A new generation of PBI membranes with improved performance in Vanadium redox-flow batteries

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Background

The cell membrane is a critical component as it defines the performance and energy efficiency of vanadium redox-flow batteries (VRFB). State-of-the-art are ion exchange membranes, which are based on the perfluorinated polymer backbone, such as Nafion® or Fumasep®. These membranes exhibit good stability in the electrolyte solution upon cycling, however there are also downsides: the poor membrane selectivity towards vanadium permeability leads to faster self-discharge of the battery. Moreover, the high cost of the currently used membranes reduces the competitiveness of the battery systems. In addition, fluorinated polymers have very limited recyclability and substantial environmental concerns. Para-polybenzimidazole (p-PBI) polymer is a promising candidate to meet these requirements. The conventional production process of PBI membranes uses organic solvents, leading thus to the accumulation of waste and rising the membrane price. We have introduced a production process without organic solvents for the p-PBI membrane, currently used for high temperature PEM fuel cells. A novel method for the **transformation of p-PBI gel membranes into dense p-PBI films** has been recently developed [1]. The new dense PBI membranes show significantly lower vanadium crossover. They also show good ionic conductivity and promising performance in vanadium redox-flow batteries [2].

Novel dense p-PBI membrane

Gel p-PBI

1. *H_2O washing*
2. *Controlled drying*

Dense p-PBI

Thickness:
- Gel p-PBI: 350 µm
- Dense p-PBI: 30 µm
- Dense p-PBI (H_2SO_4 doped): 50 µm

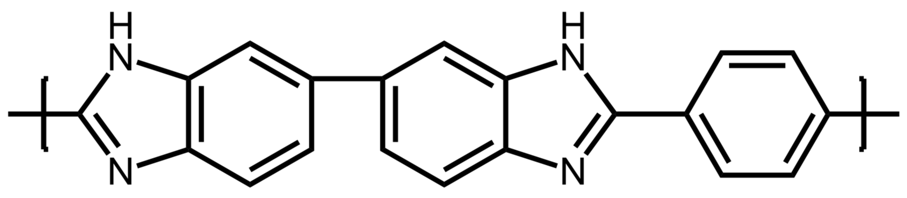
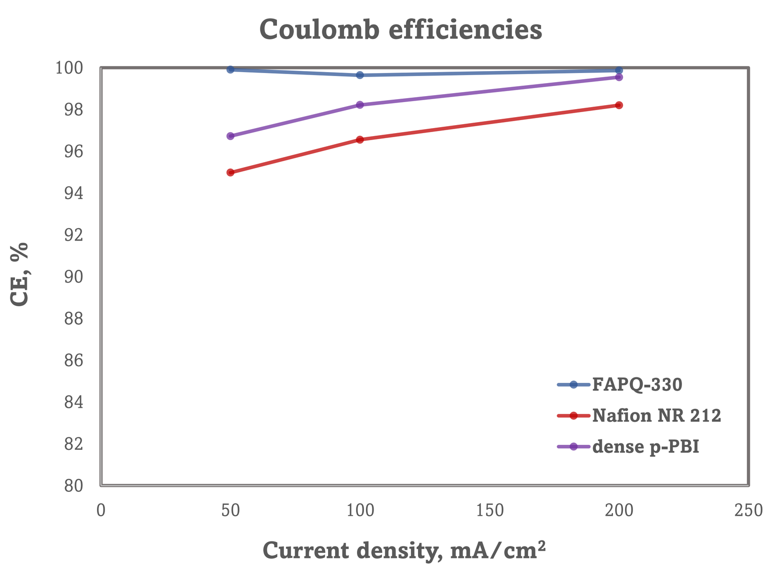


