Material Development for Redox Flow Batteries at PNNL

2025 OE Peer Review

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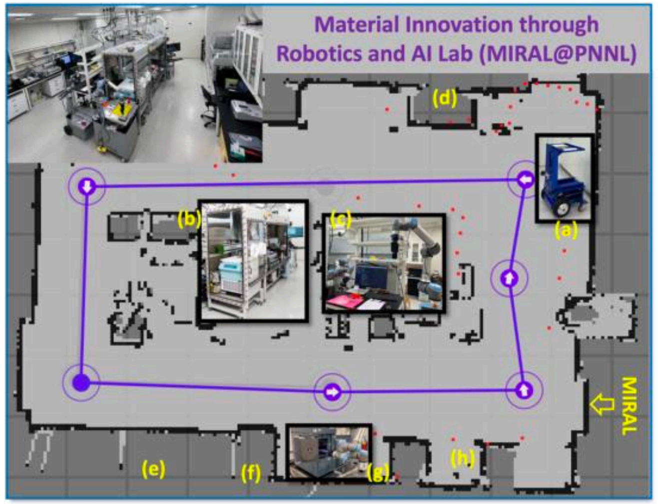
Project Overview

- **Project Goal:**

  This project will develop advanced redox flow battery (RFB) electrolytes and membranes systems to achieve substantially improved cost and performance metrics for redox flow technology.

    - Aqueous soluble organic (ASO) anolyte (Feng)
    - ASO catholyte
    - Membrane development of ASO systems
- **Current Practice:**
  - Vanadium-based flow batteries suffer from high cost and limited stability
  - Development of RFBs using earth abundant materials
- **Why PNNL:**
  - A materials innovation powerhouse for flow battery R&D with a proven track record
  - Materials Innovation through Robotics and AI Lab (MIRAL)
  - Grid Storage Launchpad: the most comprehensive grid energy storage R&D facility

MIRAL



- **Innovation:**
  - Identify new catholyte active molecules and novel separation mechanisms for membrane development
- **Impact:**
  - Low-cost and adaptable energy storage systems to support the modernization of the nation's power grid.
  - Diversify energy storage material sources by prioritizing earth-abundant materials.
- **Alignment:**
  - This project aligns with OE's mission towards development to strengthen and modernize our nation's power grid to maintain a reliable, affordable, secure, and resilient electricity delivery infrastructure.

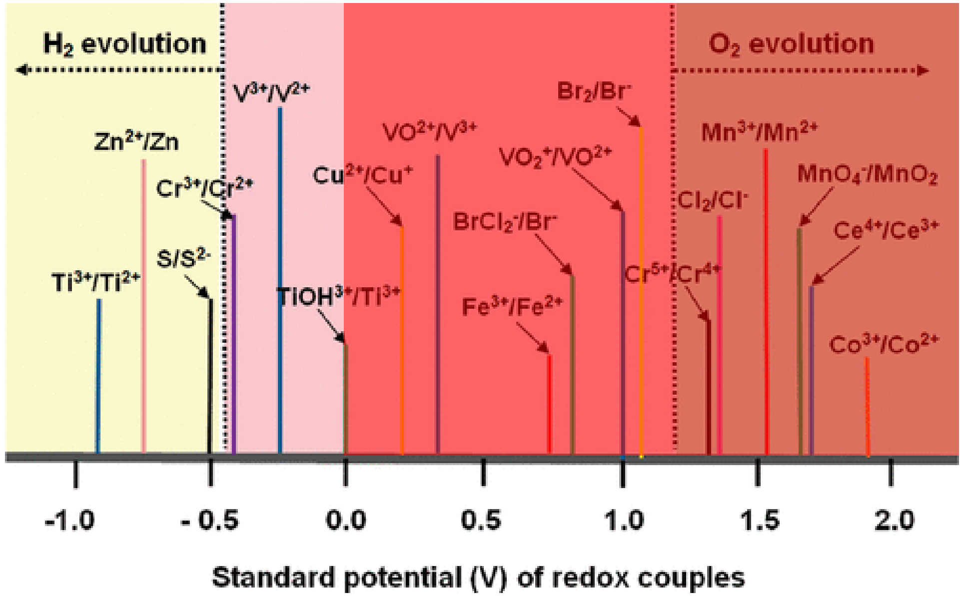
Redox flow batteries and major challenges

