Advanced Membranes for Vanadium Redox Flow Batteries (VRB)

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Project

- Separation of energy and power
- Robust battery. Allows for deep discharge and long life cycles
- Several US companies looking to commercialize this technology

Cost is focus since current capital costs range between $500-1000/kWh
Cost of VRB

- Cost calculated based on shunt-pumping losses and delivered power and energy capacity.

- Two types of VRB configurations
  1. Power intensive: 1 MW/0.25 MWh (Power quality applications)
  2. Energy intensive: 1 MW/4 MWh (Load following)

- In both scenarios the membrane separator takes up a significant portion of total cost

- Nafion™ $250-500/m²; Perfluorinated polymer (primarily C-F)

**Sandia is developing low cost, hydrocarbon polymer (C-H) with better performances than Nafion**

Evolution of VRB membranes

GEN 1 material:
+ Performance equivalent to PFSAs
- Durability, after 179 cycles oxidation of film

Test credit Soo-Han Kim 2012

Ex-situ: 0.1M $V^{+5}$

$V^{+5}$ oxidizing un-substituted aryl rings
Evolution of VRFB membranes

Substitute $-\text{SO}_3\text{H}$ on all aryl groups

GEN 4 material

Hydrophilic segment
Controls ions and water flow

Hydrophobic segment
Mechanical support

Ions and water transport

Patent submitted Nov 2014  US 62/075,693
Membrane Durability

Ex situ durability

25 mL of 1.7 M $V^{5+}$, 5M $SO_4^{2-}$
200mg of membrane

Monitored $V^{4+}$ production by UV-Vis

Before 1.7M $V^{5+}$ exposure

48 hrs

After 1.7M $V^{5+}$ exposure

GEN4 stability greater than GEN1 and GEN2

Test credit Zhijang Tang
ORNL
Membrane Performance

Tested in 2M mixed-acid VRB

- Good performance: Columbic efficiency 95%, voltage efficiency 94% and energy efficiency 90%
- Much higher charge retention compared to Nafion
- Small capacity decay with time, but large drops in part to solution leaking [test run time nearly 4 months]

GEN4 good performance much better capacity retention than Nafion
Membrane Performance

Xiaoliang, PNNL

Membrane after 300 cycles

- After cycling the membrane it shows some discoloration (white spots)
- IR analysis of active and non active area shows very little difference, suggesting little to no decomposition

We are looking into several alternatives

GEN4 may still need a few modifications, but almost there
Membrane Scalable, Cost?

- Feasible to scale chemistry? Yes
- Cost? Silicon dioxide (low volume pricing Sigma-Aldrich $64/kg) assume SiLk costs were not extremely far off from this value since cost was never an issue [Nafion $5000/kg approximately $250/m2]
Summary/Conclusions

- Gen4 significantly improved durability over Gen 1&2
- Gen4 VRB performance better than Nafion212
- Gen4 charge retention much better than Nafion 212
- Gen4 structure as presented, requires slight modification

Future Tasks

- Developing Gen4 with oxidative resistance hydrophobic domain
- Cost model development with external partner
- Further develop details in commercialization path forward
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Questions?

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Outside interest

With ProtonOnsite proved alkaline electrolysis is feasible

With IP developed in the OE program, EERE fuel cell awarded SNL incubator project for intermediate temperature PEM fuel cell – Results very promising

Lower ASR in SNL over Nafion
Higher power in SNL over Nafion

Work with Dr. Zawodzinski

Showing promising data for multiple applications