Optimising polybenzimidazolium membranes for use in vanadium redox flow batteries

J. Duburg[1], B. Chen[2], S. Holdcroft[2], L. Gubler[1]
[1] Paul Scherrer Institut (PSI), Electrochemistry Laboratory, 5232 Villigen PSI, Switzerland
[2] Simon Fraser University, Department of Chemistry, V5A 1S6 Burnaby, Canada

Introduction

- The all-vanadium redox flow battery (VRFB) is a promising energy storage device for an intermediate timescale (daily to weekly discharge). However, optimisation of the membrane in terms of energy efficiency and capacity retention is needed before wide scale implementation can occur.

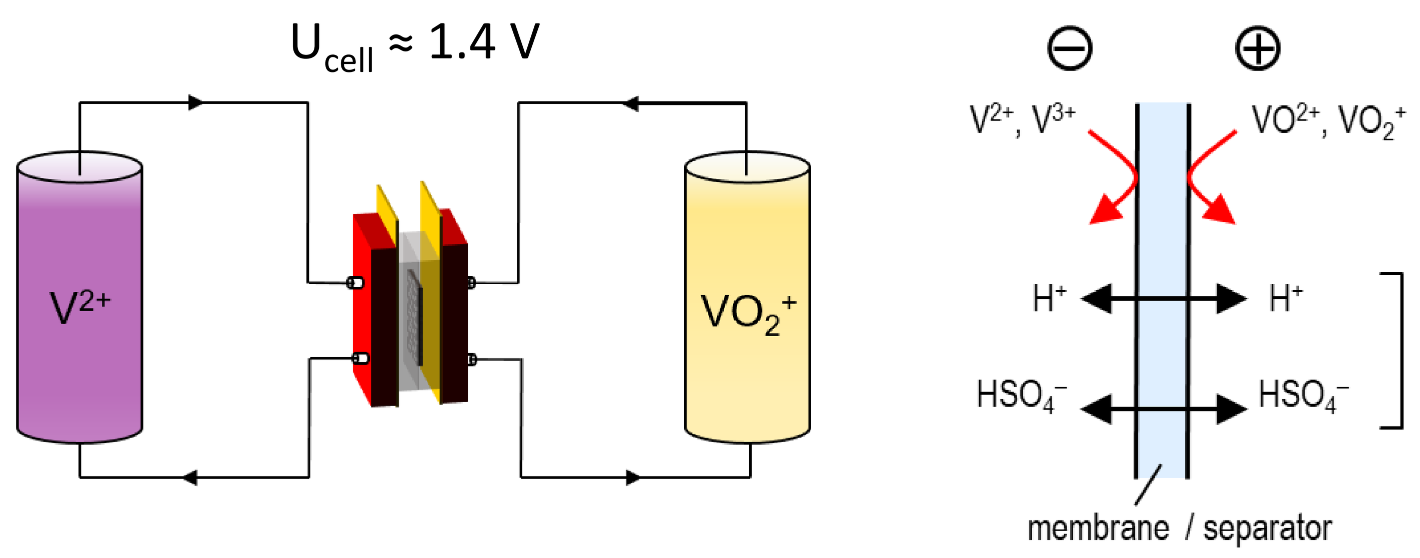


Figure 1: Schematic of a VRFB cell (L) and the corresponding membrane requirements (R).

- So far, polybenzimidazolium membranes have not yet been extensively studied for VRFB applications [1], with their main use being found in AEM fuel cell and electrolysis systems [2].

