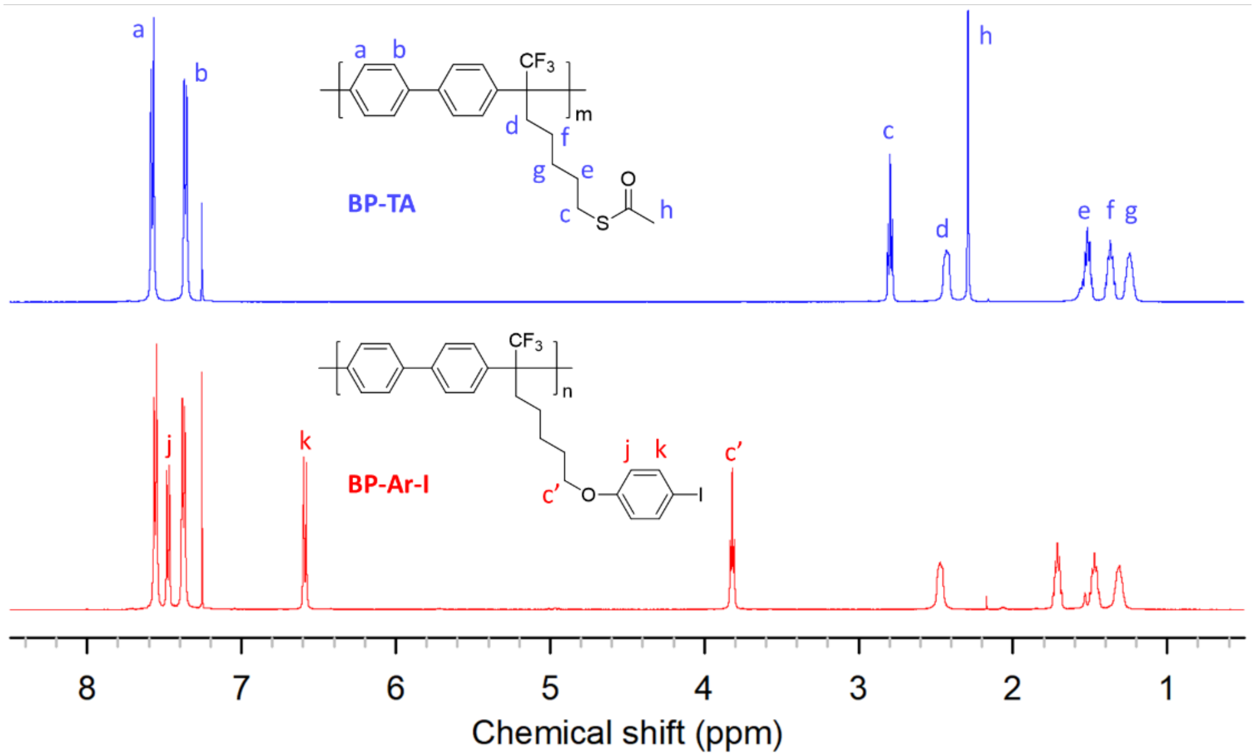



**Figure S2.** $^1$H NMR spectra ($CDCl_3$) of synthesized polymers: BP-TA (blue) and BP-Ar-I (red). BP-TA δ (ppm) = 7.57 (d, 4H), 7.36 (d, 4H), 2.8 (t, 2H), 2.43 (m, 2H), 1.52 (m, 2H), 1.37 (m, 2H), 1.24 (m, 2H); BP-ArI δ (ppm) = 7.57 (d, 4H), 7.49 (d, 2H), 7.39 (d, 4H), 6.60 (d, 2H), 3.82 (t, 2H), 2.47 (m, 2H), 1.71 (m, 2H), 1.47 (m, 2H), 1.31 (m, 2H). Related to the polymer Synthesis and characterization section in the main test.

