



Contents lists available at ScienceDirect

## Chemical Engineering Journal

journal homepage: [www.elsevier.com/locate/cej](http://www.elsevier.com/locate/cej)

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

Chanho Noh<sup>a,1</sup>, Dmytro Serhiichuk<sup>b,c,d,1</sup>, Najibah Malikah<sup>b,d</sup>, Yongchai Kwon<sup>a,e,\*</sup>, Dirk Henkensmeier<sup>b,d,f,\*</sup>

<sup>a</sup> Graduate School of Energy and Environment, Seoul National University of Science and Technology, Nowon-gu, Seoul 01811, Republic of Korea

<sup>b</sup> Center for Hydrogen and Fuel Cell Research, Korea Institute of Science and Technology, Seongbuk-gu, Seoul 02792, Republic of Korea

<sup>c</sup> Chemical Technology Faculty, NTUU Igor Sykorsky Kyiv Polytechnic Institute, Kyiv 03056, Ukraine

<sup>d</sup> Division of Energy & Environment Technology, KIST School, University of Science and Technology, Seongbuk-gu, Seoul 02792, Republic of Korea

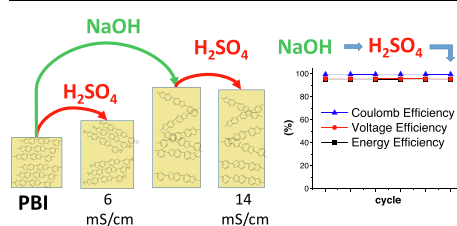
<sup>e</sup> Department of Chemical and Biomolecular Engineering, Seoul National University of Science and Technology, Nowon-gu, Seoul 01811, Republic of Korea

<sup>f</sup> Green School, Korea University, Seongbuk-gu, Seoul 02841, Republic of Korea

## 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  $4 \times 10^{-15}$  to  $1.6 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$ .
- 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

## Keywords:

PBI  
Alkaline pre-treatment  
Conductivity  
Vanadium permeability  
VRFB

## 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  $9 \times 10^{14} \text{ S s m}^{-3}$ , 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  $40 \text{ mA cm}^{-2}$ .

\* Corresponding authors at: Graduate School of Energy and Environment, Seoul National University of Science and Technology, Nowon-gu, Seoul 01811, Republic of Korea (Y. Kwon). Center for Hydrogen and Fuel Cell Research, Korea Institute of Science and Technology, Seongbuk-gu, Seoul 02792, Republic of Korea (D. Henkensmeier).

E-mail addresses: [kwonyc@seoultech.ac.kr](mailto:kwonyc@seoultech.ac.kr) (Y. Kwon), [henkensmeier@kist.re.kr](mailto:henkensmeier@kist.re.kr) (D. Henkensmeier).

<sup>1</sup> Both authors contributed equally.