Washington University in St. Louis
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LOW COST, HIGH PERFORMANCE ANION EXCHANGE MEMBRANES FOR GRID-SCALE ENERGY STORAGE AND OTHER ELECTROCHEMICAL DEVICES

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T-018608

Technology Description

Engineers in Prof. Vijay Ramani's laboratory have developed a variety of robust, versatile anion exchange membrane (AEM) materials that achieve high performance through superior ion selectivity. These mechanically and chemically stable membranes have the potential to dramatically reduce costs and increase lifetimes compared to conventional AEMs. They could be used as separators in redox flow batteries (RFBs) for grid-scale energy storage or in other electrochemical devices with applications in water desalination, electrolysis/hydrogen production or fuel cells.

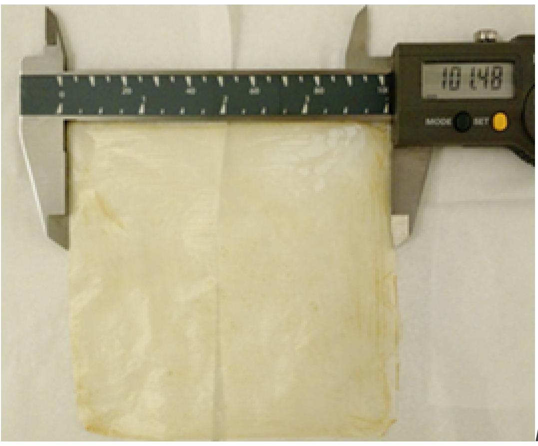
This technology includes the membrane materials as well as high throughput, scalable production methods, including:

Tunable polymeric separator (WUSTL Technology T-017637): Polystyrene-*block*-poly(ethylene-*ran*-butylene)-*block*-polysteyrene (SEBS)-based anion exchange membranes with high selectivity that efficiently separate anolyte and catholyte solutions and are stable in acidic, RFB conditions. The mechanical properties (rigidity and elasticity) of these materials can be adjusted by changing the proportion of the polymers in the membrane. Additional features can be tuned by selecting the cation and customizing the functionalization.

Doped AEMs (WUSTL Technologies T-018566, T-018608, T-018611): AEMs with a variety of properties depending on the cation, functionalization and backbone [SEBS polymer or QPEK-C (chloromethylated cardo-polytherketone) composite]. This includes:

1. reinforced AEMs with very low permeability that protects them from being degraded due to water uptake;
2. functionalization with a large cation (TRIS) to improve ion selectivity; and
3. nanocomposite membranes with metal-oxide fillers that can be incorporated into QPEK-C materials to improve mechanical properties and reduce permeability while improving performance (selectivity and conductivity).

These AEMs perform as well or better than conventional AEMs at ~1% of the cost. This is particularly useful for RFBs where membranes account for about 20% of the system costs.



Lab scale prototype *- membrane sample shows long term storage with no performance degradation (capacity or efficiency) over >500 hours of cycling.*

Stage of Research

Lab scale synthesis and performance: The inventors have synthesized a variety of membrane materials at lab scale and demonstrated their performance and stability (conductivity, cycling performance, water uptake etc.) in electrochemical devices (RFB cells at ~20Wh). These materials exhibit different properties that can be tuned/optimized based on the intended application. For example:

A SEBS-based AEM separator in a Vanadium-Cerium Redox Flow Battery had an energy efficiency of 86% at current density of 50 mA/cm^2 , maintained its mechanical integrity and performed 4 times better than commercial membranes in terms of capacity retention.

SEBS functionalized with a TRIS cation had low ion exchange capacity (0.65 mmol/g); high chloride conductivity (1.45 mS/cm at 40°C) and high tensile strength (4 MPa) to simulate conditions in an operating RFB.

Reinforced materials [SEBS and QPEK-C] had low water uptake and swelling ratios to prevent membrane degradation in desalination and other applications

Future work: The inventors plan future studies to scale up production (beyond 10 cm x 10 cm), test additional applications, and develop processes for roll-to-roll production.

Applications

- **Anion exchange membranes (AEMs)** for energy storage and conversion systems, with end user applications including:
  - **redox flow battery (RFB) separator -** for grid-scale storage of renewable energy (e.g., solar, wind), distributed storage and load-level management
  - **water electrolysis** – hydrogen production, alkaline water electrolyzers
  - **alkaline fuel cells**
  - **water desalination** - reverse electrodialysis and capacitive deionization

Key Advantages

- **Low cost:**
  - membrane is fabricated from inexpensive polymers and earth-abundant materials
  - membrane end-product is estimated to be ~1% of the cost of current AEMs (e.g., Nafion)
  - lowers total electrical consumption for water desalination

    - scalable fabrication processes achieve AEMs with large surface area and potential for roll-to-roll manufacturing
    - predict capital costs of <$100/KWh for RFB application because battery architecture allows for capacity scale up with sub-linear scaling of costs (~1/4 cost of lithium ion battery at 100GWh/year and above)
- **High performance**
    - high ionic conductivity and ion exchange capacity (IEC) due to **superior ion permselectivity**
    - long-term cycling performance and long term energy storage with no performance degradation could improve lifetime of redox flow batteries and other electrochemical devices
- **Robust and versatile –** tunable features can be optimized for end user application
    - mechanically stable with high tensile strength for applications with large active areas and high stress such as desalination
    - chemically stable to maintain performance in harsh acidic or alkaline environments, particularly for fuel cells/electrolysis/hydrogen production
    - rigidity and elasticity can be adjusted for desired application by changing the proportion of the polymers in the membrane
    - physical strength, water uptake and degree of functionalization can be adjusted with different cations and functionalization of the membrane (e.g., membrane reinforcement prevents degradation from water uptake)
- **Thin –** batch process produces uniform membranes down to 30 microns thick

Publications

- S. Sankarasubramanian, Y. Zhang, V. Ramani, Methanesulfonic acid-based Electrode-decoupled Vanadium-Cerium Redox Flow Battery Exhibits Significantly Improved Capacity and Cycle Life, *Sustainable Energy and Fuels*, 3, 2417-2425 (2019)
- Z. Wang, J. Parrondo, V. Ramani, Anion Exchange Membranes Based on Polystyrene-BlockPoly(ethylene-ran-butylene)-Block-Polystyrene Triblock Copolymers: Cation Stability and Fuel Cell Performance, *Journal of The Electrochemical Society*, 164 (12) F1216-F1225 (2017)
- Wang, Z., Parrondo, J., & Ramani, V. (2017). Polystyrene-block-poly (ethylene-ran-butylene)-block-polystyrene triblock copolymer separators for a vanadium-cerium redox flow battery. *Journal of The Electrochemical Society*, 164(4), F372-F378.

Patents

- Triblock Copolymer Based Anion Exchange Membranes (AEMs) as Separators in Electrochemical Devices (U.S. Patent Application, Publication No. US20190044158A1)
- Doped Anion Exchange Membranes (AEMs) for Highly Selective Separators in Electrochemical Devices (PCT Application filed 7/30/19)

Website

- Ramani Lab