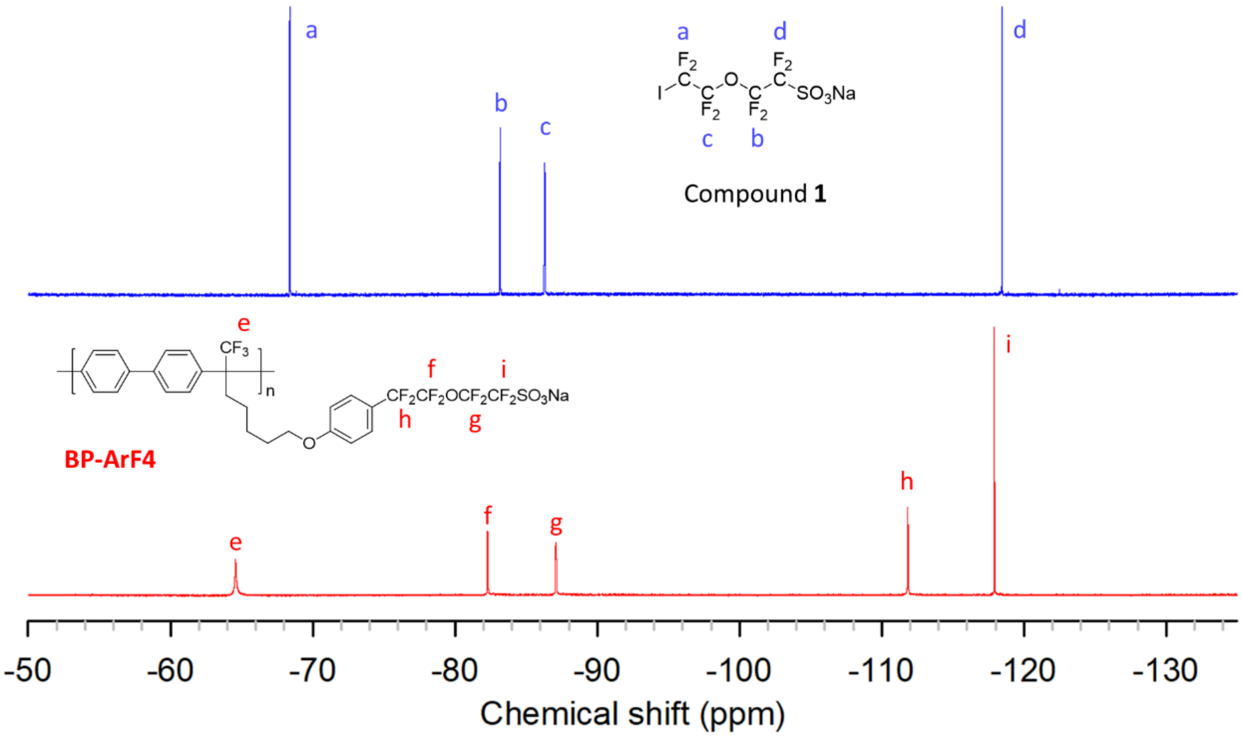



**Figure S3.** $^{19}F$ NMR spectra of synthesized polymers: Compound **1** ($D_2O$ solvent, blue) and BP-Ar-**I** (DMSO-$d_6$, red). Compound **1**, δ (ppm) = -68.38 (t, 2F), -83.17 (t, 2F), -86.31 (t, 2F), -118.46 (t, 2F); BP-Ar**I**, δ (ppm) = -64.57 (s, 3F, $-CF_3$), -82.25 (t, 2F), -87.08 (t, 2F), -111.82 (t, 2F), -117.92 (t, 2F). Related to the polymer Synthesis and characterization section in the main test.