- Decoupling of power and capacity
- High safety
- Easy recycling after service life

- Limited library of available molecules, particular for catholyte
- Molecular engineering is often required to tune properties of redox potential and solubility etc.
- Lack of suitable membranes for ASO systems

Challenge on catholyte material development

Electrochemical potential window

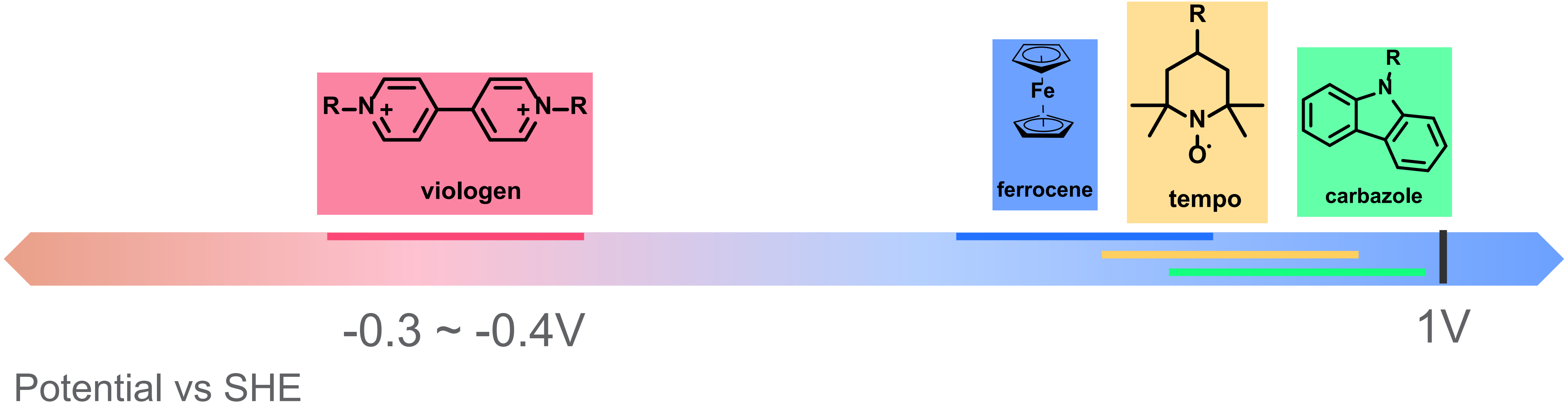


TEMP ring opening degradation

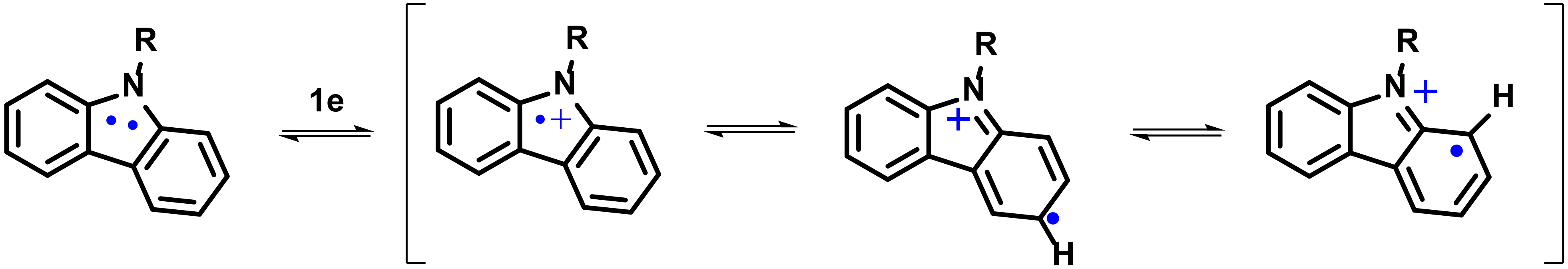
Ferrocene ring hydrogenation

Adv. Funct. Mater. 2022, 2203032
Energy Environ. Sci., 2022, 15, 1315–1324
Chem. Rev. 2011, 111, 5, 3577–3613

Carbazole (Cz) based catholyte



High redox potential within water window



How we stabilize the radical cation?

