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Optimizing the performance of meta-polybenzimidazole membranes in vanadium redox flow batteries by adding an alkaline pre-swelling step

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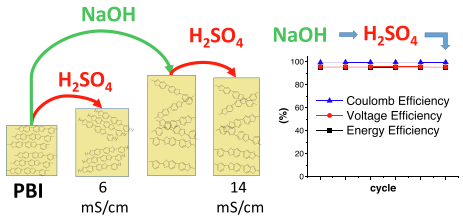
HIGHLIGHTS

- Alkaline pre-swelling increases conductivity of sulfuric acid doped PBI 3–10 times.
- Pre-swelling in 4 M NaOH reduces VO^{2+} permeability from 4 10^{-15} to 1.6 10^{-15} m^2 s^{-1}.
- Selectivity (conductivity/permeability) was increased 7 times.
- Energy efficiencies of 91.3% at 80 mA cm^{-2} and 95.4% at 40 mA cm^{-2} were achieved.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybenzimidazole (PBI) is a promising material for vanadium redox flow battery (VRFB) membranes. It shows a low permeability for vanadium ions, a conductivity in the range of 5 mS cm^{-1} in contact with 2 M sulfuric acid, and resists degradation by VO_2^+. Recent literature showed that the conductivity of PBI can be increased to 18 mS cm^{-1} by pre-swelling the membrane with phosphoric acid (PA), and up to 590 mS cm^{-1} by casting a sulfonated *para*-PBI membrane from polyphosphoric acid before immersion in sulfuric acid. However, these membranes show an increased permeability towards VO^{2+} ions, and thus reduced coulomb efficiency in the VRFB. Here we investigate pre-swelling in 4 M alkaline solution. It increases the conductivity in 2 M sulfuric acid to 56 (potassium hydroxide) and 12 mS cm^{-1} (sodium hydroxide). In 3 M sulfuric acid, the NaOH swollen membrane (4N3S) shows 14 mS cm^{-1}, corresponding to an area resistance of 69 mΩ cm^2 for a 10 μm thick membrane, lower than that of Nafion 115 (192 mΩ cm^2) and even Nafion 212 (89 mΩ cm^2). The selectivity (conductivity/permeability) is $9{\cdot}10^{14}$ S s m^{-3}, 7, 30 and 1000 times higher than for standard PBI, PA and polyphosphoric acid pre-swollen membranes, respectively. A VRFB with a 5 μm thick 4N3S membrane showed energy efficiencies of 91.3% at 80 mA cm^{-2} and 95.4% at 40 mA cm^{-2}.

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