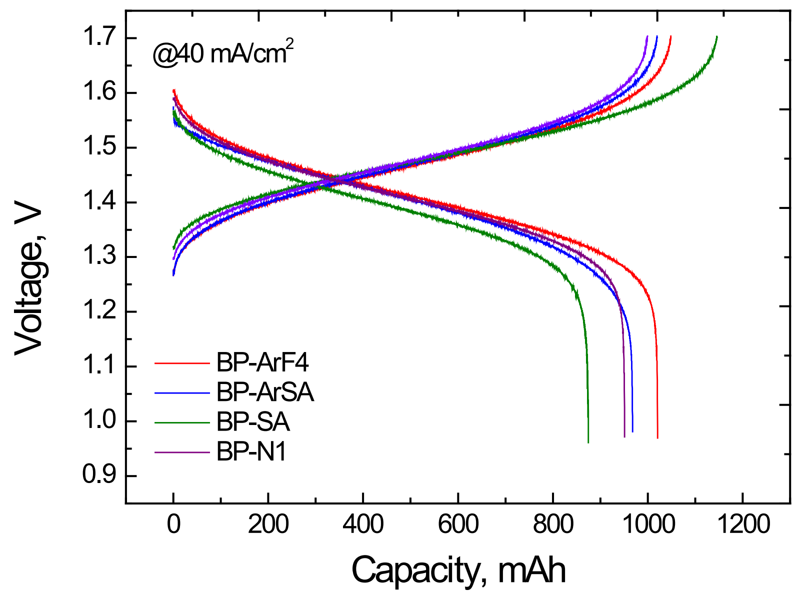



**Figure S4.** Charge-discharge curves for BP-ArF4, BP-ArSA, BP-SA, and BPN1 at current density of 40 mA/cm$^2$.

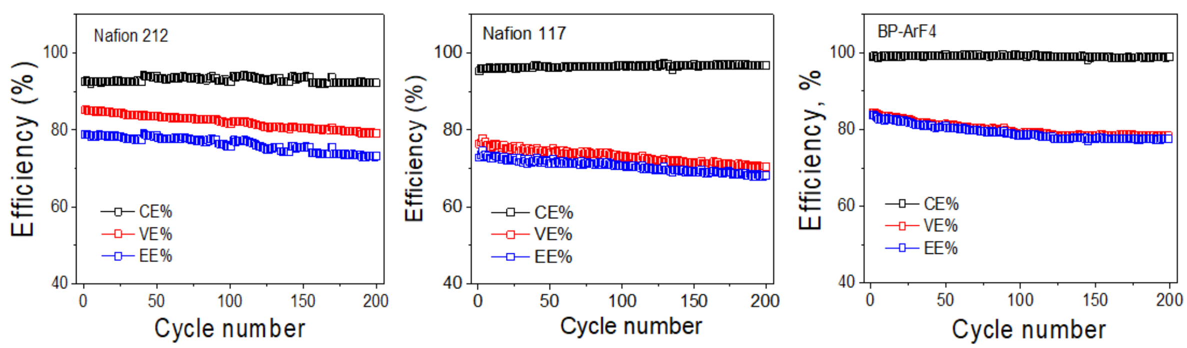



**Figure S5.** Comparison of VRFB cycle stability of BP-ArF4 membrane with Nafion 212 and 117 at 100 mA/cm$^2$.

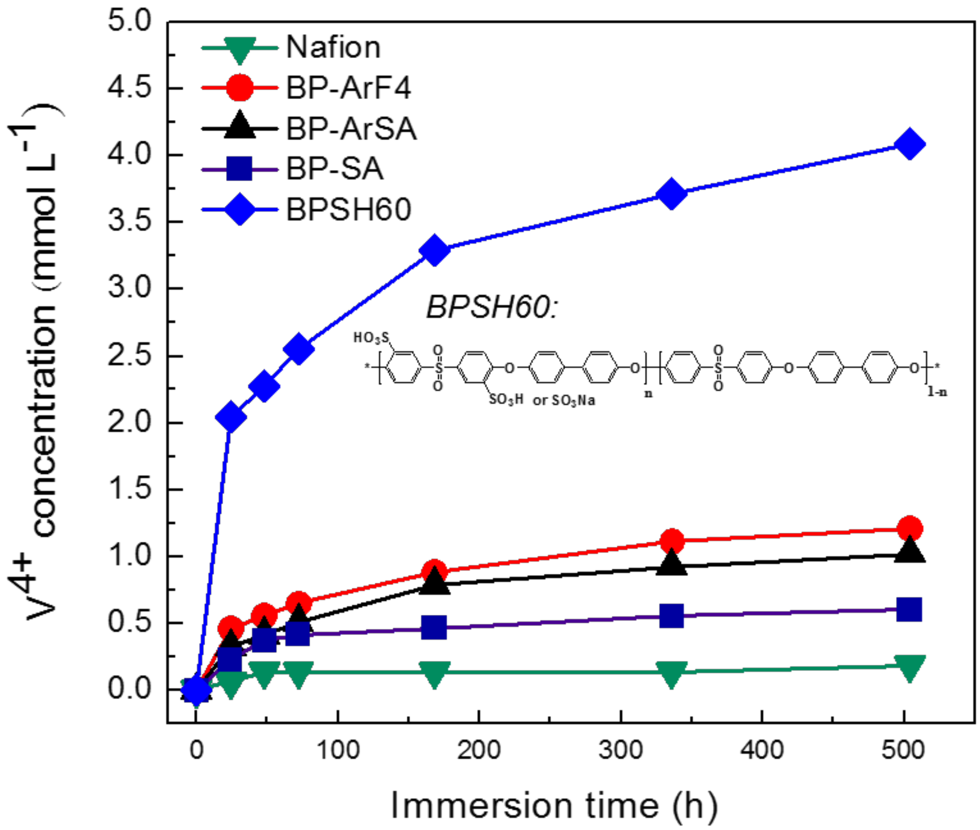



**Figure S6.** Chemical stability test results show increase of $V^{4+}$ ions concentration with time of electrolyte (0.1 M $V^{5+}$ in 4.0 M $H_2SO_4$) solutions containing IEMs at room temperature. We also compare our biphenyl-based sulfonated membranes with another hydrocarbon PEM, BPSH-60. Related to the VRFB performance section in the main test.