Radical cation stabilization strategy

spin delocalization

Dimerization for stabilization

- Lowers the local spin density at any one reactive site.
- Reduces reactivity toward water or oxygen.
- Minimizes the likelihood of further degradation or side reactions.

Flow battery cycling performance

Cell testing condition:

25mL 0.1M SV 0.2M Na_2SO_4; 5.5 mL ~0.1M bi-Cz-01 0.2 M Na_2SO_4

N212 water soak RT OVN; 40mL/min; GFC020 electrode; 10mA/cm^2

Cz-based material development roadmap

- Utilize MIRAL to accelerate the development

Achieved ● **A** **Baseline data & know-how**
Chemists synthesize mono- & bi-Cz seeds

In progress ● **B** **HTP solubility workflow**
- Active-learning model prioritizes hydrotrope & micro-emulsion recipes

Pending ○ **C** **Virtual design of new Cz molecules**

Pending ○ **D** **MIRAL automated validation & parallel solubility push**

Model compound confirmation of radical cation stabilization strategy

Advancing Bi-Cz Solubility

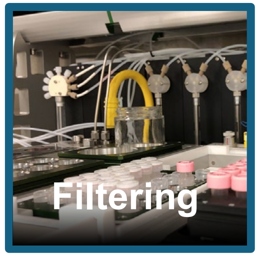
1 Domain Expertise
Establishing a foundation with baseline experiments

2 HTP/ML Screening
Optimizing formulations with high-throughput screening

3 Next-Gen Derivatives
Developing new derivatives using virtual libraries

4 MIRAL Platform
Validating and enhancing solubility with automation


Lab Mobility


Filtering


Capping


Solid Additions


Liquid Additions


Imaging

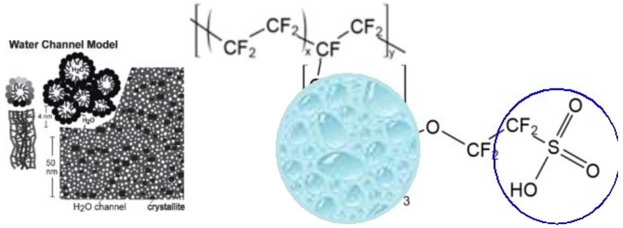
ASO flow battery membrane development

The membrane is the most underdeveloped component in the field of redox flow batteries

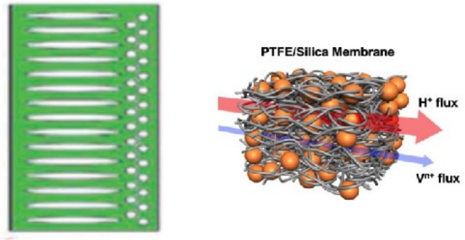
Functionality requirements

- High ionic permselectivity
- Low electric resistance
- High stability
- Low cost