- Hexamethyl-p-terphenyl polybenzimidazolium (HMT-PMBI) membranes are described as Xtype, with:

$$X = \frac{R\ units\ per\ repeating\ unit}{4} \cdot 100$$

dm : Degree of methylation
dx : Degree of crosslinking

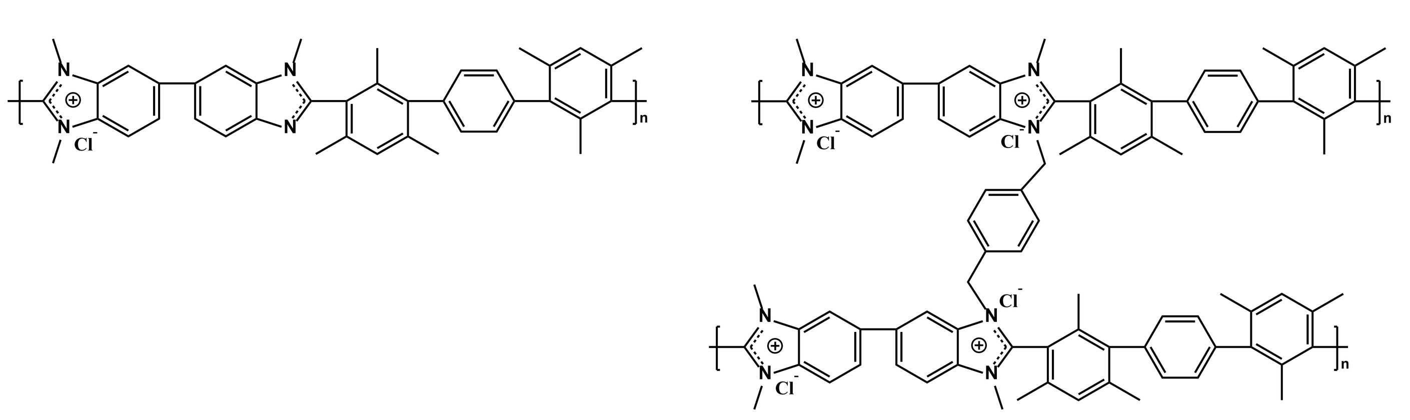


Figure 2: Molecular structure of 75dm HMT-PMBI (L) and crosslinked 75dm25dx HMT-PMBI (R).