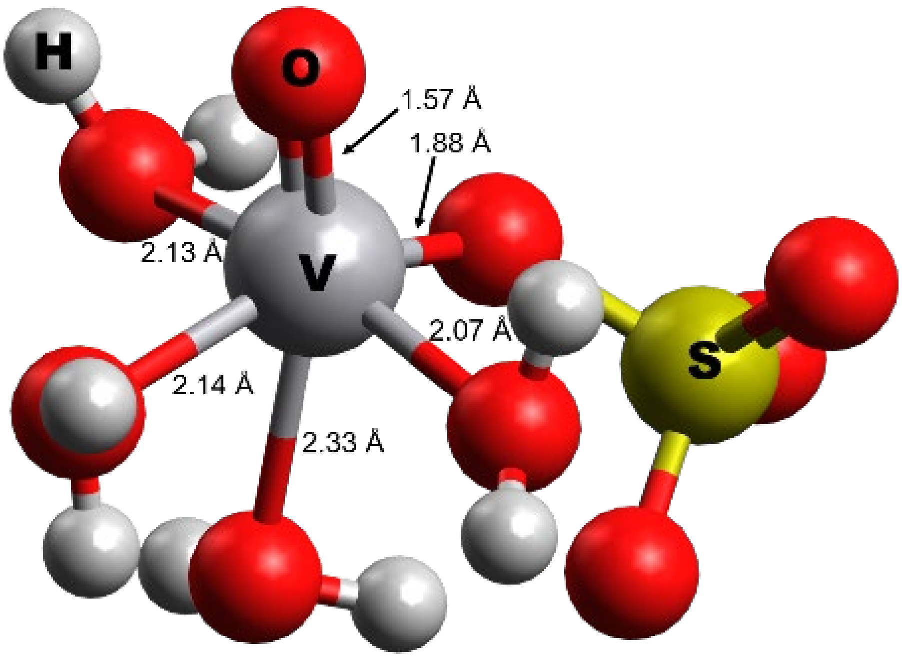



**Figure S7.** Optimized structures of $VO(SO_4)(H_2O)_4$. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

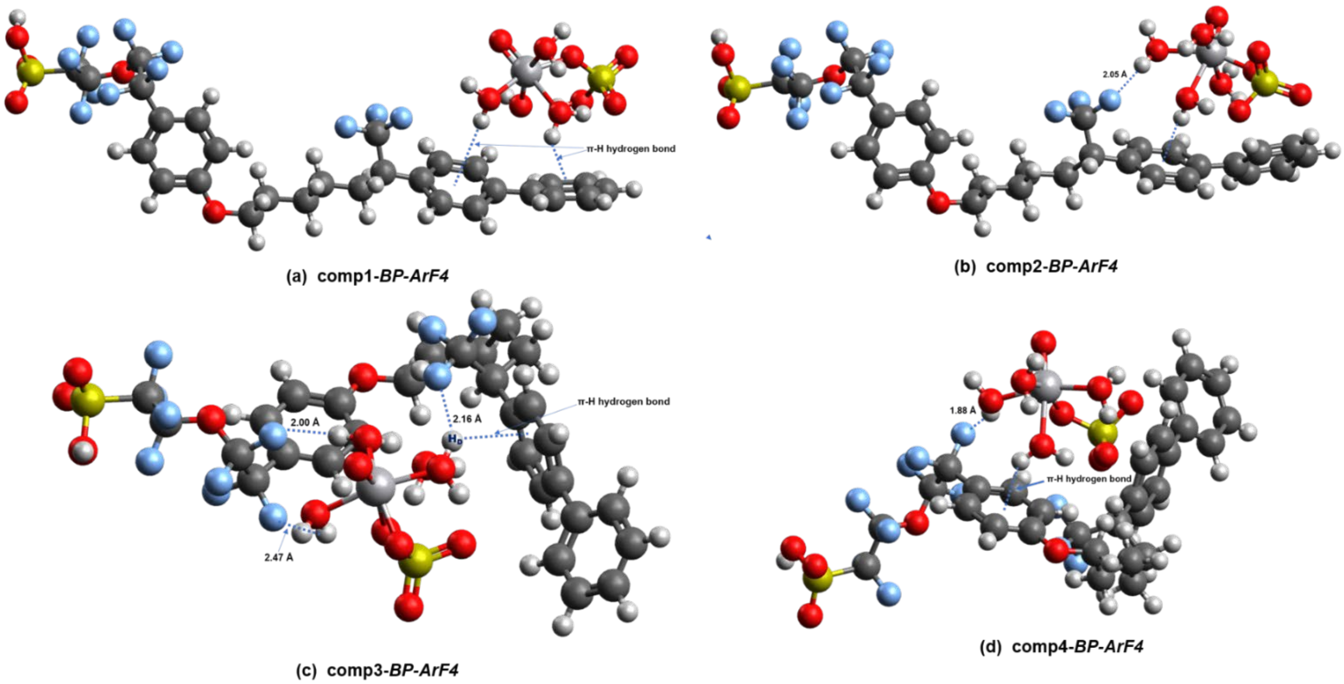



**Figure S8.** Optimized structures of BP-ArF4 --- vanadium ion complexes. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

