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MEMBRANES FOR ALL-IRON, ALL-SOLUBLE FLOW BATTERIES

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INTRODUCTION

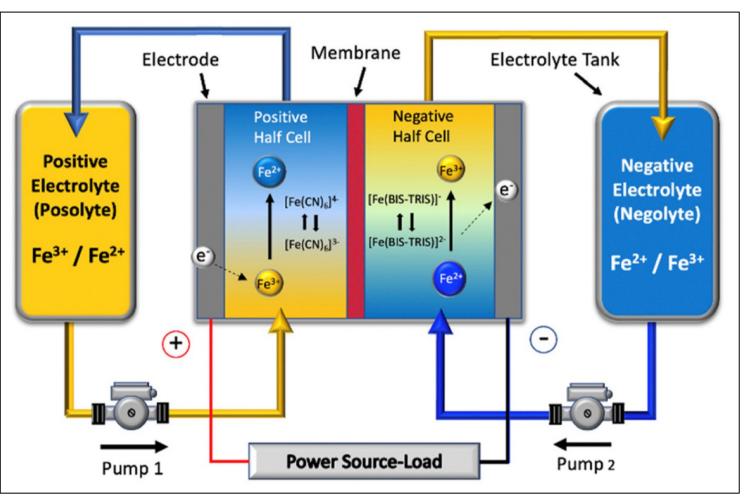


Figure 1. Schematic diagram of a flow battery system¹

This work looks at the suitability of various commercial membranes for all-iron, all-soluble FBs.

- Climate change highlights the need for long-duration energy storage.
- Flow batteries (FB) are a promising candidate to address this need.
- Typical electrolyte chemistry is the all-vanadium FB, but this is expensive.
- All-iron, all-soluble iron FB is a promising cost-effective alternative.
- Few membranes have been tested with all-iron, all-soluble iron FBs.

Iron

electrolyte:

 $0.5 \text{ M K}_{3}[\text{Fe}(\text{CN})_{6}]$

+ I.0 M NaCl

Vanadium

electrolyte:

 0.5 M VO_{2}^{+}

+ 2 M H₂SO₄

METHODOLOGY

Membranes Investigated					
Cation exchange	Anion exchange				
membranes	membranes				
Nafion® 117,	Fumasep				
Aquivion E98-05,	FAP-450,				
Fumasep FS-930,	Fumasep				
Fumasep E-620(K),	FAA-3-30,				
Dongyue DMV850,	Fumasep				
PFSA D15-R ePTFE	FAAM-20				

- Chemical stability testing with electrolytes
- Tensile testing of "dogbone" samples
- Thermogravimetric analysis
- lon exchange capacity titrations
- Electrochemical impedance spectroscopy

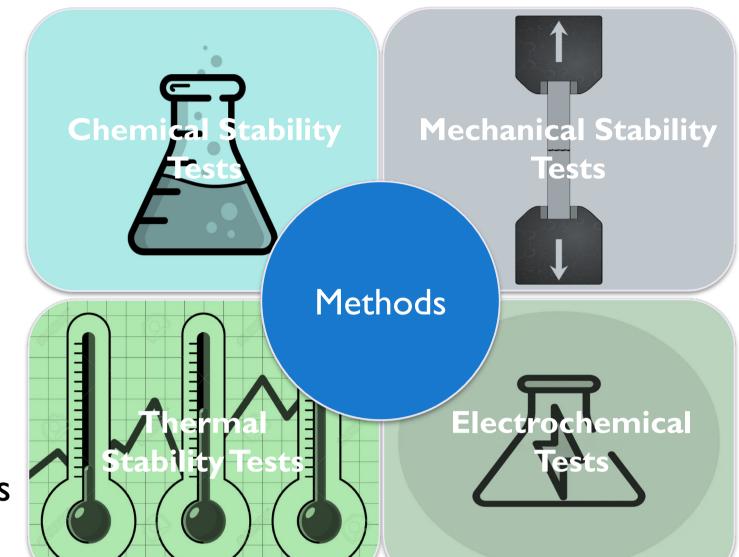


Figure 2. Schematic summarizing testing regime of commercial membranes

CHEMICAL STABILITY TESTING

Membranes must be able to withstand the highly oxidative environments found in FBs.²