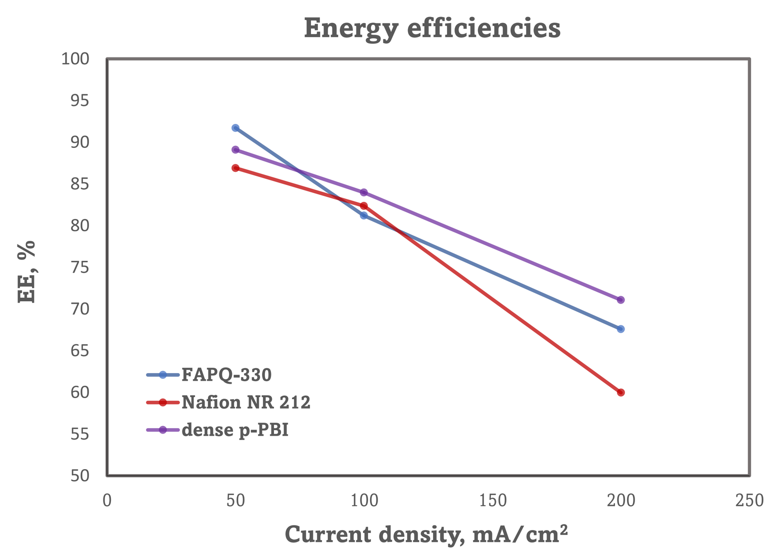
Figure 1: p-PBI chemical structure

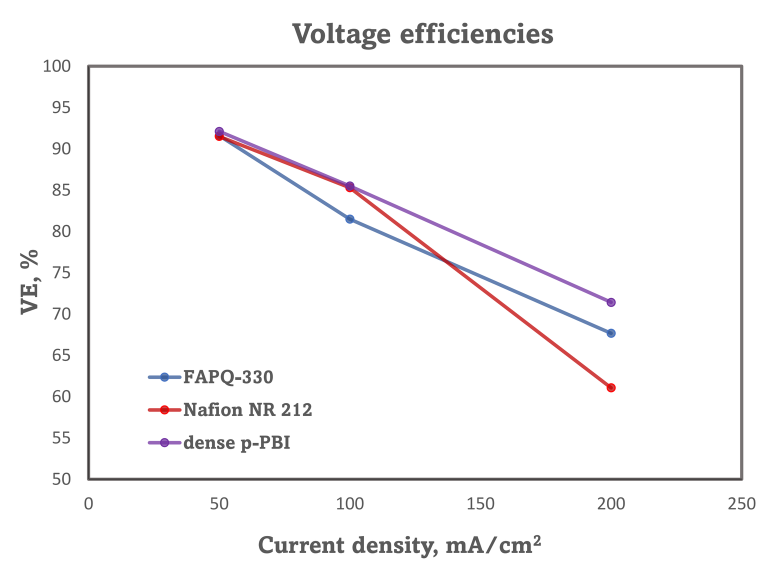
Key advantages:
- Competitive performance with state-of-the-art technology
- Lower Vanadium (IV) permeability
- Environmentally benign (non-fluorinated)
- Cost-competitive
- The production process for the dense p-PBI membrane does not require organic solvents