Ion-exchange membrane



Porous membrane



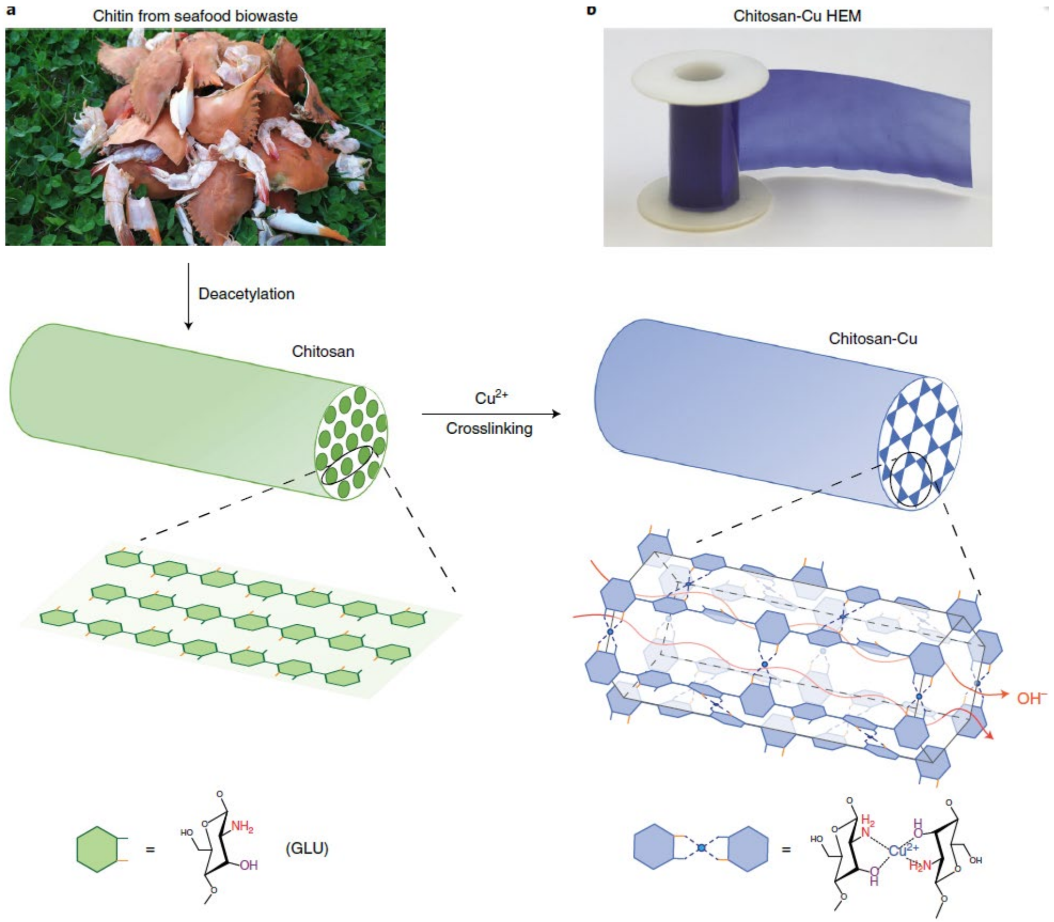
Challenges:

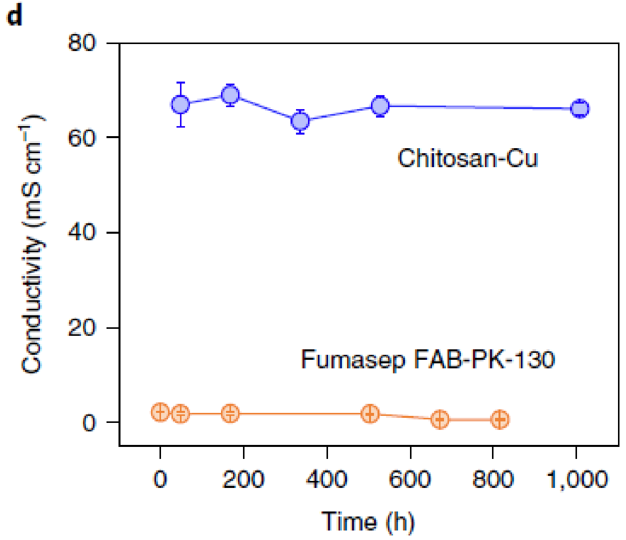
- No Specifically designed membrane available for ASO system
- Poor selectivity, leading to active redox species crossover.
- Instability (e.g., electrolyte pH > 11)
- Low ionic conductivity, resulting in high membrane resistance.
- High cost

