Advanced Membranes for Flow Batteries: Anion Exchange Membranes

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2019 Budget = $300k
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Membrane Basics

The performance of flow batteries are influenced by membrane properties. Membrane conductivity dictates battery round trip efficiency and membrane selectivity regulates capacity retention.

• Due to cost concerns of acidic vanadium flow batteries, this is driving R&D interest in pH neutral and high pH environments typically used in aqueous organic and non aqueous flow batteries.
• New flow battery chemistries being developed under a variety of pHs.

In acidic environments (VRFB)
CEM used pH < 7

In alkaline environments
AEM used pH > 7
Anion Exchange Membrane (AEM) Basics:

1. Polymer that contains bound positive charges.
2. *Alkaline stable* AEM allows for new electrochemical applications.
3. There is no widely accepted *alkaline stable* “state of the art” AEM.

Growth of AEM interest 2001 - 2017

Handful of small AEM companies
Recent independent stability survey of AEM

- Growth and interest in AEMs, but need to objectively determine best AEM candidates
- Third party lab investigated accelerated membrane durability under alkaline conditions by soaking films in 1 M KOH for 1000 hrs at 80 °C and monitoring any loss in 1. IEC  2. Conductivity  3. Mechanical

Credit: Kelly Meeks and Bryan Pivovar NREL
IEC and Conductivity stability:

- Hydroxide ion is a strong base and nucleophile.
- Three different mechanisms result in IEC and conductivity loss.

Acceptable loss < 5%

Sandia polymer, PPN6 passed this test!

64% of surveyed polymers saw less than a 5% loss in IEC (Sandia polymer is PPN6).

but

42% of surveyed polymers saw less than a 5% loss in conductivity (Sandia polymer is PPN6).
Mechanical stability:

Only 20% of films maintained mechanical properties. Only three poly(phenylene) type structures survived (PPN6 is the Sandia polymer). All other types of backbones look to degrade. PPN6 showing encouraging durability.

Credit: Kelly Meeks and Bryan Pivovar NREL
Membranes for Flow Batteries (FB)

- Membranes for flow batteries = precise control of IEC. Too High IEC = high crossover, capacity loss. Too Low IEC = low conductivity, low efficiency. Need to optimize polymer IEC which is dependent on polymer structure and battery chemistry.
- Recently discovered a processing issue that was affecting IEC control = performance in flow battery applications.
Aqueous Soluble Organic FB:

Polymer with large amount of alkyl bromide (4-5) Process 1 partial conversion.

SNL = Low resistance

SNL 3.5 x lower resistance than Selemion DSV

Target 1x10^-10 cm^2/s
SNL 6 x 10^-9 cm^2/s
Selemion DVS 1x10^-12 cm^2/s

Unpublished work from Dr. Aziz labs

Process 1 No reaction

Polymer with low amount of alkyl bromide (1-2) Process 1 no reaction.
Dissolve in CCl₃H

Using Process 1 poor IEC control: experimental IEC (2.3 eq/g) always lower than theoretical (2.7 meq/g).

Heterogeneous reaction rate dependent on polarity of polymer.
Polymer Process 2:

Dissolve in DMSO

Add amine to polymer

Process 2 improves control of IEC: Experimental IEC (2.68 eq/g) now matches theoretical (2.7 meq/g). Submitted non provisional patent SD15069.0.
Conclusions:

• High interest in alkaline stable anion exchange membranes.
• Various polymers are being investigated, but the SNL polymer has shown promising durability in comparison tests.
• Issues in controlling polymer IEC was due to processing conditions (Process 1).
• Developed Process 2 which has shown full conversion of alkyl bromide to ammonium; IEC control. Submitted non-provisional patent.

Future Tasks:

• Flow battery test of AEMs synthesized by Process 2
• Membrane commercialization

Patents/Papers:

• Acid-catalyzed benzoylation reactions of Diels-Alder polyphenylenes in Polymer (December 2018), 158, 190-197. Fujimoto, Cy; Sorte, Eric; Bell, Nelson; Poirier, Cassandra; Park, Eun Joo; Maurya, Sandip; Lee, Kwan-Soo; Kim, Yu Seung.
Thank You

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Questions?

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