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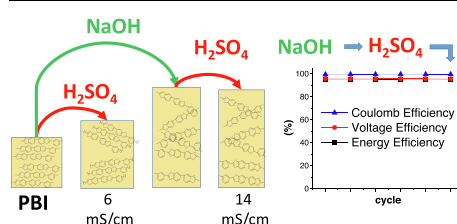
## Optimizing the performance of meta-polybenzimidazole membranes in vanadium redox flow batteries by adding an alkaline pre-swelling step

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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  $\text{VO}_2^+$  permeability from  $4 \cdot 10^{-15}$  to  $1.6 \cdot 10^{-15} \text{ m}^2 \text{ s}^{-1}$ .
- Selectivity (conductivity/permeability) was increased 7 times.
- Energy efficiencies of 91.3% at  $80 \text{ mA cm}^{-2}$  and 95.4% at  $40 \text{ mA cm}^{-2}$  were achieved.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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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  $5 \text{ mS cm}^{-1}$  in contact with 2 M sulfuric acid, and resists degradation by  $\text{VO}_2^+$ . Recent literature showed that the conductivity of PBI can be increased to  $18 \text{ mS cm}^{-1}$  by pre-swelling the membrane with phosphoric acid (PA), and up to  $590 \text{ mS cm}^{-1}$  by casting a sulfonated *para*-PBI membrane from polyphosphoric acid before immersion in sulfuric acid. However, these membranes show an increased permeability towards  $\text{VO}_2^+$  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  $12 \text{ mS cm}^{-1}$  (sodium hydroxide). In 3 M sulfuric acid, the NaOH swollen membrane (4N3S) shows  $14 \text{ mS cm}^{-1}$ , corresponding to an area resistance of  $69 \text{ m}\Omega \text{ cm}^2$  for a  $10 \mu\text{m}$  thick membrane, lower than that of Nafion 115 ( $192 \text{ m}\Omega \text{ cm}^2$ ) and even Nafion 212 ( $89 \text{ m}\Omega \text{ cm}^2$ ). The selectivity (conductivity/permeability) is  $9 \cdot 10^{14} \text{ S s m}^{-3}$ , 7, 30 and 1000 times higher than for standard PBI, PA and polyphosphoric acid pre-swollen membranes, respectively. A VRFB with a  $5 \mu\text{m}$  thick 4N3S membrane showed energy efficiencies of 91.3% at  $80 \text{ mA cm}^{-2}$  and 95.4% at  $40 \text{ mA cm}^{-2}$ .

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