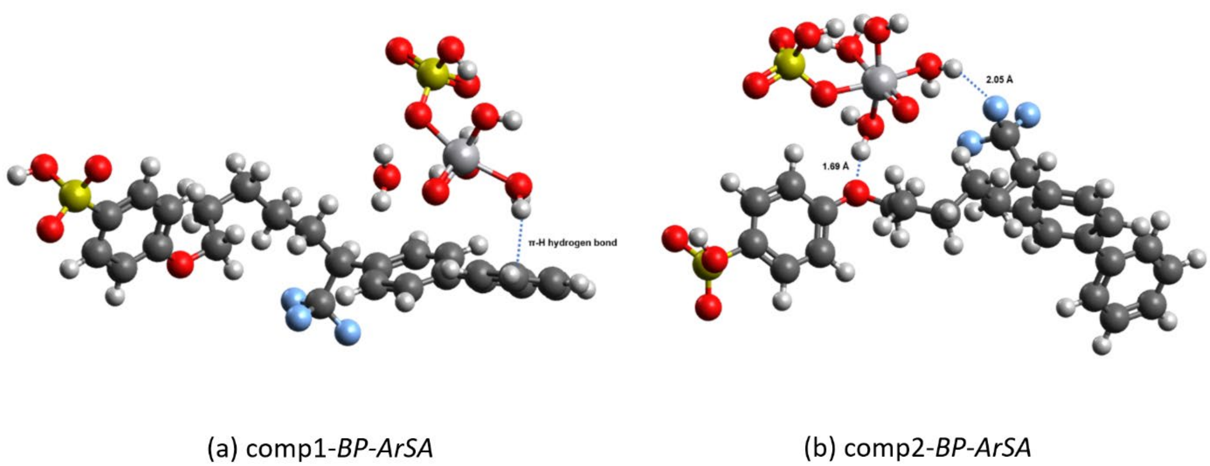
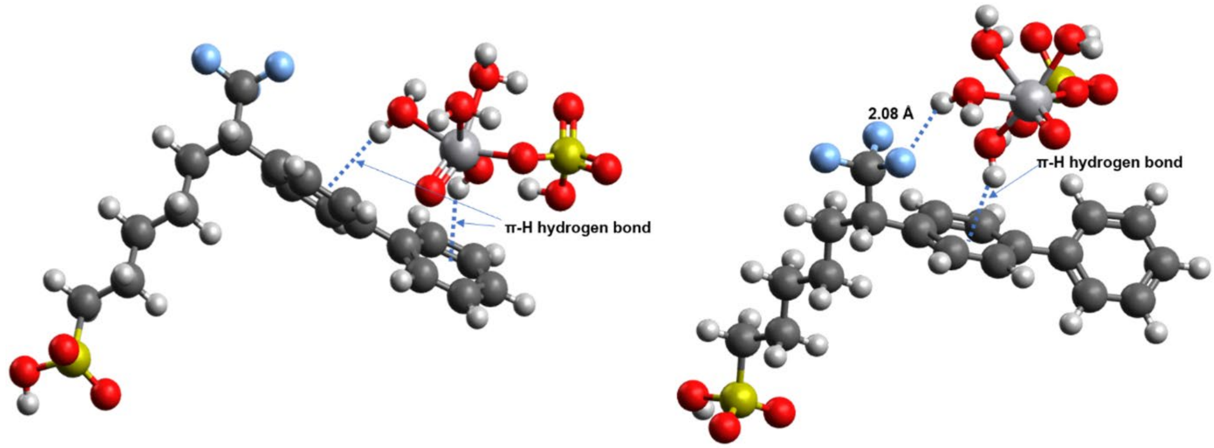
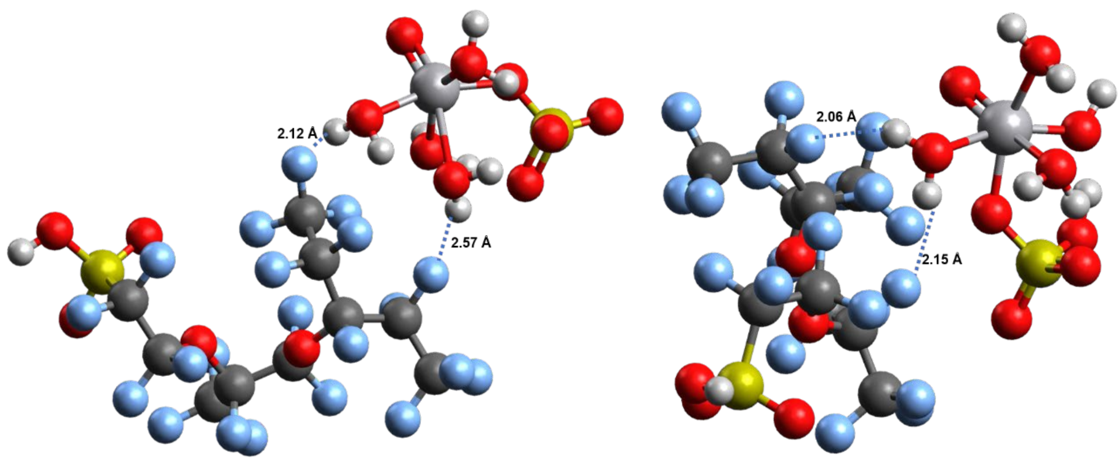



**Figure S9.** Optimized structures of BP-ArSA --- vanadium ion complexes. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.




(a) comp1-*BP-SA* (b) comp2-*BP-SA*

**Figure S10.** Optimized structures of BP-SA --- vanadium ion complexes. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.




(a) comp1-*Nafion* (b) comp2-*Nafion*

**Figure S11**. Optimized structures of *Nafion* --- vanadium ion complexes. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

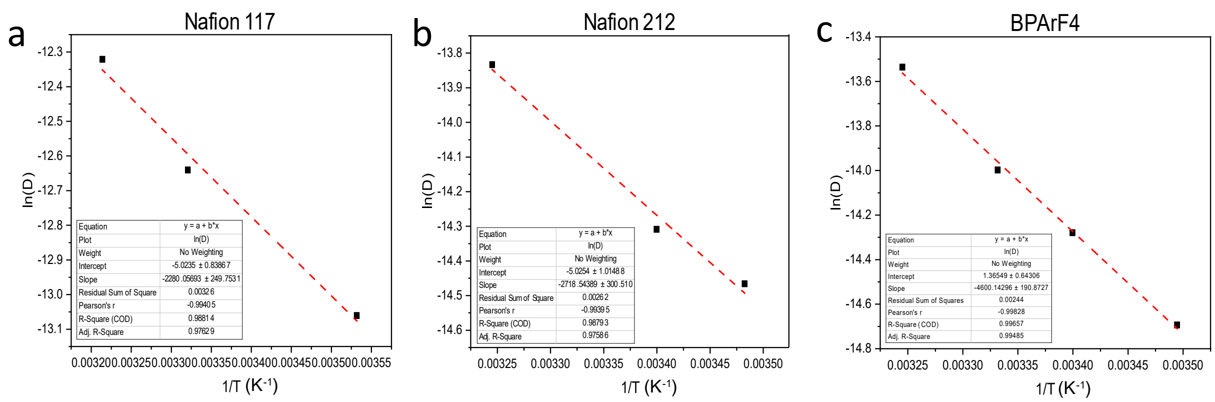



**Figure S12**. Arrhenius plot of the temperature dependence of vanadium permeability for: **a.** Nafion 117, **b.** Nafion212, and **c.** BP-ArF4. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