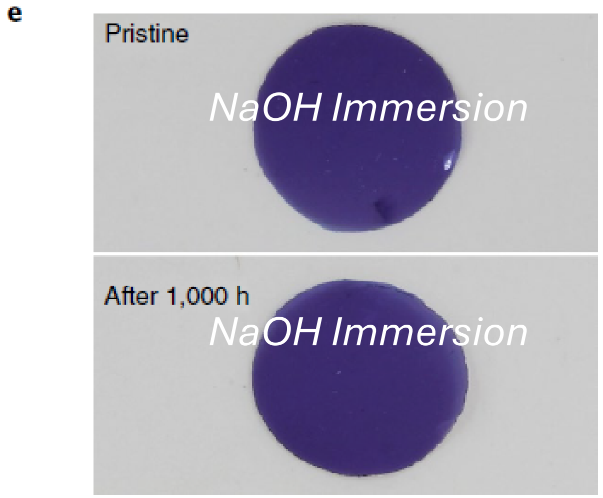
Wei et al. Adv. Energy Mater. 2013, 3, 1215
Schmidt-Rohr et al. Nat. Mater. 2008, 7, 75.
H. Z. Zhang et al. *Energy Environ. Sci.* 2011 , 4 , 1676 .

Membrane Development for ASO systems

Cu-chitosan based ion-exchange membranes for ASO RFBs







This membrane exhibits:

1. High hydroxide ion conductivity (~61 mS cm^{-1}).
2. Good alkaline stability (e.g., 80°C, 3M NaOH).

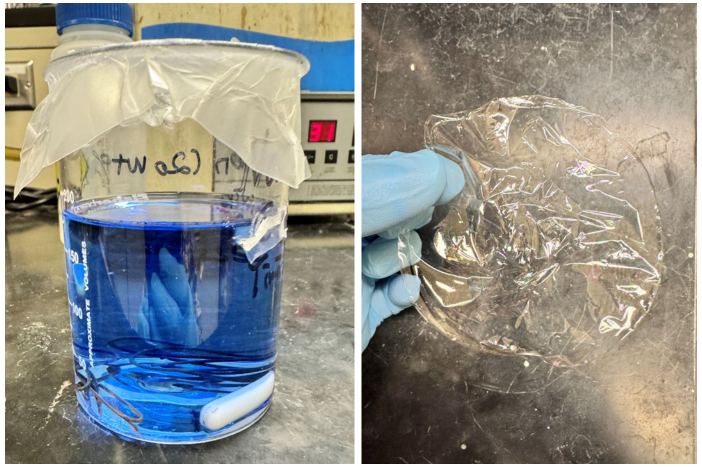
It is a promising candidate for the SSO RFBs.

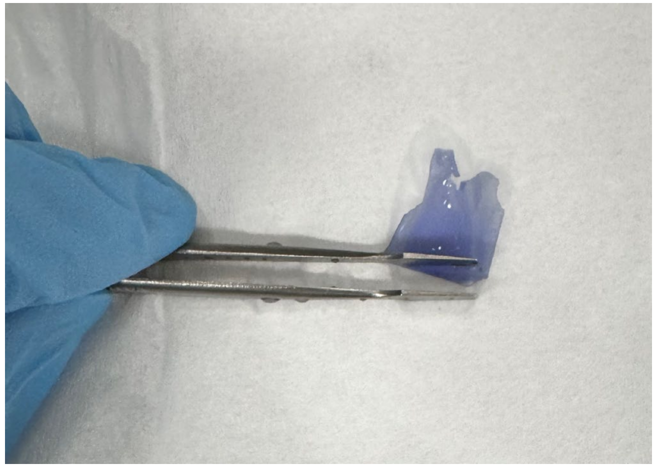
Nature nanotechnology 17, no. 6 (2022): 629-636

Instability in a functional ASO RFBs

Cu-chitosan based ion-exchange membranes for ASO RFBs

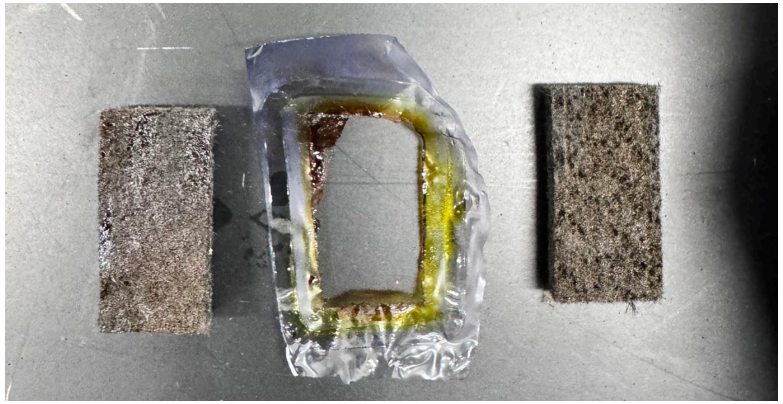
- Successful membrane preparation: High hydroxide conductivity.