Properties in acidic media

Electrolyte affinity

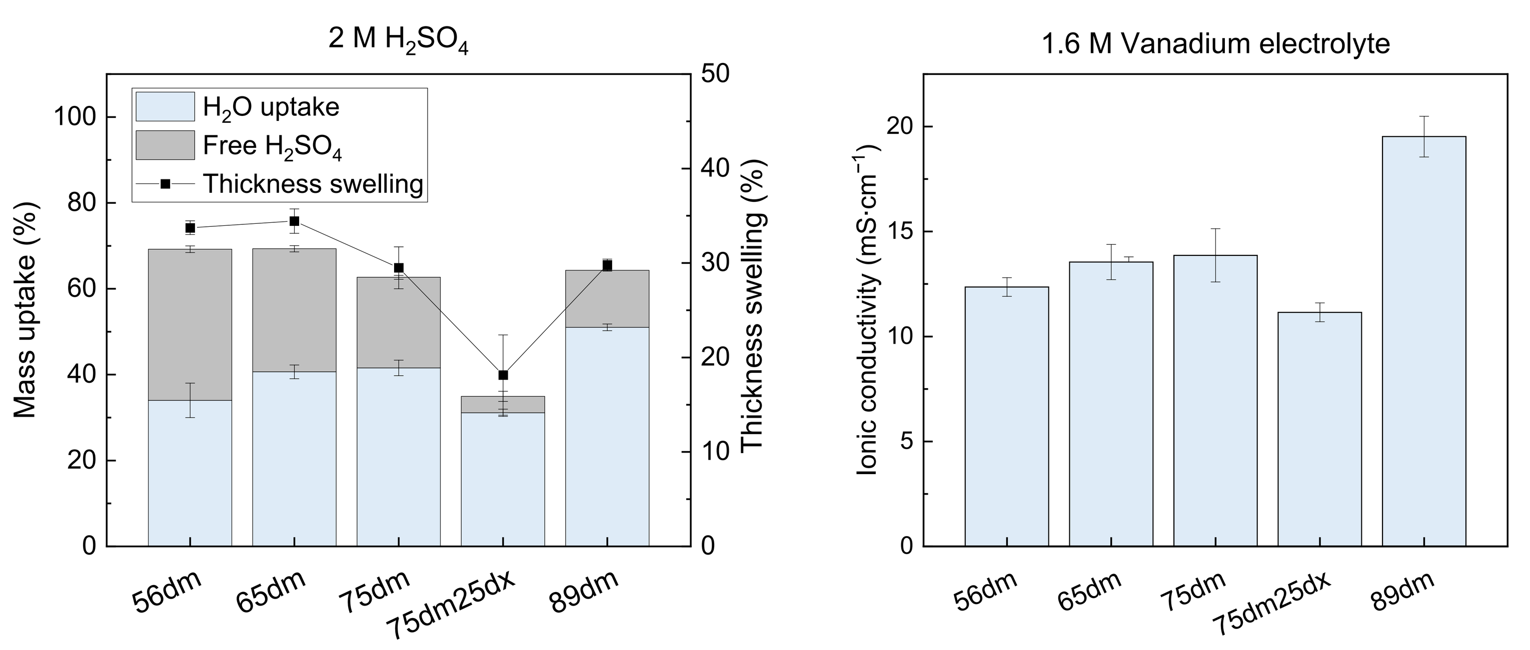


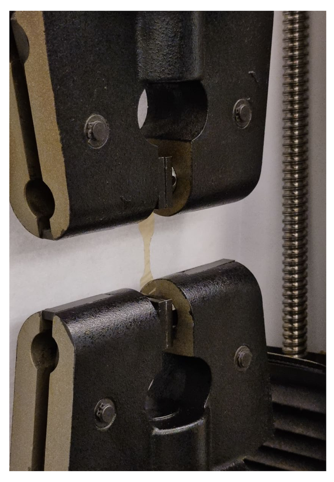
Figure 3: Electrolyte uptake and thickness swelling in 2 M H_2SO_4 (L) and ionic conductivity in 1.6 M vanadium electrolyte (R) of various HMT-PMBI membranes.

- In contact with 2 M H_2SO_4, HMT-PMBI membranes with a higher degree of methylation exhibit a higher water uptake, whereas their free acid content is reduced.

- Crosslinking the membrane decreases the thickness swelling, thereby reducing the electrolyte uptake.

- An increase in methylation, increases the ionic conductivity of the membrane in a 1.6 M vanadium electrolyte, with a small decrease in ionic conductivity observed for the crosslinked derivative.

Mechanical stability in the vanadium electrolyte



Membrane	Stress (MPa)	Elongation at break (%)	Young's modulus (MPa)
56dm	32	46	345
65dm	30	53	301
75dm	28	44	307
75dm25dx	29	25	293
89dm	25	50	259

Figure 4: Mechanical properties of HMT-PMBI swollen in a 1.6 M vanadium electrolyte.

- The mechanical integrity weakens with increasing degree of methylation.