**Table S1.** Binding energy between the vanadium ion/BP-ArF4 and vanadium ion/Nafion. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

| Complexes | Binding Energy (kcal/mol) |
|---|---|
| **comp1-*BP-ArF4*** | 23.9 |
| **comp2-*BP-ArF4*** | 22.6 |
| **comp3-*BP-ArF4*** | 33.8 |
| **comp4-*BP-ArF4*** | 26.3 |
| **comp1-BP-ArSA** | 14.2 |
| **comp2-BP-ArSA** | 20.5 |
| **comp1-BP-SA** | 21.4 |
| **comp2-BP-SA** | 19.0 |
| **comp1-*Nafion*** | 13.7 |
| **comp2-*Nafion*** | 21.0 |

**Table S2.** Activation energy of Nafion 117, Nafion 212 and BP-ArF4 obtained by measuring vanadium ion permeability at different temperature. Related to the SAXS and DFT studies: selective ion transport mechanism section in the main test.

| Membrane | Activation Energy (kcal/mol) |
|---|---|
| **Nafion 117** | 4.53 |
| **Nafion 212** | 5.40 |
| **BP-ArF4** | 9.14 |

**Table S3**. Comparison of $VO^{2+}$ permeability and resistivity of membranes reported from literatures. Related to the breaking the trade-off limitations in IEMs section in the main test.

| Samples | Type of membrane | $VO^{2+}$ Permeability ($\times 10^{-7}$ $cm^2$/min) | Resistivity (Ω·cm) | Ref. |
|---|---|---|---|---|
| S-Radel | PEM | 2.1 | 46.79 | 1 |
| SPEEK | PEM | 11-12 | 59-61 | 2 |
| SPTKK | PEM | ~1.8 | 73.5 | 3 |
| SPTK | PEM | ~0.7 | 95.2 | 3 |
| SPAES | PEM | ~1.6 | ~70-80 | 4 |
| SPBI30 | PEM | 0.17 | 86 | 5 |
| BPSH60 | PEM | 210 | 8.3 | 6 |
| N115 | PEM | 33 | 39.4 | 7 |
| XL100 | PEM | 25.7 | 86.1 | 8 |
| SPFEK | PEM | 9.85 | 58.82 | 9 |
| Nafion117 | PEM | 37 | 16.9 | 10 |
| Nafion212 | PEM | 41 | 13.5 | 6 |
| BP-ArF4 | PEM | 10 | 17.36 | This work |
| QA-PFE | AEM | ~0 | ~200 | 11 |
| QPPAE-2/1 | AEM | ~0 | 154 | 12 |
| QPPP-2 | AEM | 0.09 | 400 | 13 |
| QPEK-C-TMA+ | AEM | 4.8 | 179 | 14 |
| C6QPSF | AEM | 0.5 | 63 | 15 |
| PAEK-API | AEM | 1.31 | 250 | 16 |
| QDAPP | AEM | 1.8 | 108 | 17 |
| PSF-TMA | AEM | 0.26 | 250 | 18 |
| PyPPEKK | AEM | 0.684 | 143 | 19 |

**Table S4**. Comparison of VRFB efficiencies, self-discharge time, and capacity retention/decay rate with PEMs and AEMs reported from literatures. Related to the breaking the trade-off limitations in IEMs section in the main test.