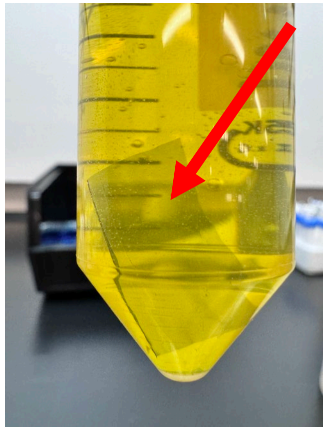


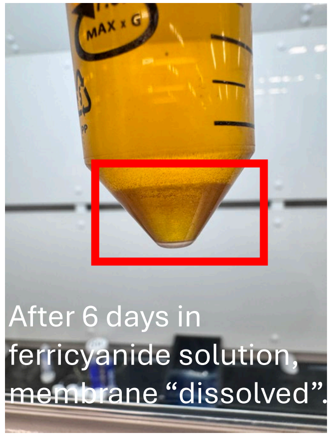
Hydroxide ion conductivity of Cu-Chitosan membrane: *~92.7 ± 5.4 mS/cm*

- Failed membrane test: Membranes dissolved during the test (1M DHPS paired with potassium ferricyanide)



Why?



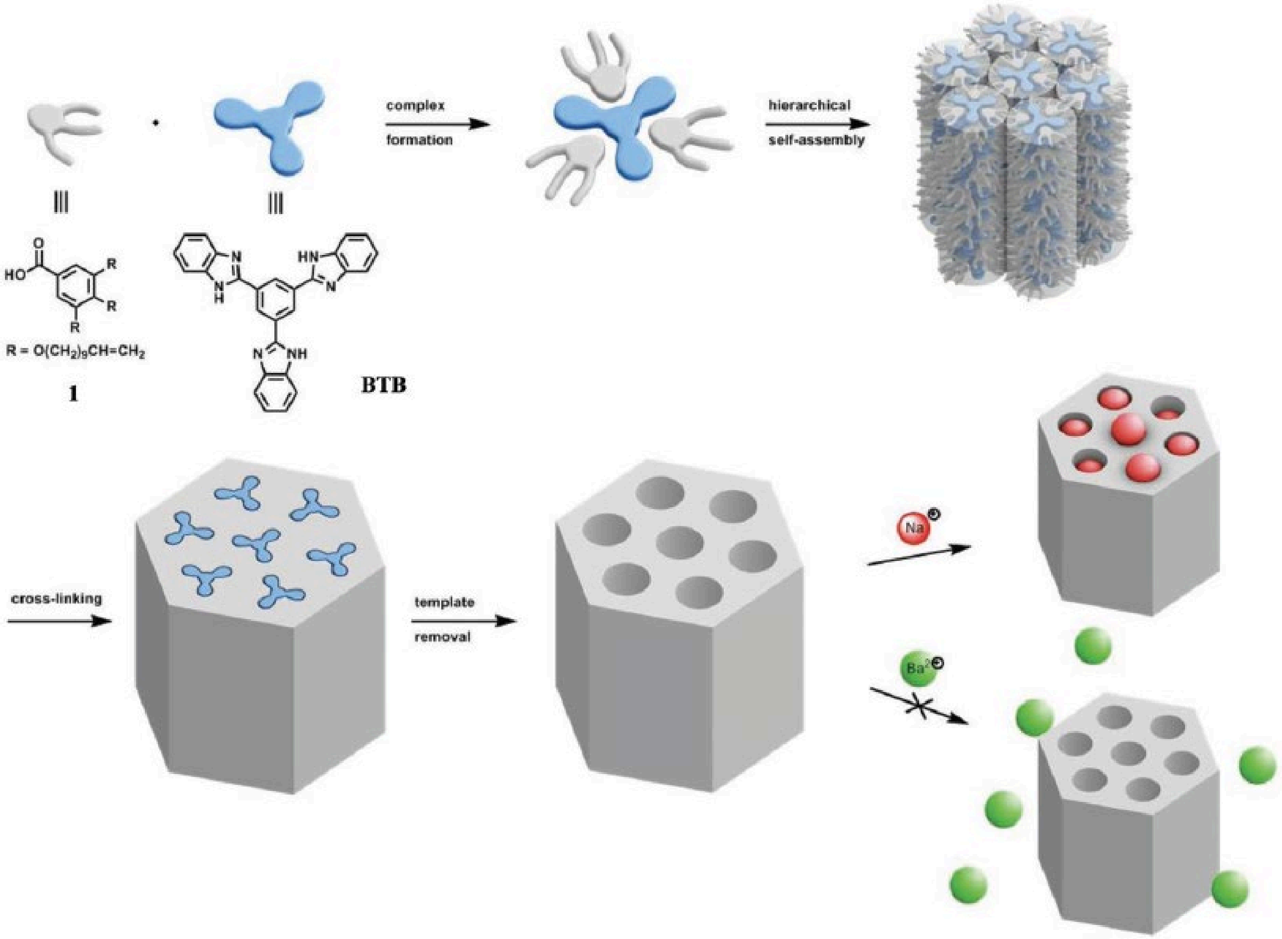


After 6 days in ferricyanide solution, membrane “dissolved”.

The Cu-chitosan membrane exhibits poor stability in ferricyanide solutions, irrespective of pH.

