Composite membrane for the VRFB: Bilayer of a porous separator and a polybenzimidazole 'Skin'

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Introduction

Ion-exchange membranes are performance and cost relevant components of redox flow batteries. Currently used materials are largely 'borrowed' from other applications that have different functional requirements [1]. The vanadium redox flow battery (VRFB) already comprises an ionically conducting solution in the form of the positive and negative electrolyte. Hence, it would be desirable to use a porous material imbibed with electrolyte as a separator, as in conventional batteries, which would dramatically reduce cost. The development goal for a separator based on a porous material is to prevent excessive crossover of vanadium ions while maintaining a low ohmic resistance.

We present a composite membrane for the VRFB consisting of a porous propylene (PP) separator of 30 μm thickness laminated with a thin meta-polybenzimidazole (mPBI) layer. PBI is known to swell in acidic solutions and develop ion conductivity. With a low PBI film thickness in the micron range, we expect a low ohmic resistance of the membrane comparable to that of state-of-the art ion exchange membranes.

Experimental

PBI films are prepared by solution casting, using dimethylacetamide (DMAC) as solvent, to obtain thicknesses in the range of 0.2 to 10 μm. The PBI films were subsequently laminated to a porous polypropylene support (TreoPore® PDA-30, Treofan (Germany) of 30 μm thickness. Alternatively, the PBI can be sprayed with defined loading onto the PP support (*Figure 1*).

PP-PBI composite membranes with PBI layer thickness ranging from 0.2 to 10 μm were tested at room temperature in single laboratory cells of 25 cm^2 active area and compared to a cell with Nafion 212 membrane. Toyobo carbon felt electrodes (Japan), type AAF304ZS, were used. The vanadium electrolyte was purchased from Oxkem (United Kingdom) and contained 1.6 M vanadium in 2.0 M sulphuric acid and 0.5 M phosphoric acid. Details on the experimental procedure can be found in our recently published article [3].

Figure 1. Composite membranes consisting of polybenzimidazole (PBI) sprayed from a DMAC solution at different loadings onto a porous polypropylene (PP) support.

Results

For the measurement of the ohmic resistance of composite membranes with different PBI layer thicknesses, a hydrophilic polyethylene substrate was used. Samples were equilibrated in vanadium electrolyte (1.6 M V, 2.0 M H_2SO_4) prior to assembly in a through-plane Swagelok conductivity cell. The ohmic resistance of bilayer membranes as a function of PBI layer thickness is shown in *Figure 2*.

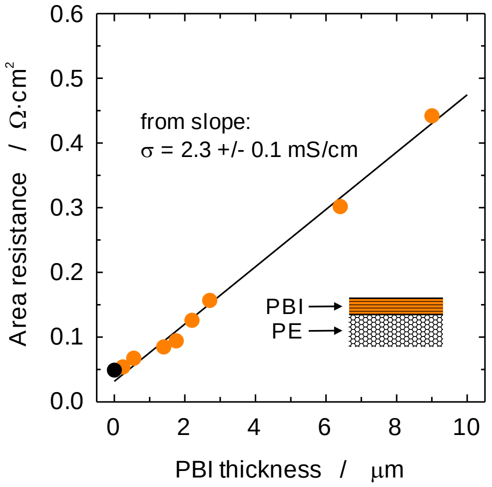

Figure 2. Through-plane resistance of bilayer membranes equilibrated in vanadium electrolyte vs. thickness of the polybenzimidazole (PBI) layer. (Source DOI: 10.1149/1945-7111/ab945f, license CC BY 4.0)

The regression lines yields a slope of ~30 mΩ·cm^2 per μm of PBI film thickness. This offers the prospect of designing a composite membrane-separator with low ohmic resistance.

Charge-discharge cycles at a current density of 150 mA·cm^{-2} for composite membranes with different PBI layer thickness are shown in *Figure 3*, compared against results obtained with Nafion 212. Membranes with a PBI thickness of up to 1 µm show better performance than Nafion 212, i.e., a lower cell voltage during charge and a higher cell voltage during discharge. Samples with PBI thickness of 3 and 10 µm show inferior performance as a result of high ohmic resistance. With the composite membranes, higher discharge capacity is obtained compared to Nafion 212 except for the sample with 10 µm thick PBI.

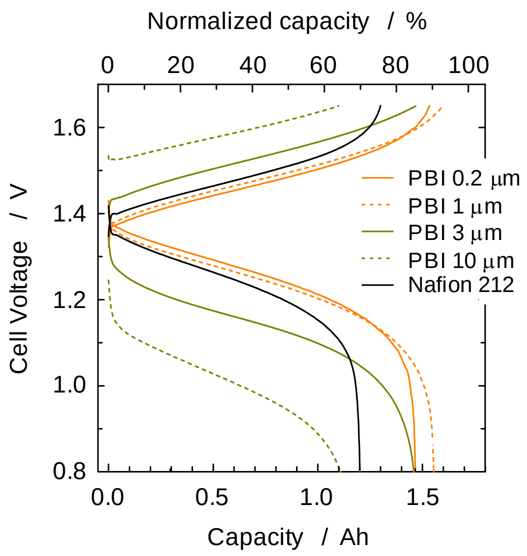

Figure 3. Charge-discharge cycling test at a current density of 150 mA·cm^{-2}. (adapte from DOI: 10.1149/1945-7111/ab945f, license CC BY 4.0)

The charge-discharge energy efficiency, which is the product of coulombic efficiency and voltaic efficiency, for different current densities is shown in *Figure 4*. The composite membranes with a PBI thickness of 1 µm and below show improved performance compared to Nafion 212, which is a result of improved coulombic efficiency and comparable voltaic efficiency. Thicker PBI layers induced increasing ohmic losses, leading to poor round-trip efficiency at practical current densities of >100 mA·cm^{-2}. These results demonstrate that with a careful choice of constituents and architecture, it is possible to prepare membranes with high performance, high efficiency and low cost for next generation VRFB systems.

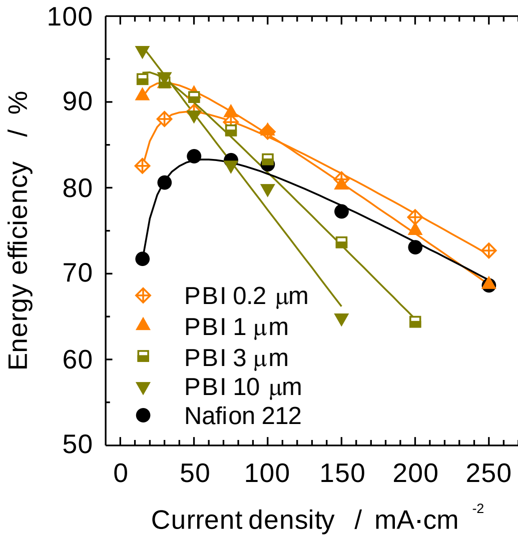

Figure 4. Charge-discharge cycling efficiency as a function of current density. (Source DOI: 10.1149/1945-7111/ab945f, license CC BY 4.0)

Conclusion

Composite membranes with asymmetric architecture consisting of a porous polyolefin separator and a thin topcoat of polybenzimidazole (PBI) are of potential interest as separator in next generation vanadium redox flow batteries. With a PBI layer thickness of 1 µm, cell performance is competitive to Nafion 212 over the entire current density range investigated.

Acknowledgements

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References

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