Performance in VRFB

Efficiency

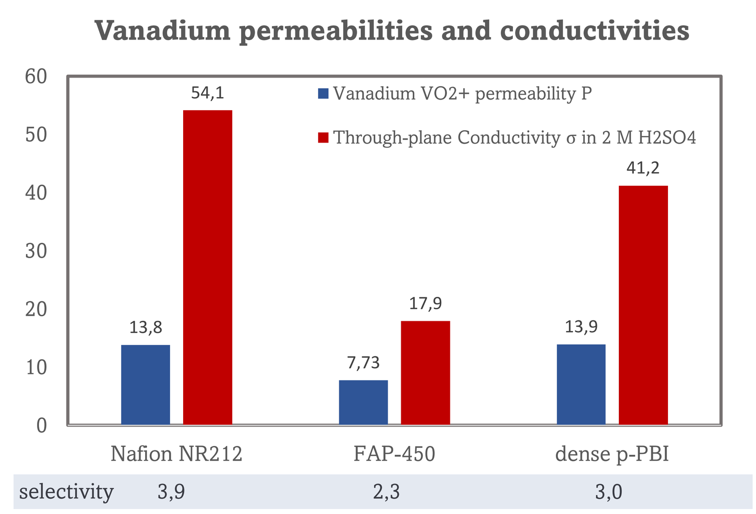






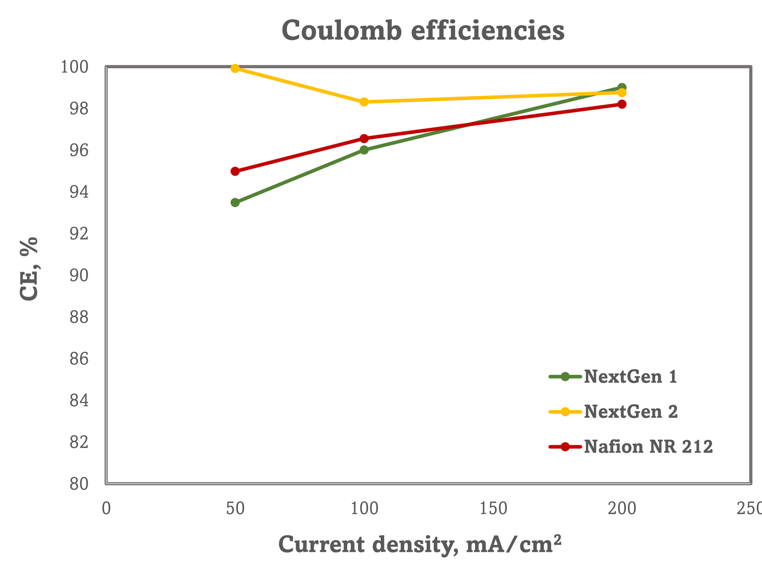
- Dense p-PBI membranes are comparable with Nafion® in terms of performance
- Dense p-PBI membranes show **better** performance than Fumasep® at high current densities

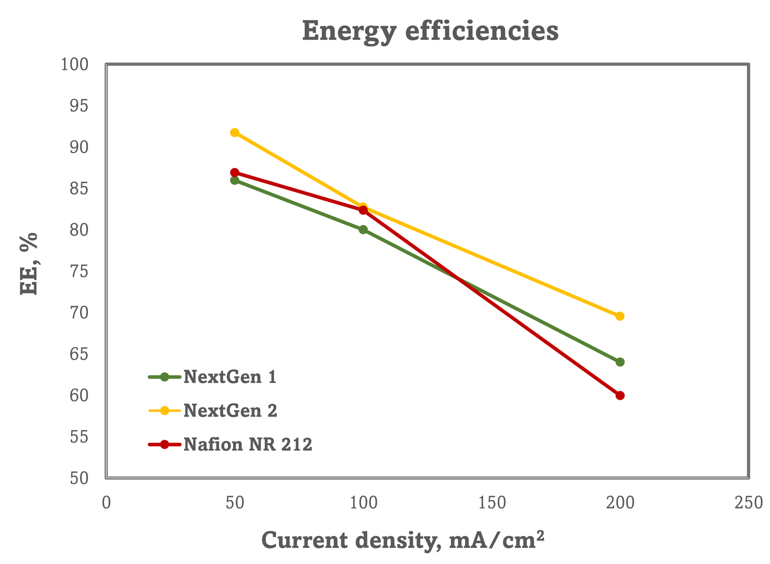
Ex-situ measurements



- Dense p-PBI membranes show **similar** permeability to Nafion®
- Dense p-PBI membranes show **higher** ionic selectivity than Fumasep®

Next generation membranes





Preliminary tests for next generation dense PBI structures demonstrate promising performance compared to state-of-the-art membranes such as Nafion®.

Conclusion

Initial testing has successfully demonstrated the applicability of dense p-PBI membrane for VRFB. Comparable performance has been demonstrated against fluorinated Nafion® and Fumasep® membranes.

Outlook

Further tests are required for a complete and comprehensive assessment:
- Qualification under real operating conditions
- Stress tests: long-time cycle simulations
- Work on next-generation membranes

References:

[1] L. A. Murdock, F. Huang, B. C. Benicewicz, Patent US 2021 0280883 A1
[2] L. A. Murdock, B. C. Benicewicz, L. Wang, F. Huang, Patent WO 2020 056268 A2.

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We thank Gunter Bechtloff for performing battery cycling experiments.
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