Identify new membrane material design strategy

Designing ion-exchange membranes guided by principles of molecular self-assembly



How do self-assembling molecules form membranes?

Varying molecules align through:

- *Hydrogen bonding.*
- *Hydrophobic-hydrophobic interaction.*
- *π-π stacking, etc.*

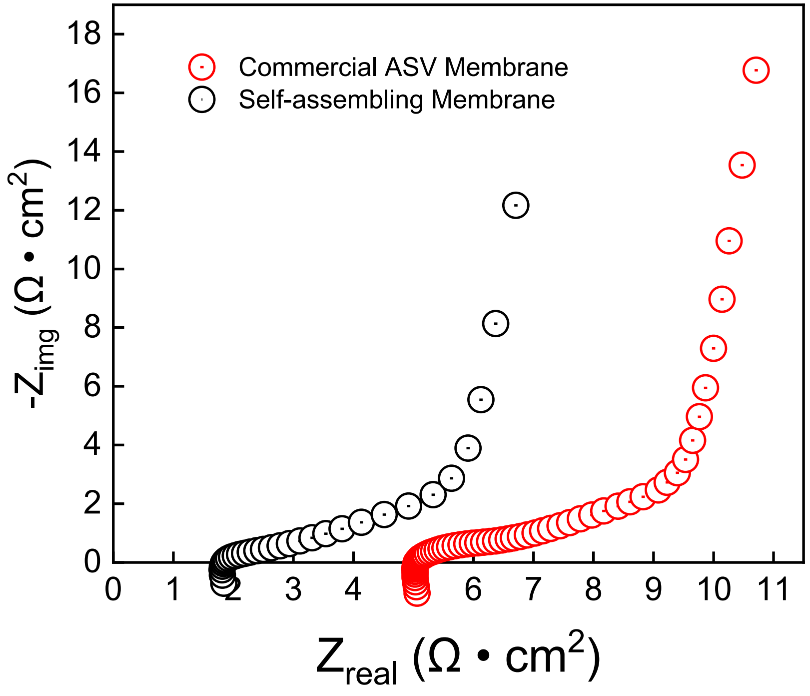
To form <u>selective membrane pores</u> and <u>size-controlled ion transport channels</u>.