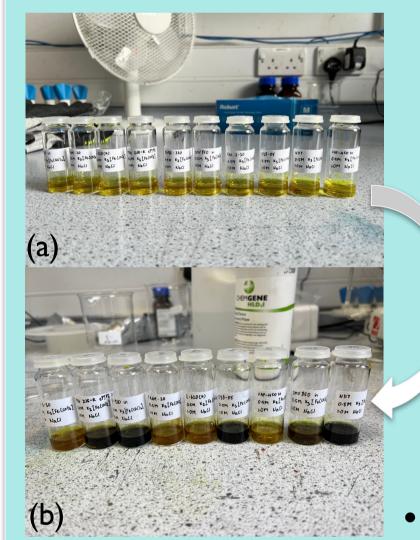


Figure 3. Photo (a) before and (b) after chemical stability test

N117
E98-05
FS-930
E-620(K)
DMV850
PFSA D15-R ePTFE
FAP-450
FAA-3-30
FAAM-20

-80% -60% -40% -20% 0% 20% 40% 60%

Mass Change in Iron Electrolyte (%)

Mass Change in Vanadium Electrolyte (%)

Figure 4. Mass change upon exposure to electrolytes

- N117, E98-05, and DMV850 possess good chemical stabilities under both iron and vanadium electrolyte conditions.
- FAP-450 and FAA-3-30 possess good chemical stability under iron electrolyte, but not when exposed to vanadium electrolyte.

MECHANICAL STABILITY TESTING

Water uptake can cause membrane swelling, resulting in loss of mechanical integrity and affecting ion pathways.³

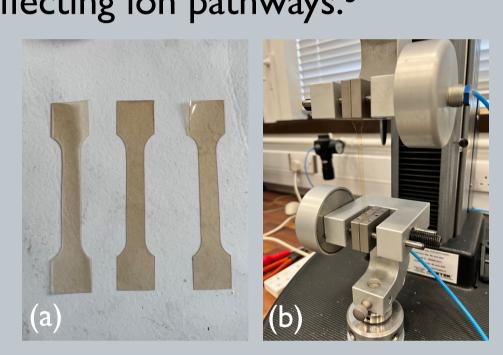


Figure 5. Photos of (a) laser-cut "dogbone" samples and (b) membrane undergoing tensile testing

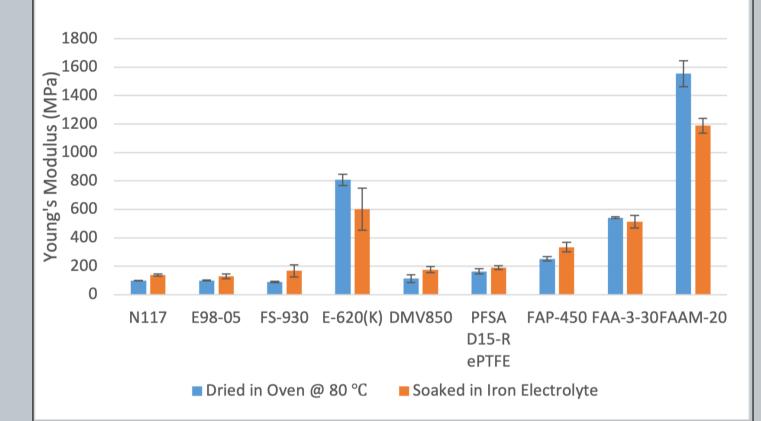
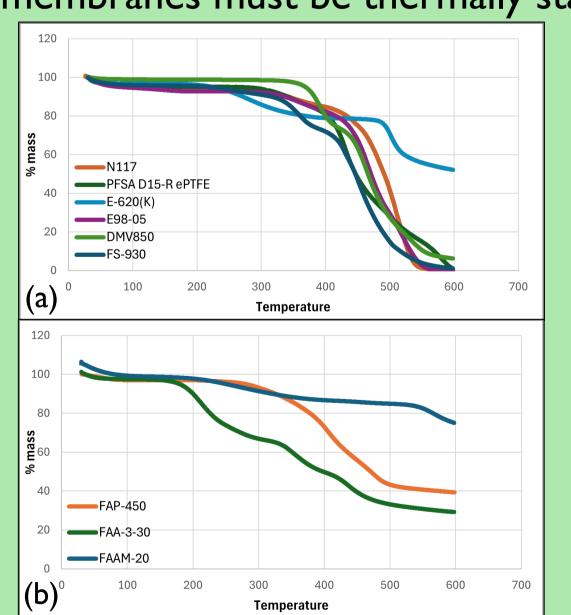


Figure 6. Young's modulus of dry and wet membranes

- E-620(K) and FAAM-20 are the two most mechanically robust membranes, but they both deform more easily when soaked in iron electrolyte.
- FAA-3-30 and FAP-450 are good candidates as they retain their mechanical properties even when soaked in iron electrolyte.