| Sample | Type | CE (%) | VE (%) | EE (%) | Current density ($mA/cm^2$) | Self-discha-rge time (hour) | Capacity retention/ Cycle # | Capacity decay rate (per cycle)/Current density ($mA/cm^2$) | Thick-ness (μm) | Vanadium sulfate/$H_2SO_4$ concentra-tion | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Nafion 115 | PEM | 91.7 | 92.3 | 84.7 | 50 | 80 | N/A | N/A | 127 | 1.5M/3M | [20] |
| Nafion 212 | PEM | 92 | 86 | 79 | 80 | 40 | N/A | N/A | 60 | 1.5M/3M | [21] |
| SPPEK | PEM | 98.8 | 75.5 | 74.6 | 60 | N/A | N/A | N/A | 20 | 1.5M/3M | [1] |
| SPEEK40 | PEM | 98.5 | 88.8 | 87.5 | 50 | 170 | N/A | N/A | 90 | 1.5M/3M | [20] |
| SPEEK50 | PEM | 97.3 | 86.3 | 84.0 | 50 | N/A | N/A | N/A | 85 | 1.5M/3M | [20] |
| SPEEK60 | PEM | 96.1 | 87.6 | 84.2 | 50 | N/A | N/A | N/A | 90 | 1.5M/3M | [20] |
| S-PAEK-40 | PEM | 89.5 | 92.2 | 82.6 | 20 | N/A | ~60%/100 | 0.4%/20 | 172 | 1M/2M | [22] |
| Nafion 117 | PEM | 90 | 94 | 84.6 | 40 | 30 | ~50%/200 | 0.25/80 | 175 | 1.5M/2M | [23] |
| SPSF-62 | PEM | 94.9 | 94.0 | 89.2 | 50 | 29 | N/A | N/A | 76 | 1.5M/3M | [24] |
| SPI-50 | PEM | 96 | 93.8 | 90.1 | 40 | 110 | 78.2%/100 | 0.218/160 | 71 | 1.5M/2M | [25] |
| SPBI-30 | PEM | ~100<br>~100 | ~85<br>~88 | ~85<br>~88 | 80<br>60 | 384 | 54.95%/500 | 0.09%/100 | 35 | 1.5M/3M | [5] |
| BP-ArF4 | PEM | 99.4<br>99.2<br>98.6<br>97.3 | 86.4<br>89.5<br>93.2<br>96.4 | 85.9<br>88.8<br>91.9<br>93.9 | 80<br>60<br>40<br>20 | 209.5 | 84%/200 | 0.08%/100 | 88 | 1.6M/4M | This work |
| QA-PFE | AEM | ~100 | ~78 | ~78 | 40 | N/A | N/A | N/A | ~50 | 1M/2.5M | [11] |
| QPPAE-2/1 | AEM | 99.3 | 88.9 | 88.4 | 50 | N/A | 70%/500 | 0.08%/50 | N/A | 1.65M/3M | [12] |
| AIEM | AEM | 95.6 | 78.5 | 75.1 | 40 | ~300 | N/A | N/A | 43 | 1.5M/2.5M | [26] |
| QPPP-2 | AEM | ~99 | ~87 | ~87 | 80 | N/A | 92%/30 | 0.26%/80 | ~35 | 1.65M/3M | [13] |
| QPEK-C-TMA+ | AEM | ~99 | ~81 | ~80 | 30 | N/A | N/A | N/A | 40 | 1.5M/3M | [14] |
| QAPPEK | AEM | 98.4 | 83.8 | 82.5 | 40 | N/A | N/A | N/A | ~40 | 1.5M/3M | [27] |
| DF-a2 | AEM | 98.5 | 84.6 | 83.3 | 50 | 35 | N/A | N/A | ~300 | 1.5M/3M | [28] |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| QS-AIEM | AEM | 98 | 91.5 | 89.7 | 50 | N/A | 70%/80 | 0.375%/N/A | ~40 | 1.5M/3M | [15] |
| PAEK-API | AEM | 96.4 | 86.5 | 83.4 | 60 | N/A | 84%/100 | 0.16%/40 | ~130 | 1.5M/3M | [16] |
| QDAPP | AEM | 99 | 85 | 85 | 200 | N/A | 94%/20 | 0.3%/N/A | N/A | 1.7M/5M | [17] |
| PyPPEKK | AEM | 98.4 | 90.3 | 88.9 | 40 | N/A | N/A | N/A | 45 | 1.5M/3M | [19] |

## Reference


(1) Wang, N.; Yu, J.; Zhou, Z.; Fang, D.; Liu, S.; Liu, Y., SPPEK/TPA composite membrane as a separator of vanadium redox flow battery. *J. Membr. Sci.* **2013,** *437*, 114-121.

(2) Dai, W.; Shen, Y.; Li, Z.; Yu, L.; Xi, J.; Qiu, X., SPEEK/Graphene oxide nanocomposite membranes with superior cyclability for highly efficient vanadium redox flow battery. *J. Mater. Chem. A* **2014,** *2* (31), 12423-12432.

(3) Chen, D.; Wang, S.; Xiao, M.; Meng, Y., Synthesis and characterization of novel sulfonated poly (arylene thioether) ionomers for vanadium redox flow battery applications. *Energy Environ. Sci* **2010,** *3* (5), 622-628.

(4) Chen, D.; Wang, S.; Xiao, M.; Meng, Y., Synthesis and properties of novel sulfonated poly (arylene ether sulfone) ionomers for vanadium redox flow battery. *Energy Conversion and Management* **2010,** *51* (12), 2816-2824.

(5) Ding, L.; Song, X.; Wang, L.; Zhao, Z., Enhancing proton conductivity of polybenzimidazole membranes by introducing sulfonate for vanadium redox flow batteries applications. *J. Membr. Sci.* **2019,** *578*, 126-135.

(6) Wang, T.; Moon, S. J.; Hwang, D.-S.; Park, H.; Lee, J.; Kim, S.; Lee, Y. M.; Kim, S., Selective ion transport for a vanadium redox flow battery (VRFB) in nano-crack regulated proton exchange membranes. *J. Membr. Sci.* **2019,** *583*, 16-22.

(7) Zhou, X.; Zhao, T.; An, L.; Zeng, Y.; Zhu, X., Performance of a vanadium redox flow battery with a VANADion membrane. *Applied Energy* **2016,** *180*, 353-359.

(8) Xie, W.; Darling, R. M.; Perry, M. L., Processing and pretreatment effects on vanadium transport in nafion membranes. *J. Electrochem. Soc.* **2016,** *163* (1), A5084-A5089.

(9) Chen, D.; Wang, S.; Xiao, M.; Meng, Y., Preparation and properties of sulfonated poly (fluorenyl ether ketone) membrane for vanadium redox flow battery application. *J. Power Sources* **2010,** *195* (7), 2089-2095.

(10) Teng, X.; Zhao, Y.; Xi, J.; Wu, Z.; Qiu, X.; Chen, L., Nafion/organically modified silicate hybrids membrane for vanadium redox flow battery. *J. Power Sources* **2009,** *189* (2), 1240-1246.