Advanced Functional Materials 26.44 (2016): 8023-8030

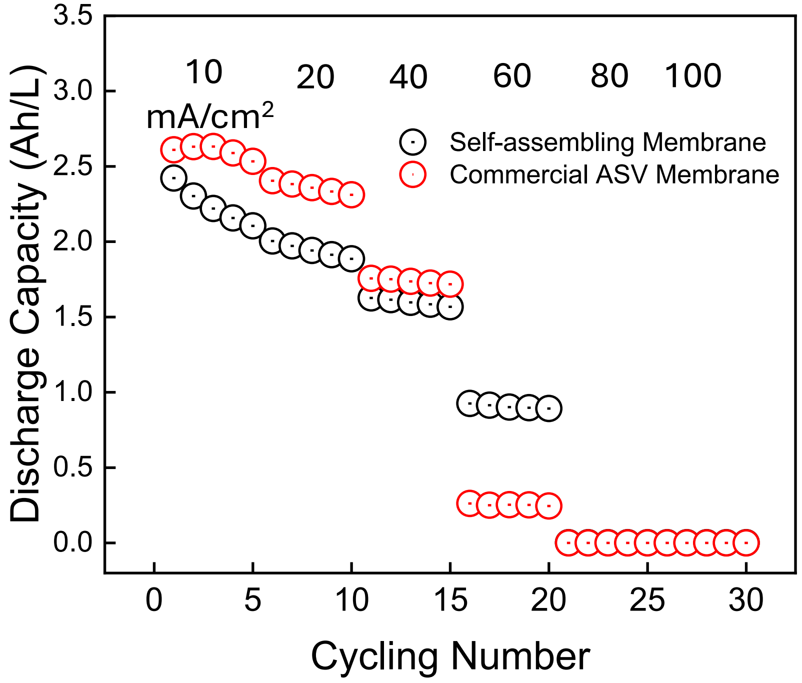
Membrane development through molecular self-assembly

Self-assembling membrane has demonstrated:

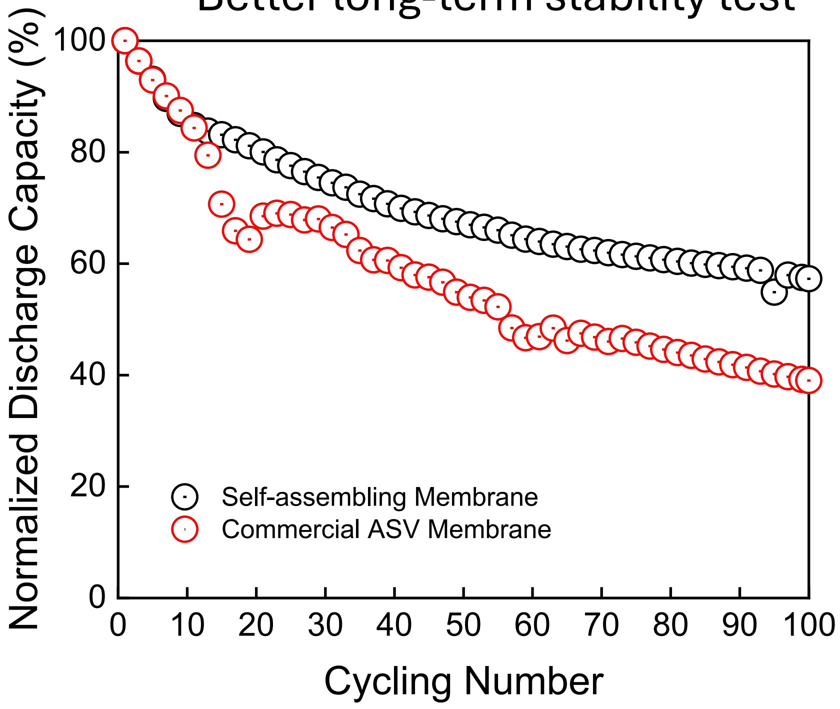
- Improved ionic conductivity



- Better rate performance



- Better long-term stability test



The self-assembling membrane outperforms the commercial ASV membrane in aqueous organic redox flow battery testing.

Acknowledgment

- PNNL is a multi-program national laboratory operated by Battelle for the US Department of Energy under contract DE-AC05-76RL01830.
- This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.
- Additional acknowledgments

Ruozhu Feng
Aaron Hollas
Peter S. Rice
Xin Zhang
Ying Chen
David Reed
Peiyuan Gao
Yangang Liang
David J. Bazak
Hyung-Seok Lim

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