Chemical stability

Day 0

Day 90

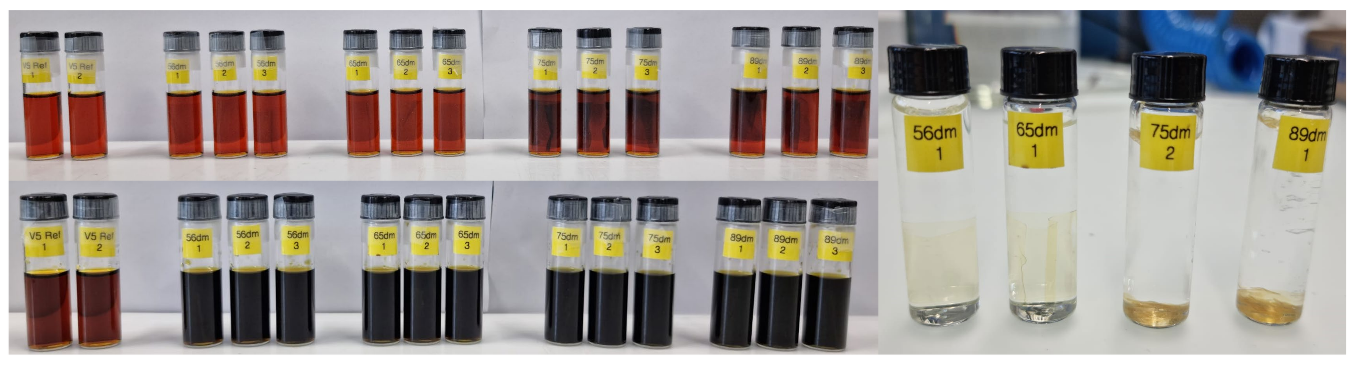


Figure 5: HMT-PMBI membranes immersed in a 1.6 M VO_2^+ electrolyte at day 0 and day 90 (L) with the samples post test (R).

- The degradation of the HMT-PMBI membranes increases with the degree of methylation.

- The samples of 75dm and 89dm exhibit mechanical instability post test.

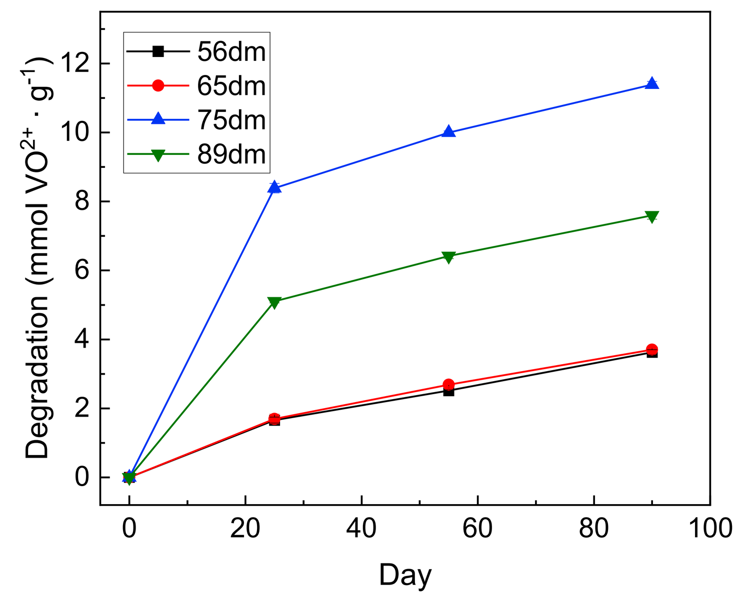


Figure 6: Chemical degradation of HMT-PMBI with the formed mmol of VO^{2+} per gram of polymer.