THERMAL STABILITY TESTING

Higher temperature operation often results in better FB performance and membranes must be thermally stable for long-duration energy storage⁴



•		
•		
•	700	600
	•	700

Membrane	T _{decomp, onset} (°C)		
NII7	271		
E98-05	354		
FS-930	309		
E-620(K)	258		
DMV850	375		
PFSA D15-R ePTFE	342		
FAP-450	313		
FAA-3-30	192		
FAAM-20	270		

- All membranes are thermally stable for FB systems
- For CEMs, membranes that possess excellent thermal stability are DMV850, E98-05, and PFSA D15-R ePTFE
- (b) 100 200 300 400 500 600 700 For AEMs, the most thermally stable membrane is Figure 7.TGA plot for (a) CEMs and (b) AEMs FAP-450

ELECTROCHEMICALTESTING

Ionic Conductivity



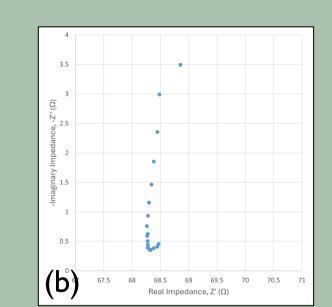


Figure 8. (a) Photo of H-cell setup, (b) Example Nyquist plot

	[mm]	[S.m ⁻¹]
N117	0.164	1.045
E98-05	0.059	0.069
FS-930	0.032	0.026
DMV850	0.047	0.158

Membrane conductivity measurement is still on-going

*Limitation of membrane versus membraneless EIS method: small • N117 performental changes heavily affect reliable measurements of thin membranes

N117 possess the highest conductivity

Ionic Exchange Capacity

Membrane	N117	PFSA D15-R ePTFE	E-620(K)	E98-05	DMV850	FS-930	FAP-450	FAA-3-30	FAAM-20
IEC [mmol/g]	0.588	1.765	1.5†	0.517	0.435	0.972	1.075	2.692	4

- For CEMs, PFSA D15-R ePTFE and E-620(K) possess high IEC
- For AEMs, FAAM-20 and FAA-3-30 possess high IEC

†Data taken from previous MSc student

REFERENCES

[1] J. J. Bailey et al., "All-iron redox flow battery in flow-through and flow-over set-ups: the critical role of cell configuration," Energy Advances, vol. 3, no. 6, pp. 1329–1341, May 2024.

[2] F. Wang, F. Ai, Y.-C. Lu, "lon selective membrane for redox flow battery, what's next?," Next Energy, vol. 1, no. 3, 2023

[3] C. A. MacHado, G. O. Brown, R. Yang, T. E. Hopkins, J. G. Pribyl, and T. H. Epps, "Redox Flow Battery Membranes: Improving Battery Performance by Leveraging Structure-Property Relationships," *ACS Energy Lett*, vol. 6, no. 1, 2021 [4] S. Yin, L. Zhou, X. Du, and Y. Yang, "Influence of temperature on performance of all vanadium redox flow battery: analysis of ionic mass transfer," *Ionics (Kiel)*, vol. 25, no. 2, 2019

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CONCLUSIONS

The most chemically stable membranes for all-iron, all-soluble FB are N117, E98-05, DMV850, and FAP-450.

The most robust membranes under dry and wet conditions are FAA-3-30 and FAP-450.

CEMs generally are more thermally stable than AEMs but all membranes are sufficiently stable for normal FB operating temperatures.

Nafion® 117 has high ionic conductivity but was less mechanically stable than many membranes. FAP-450, given its sufficient chemical, mechanical and thermal stability, should be investigated next for its ionic conductivity and potential for iron FB operation.