(11) Chen, D.; Hickner, M. A.; Agar, E.; Kumbur, E. C., Selective anion exchange membranes for high coulombic efficiency vanadium redox flow batteries. *Electrochem. commun.* **2013,** *26*, 37-40.

(12) Cha, M. S.; Lee, J. Y.; Kim, T.-H.; Jeong, H. Y.; Shin, H. Y.; Oh, S.-G.; Hong, Y. T., Preparation and characterization of crosslinked anion exchange membrane (AEM) materials with poly (phenylene ether)-based short hydrophilic block for use in electrochemical applications. *J. Membr. Sci.* **2017,** *530*, 73-83.

(13) Cha, M. S.; Jo, S. W.; Han, S. H.; Hong, S. H.; So, S.; Kim, T.-H.; Oh, S.-G.; Hong, Y. T.; Lee, J. Y., Ether-free polymeric anion exchange materials with extremely low vanadium ion permeability and outstanding cell performance for vanadium redox flow battery (VRFB) application. *J. Power Sources* **2019,** *413*, 158-166.

(14) Yun, S.; Parrondo, J.; Ramani, V., Derivatized cardo-polyetherketone anion exchange membranes for all-vanadium redox flow batteries. *J. Mater. Chem. A* **2014,** *2* (18), 6605-6615.

(15) Chen, Y.; Zhang, S.; Jin, J.; Liu, C.; Liu, Q.; Jian, X., Poly (phthalazinone ether ketone) amphoteric ion exchange membranes with low water transport and vanadium permeability for vanadium redox flow battery application. *ACS Appl. Energy Mater.* **2019,** *2* (11), 8207-8218.

(16) Ahn, Y.; Kim, D., Anion exchange membrane prepared from imidazolium grafted poly (arylene ether ketone) with enhanced durability for vanadium redox flow battery. *J. Ind. Eng. Chem.* **2019,** *71*, 361-368.

(17) Sun, C.-N.; Tang, Z.; Belcher, C.; Zawodzinski, T. A.; Fujimoto, C., Evaluation of Diels–Alder poly (phenylene) anion exchange membranes in all-vanadium redox flow batteries. *Electrochem. commun.* **2014,** *43*, 63-66.

(18) Min-suk, J. J.; Parrondo, J.; Arges, C. G.; Ramani, V., Polysulfone-based anion exchange membranes demonstrate excellent chemical stability and performance for the all-vanadium redox flow battery. *J. Mater. Chem. A* **2013,** *1* (35), 10458-10464.
(19) Zhang, S.; Zhang, B.; Xing, D.; Jian, X., Poly (phthalazinone ether ketone ketone) anion exchange membranes with pyridinium as ion exchange groups for vanadium redox flow battery applications. *J. Mater. Chem. A* **2013,** *1* (39), 12246-12254.
(20) Mai, Z.; Zhang, H.; Li, X.; Bi, C.; Dai, H., Sulfonated poly (tetramethydiphenyl ether ether ketone) membranes for vanadium redox flow battery application. *J. Power Sources* **2011,** *196* (1), 482-487.
(21) Zhang, F.; Zhang, H.; Qu, C., Influence of solvent on polymer prequaternization toward anion-conductive membrane fabrication for all-vanadium flow battery. *J. Phys. Chem. B* **2012,** *116* (30), 9016-9022.
(22) Yang, S.; Ahn, Y.; Kim, D., Poly (arylene ether ketone) proton exchange membranes grafted with long aliphatic pendant sulfonated groups for vanadium redox flow batteries. *J. Mater. Chem. A* **2017,** *5* (5), 2261-2270.
(23) Jiang, B.; Wu, L.; Yu, L.; Qiu, X.; Xi, J., A comparative study of Nafion series membranes for vanadium redox flow batteries. *J. Membr. Sci.* **2016,** *510*, 18-26.
(24) Zhang, Y.; Zheng, L.; Liu, B.; Wang, H.; Shi, H., Sulfonated polysulfone proton exchange membrane influenced by a varied sulfonation degree for vanadium redox flow battery. *J. Membr. Sci.* **2019,** *584*, 173-180.
(25) Wang, L.; Yu, L.; Mu, D.; Yu, L.; Wang, L.; Xi, J., Acid-base membranes of imidazole-based sulfonated polyimides for vanadium flow batteries. *J. Membr. Sci.* **2018,** *552*, 167-176.
(26) Qiu, J.; Zhai, M.; Chen, J.; Wang, Y.; Peng, J.; Xu, L.; Li, J.; Wei, G., Performance of vanadium redox flow battery with a novel amphoteric ion exchange membrane synthesized by two-step grafting method. *J. Membr. Sci.* **2009,** *342* (1-2), 215-220.
(27) Zhang, S.; Yin, C.; Xing, D.; Yang, D.; Jian, X., Preparation of chloromethylated/quaternized poly (phthalazinone ether ketone) anion exchange membrane materials for vanadium redox flow battery applications. *J. Membr. Sci.* **2010,** *363* (1-2), 243-249.
(28) Wang, N.; Zhang, F.; Zhang, R.; Zhou, W.; Lu, D., Sulfonation of Poly (phenylene oxide) Anion Exchange Membrane for All Vanadium Flow Redox Battery. *Int. J. Electrochem. Sci* **2019,** *14*, 5508-5520.