Cell performance

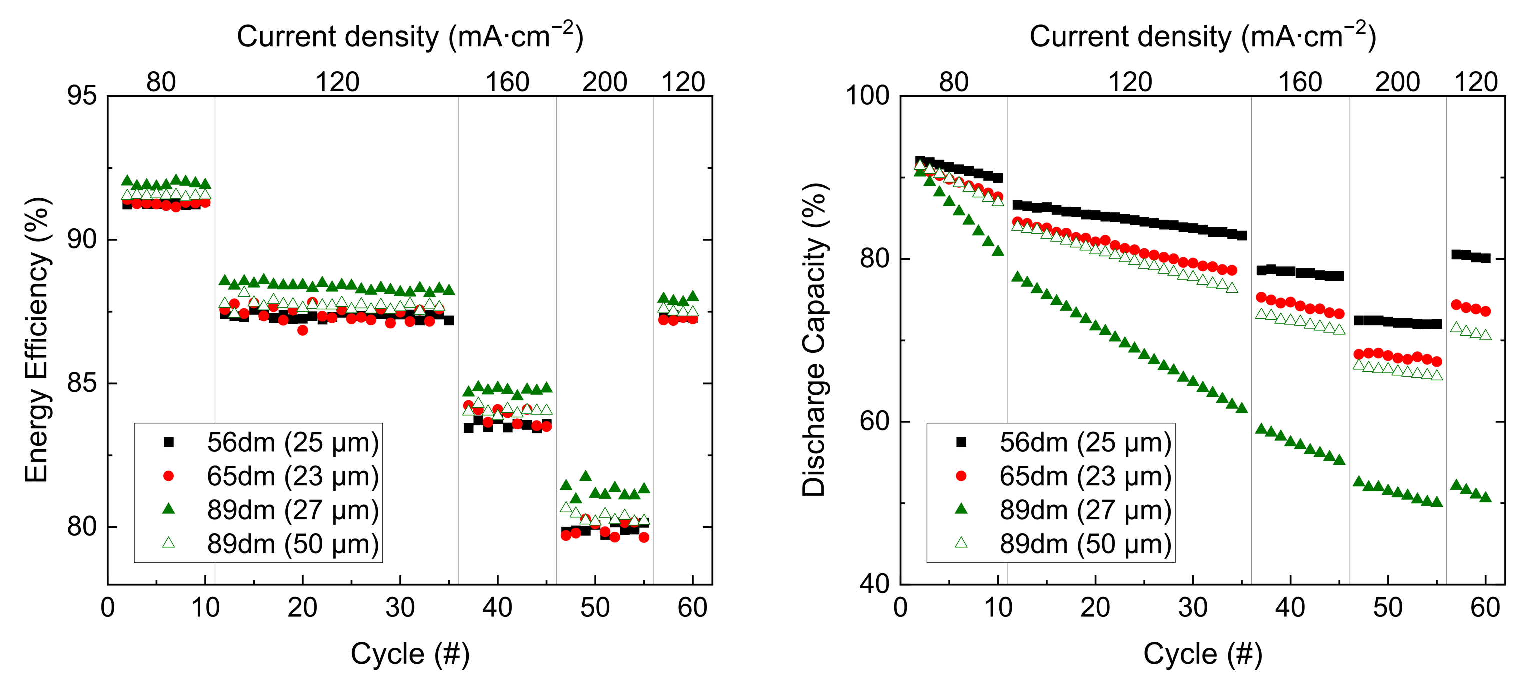


Figure 7: Energy efficiency (L) and discharge capacity (R) of HMT-PMBI at varying current densities.

- The energy efficiency is improved upon increasing the degree of methylation, whereas, the reverse trend is seen for the capacity retention.

Conclusion

- Methylation of HMT-PMBI increases the energy efficiency of the vanadium flow battery at the cost of the capacity retention. Whereas, crosslinking reduces the water uptake and ionic conductivity.

- The obtained results show that a careful balance of properties is needed to optimise HMT-PMBI membranes for VRFB applications.

References

1. Shanahan, B.; Böhm, T.; Britton, B.; Holdcroft, S.; Zengerle, R.; Vierrath, S.; Thiele, S.; Breitwieser, M. 30 µm thin hexamethyl-p-terphenyl poly(benzimidazolium) anion exchange membrane for vanadium redox flow batteries. *Electrochemistry Communications* 2019, *102*, 37-40.

2. Wright, A. G.; Fan, J.; Britton, B.; Weissbach, T.; Lee, H.-F.; Kitching, E. A.; Peckham, T. J.; Holdcroft, S. Hexamethyl-p-terphenyl poly(benzimidazolium): a universal hydroxide-conducting polymer for energy conversion devices. *Energy & Environmental Science* 2016, *9* (6), 2130-2142.

Funding from the Swiss National Science Foundation, grant number 188631, titled "Functional composite separator-membrane materials for redox flow batteries".