Ionically crosslinked highly sulfonated polyether ether ketone membranes for iron-chromium flow batteries

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Introduction

ICFB

Upscaling potential[1]
Abundant materials for electrolyte: Fe & Cr
Low electrolyte cost: 17 USD kWh^{-1}

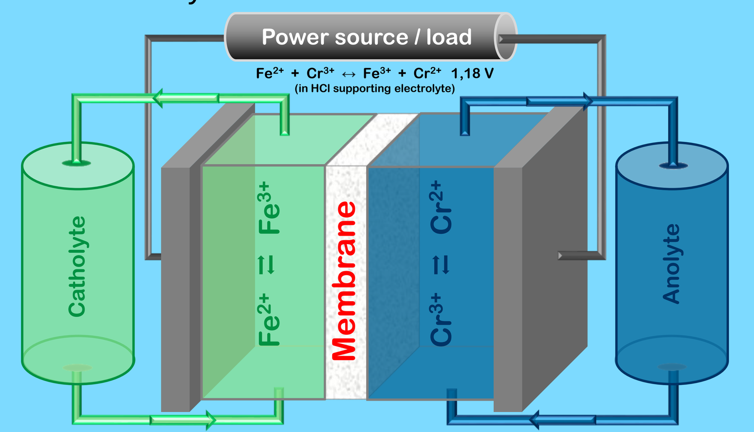


Figure 1: Schematic diagram of an ICFB.

Current challenges
PFSA membrane: Cost (≈ 500 USD m^{-2}) & regulations
Electrolyte crossover and imbalance

SPEEK membranes

PFSA alternative
Non fluorinated & stabilised by aromaticity
Rigidity: Strength + thermal/chemical stability
Lower CAPEX cost

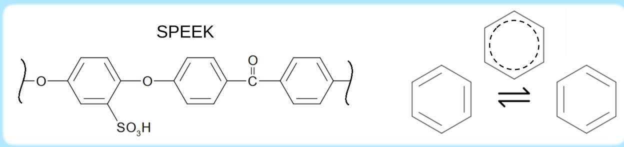


Figure 2: Molecular structure of SPEEK and aromaticity.

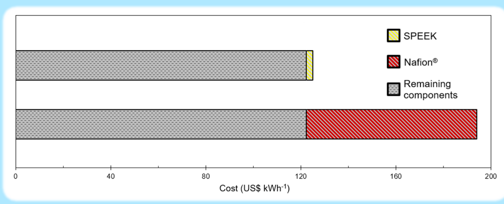


Figure 3: CAPEX cost estimation of ICFB with SPEEK/Nafion.[2]

Current challenges
Narrow H^+ channels limits thickness @ ≤25µm
DOS (57%) limitations from water solubility

Ionic crosslinking

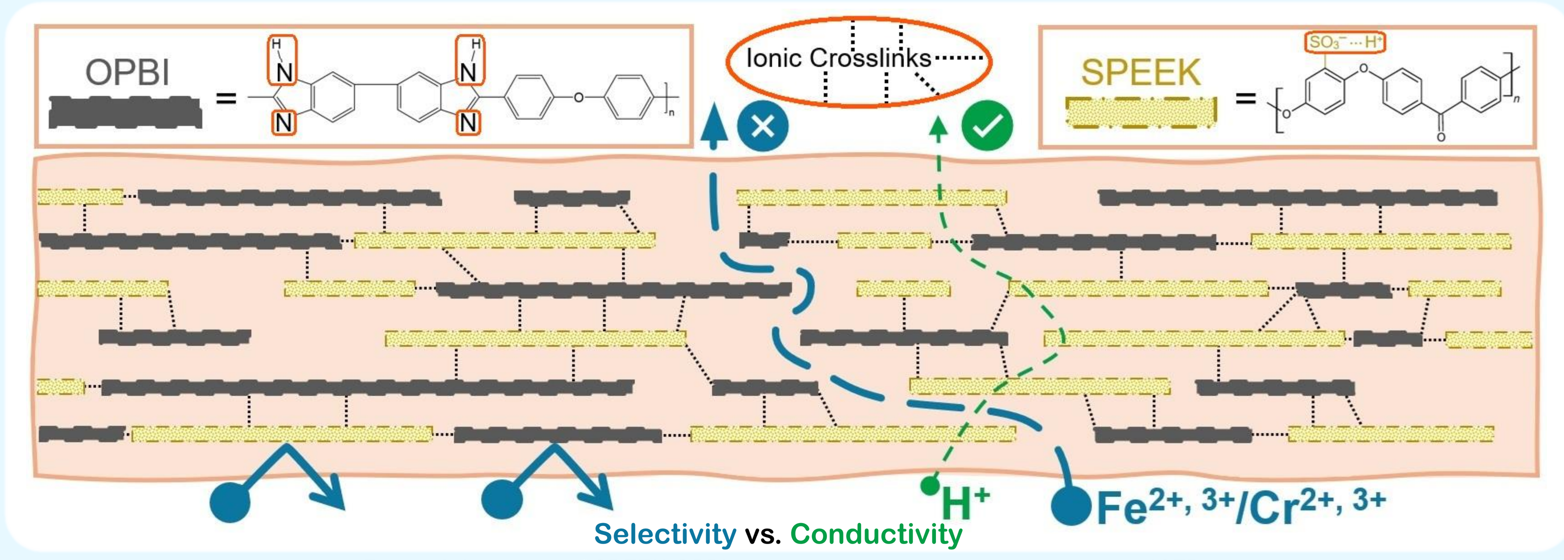
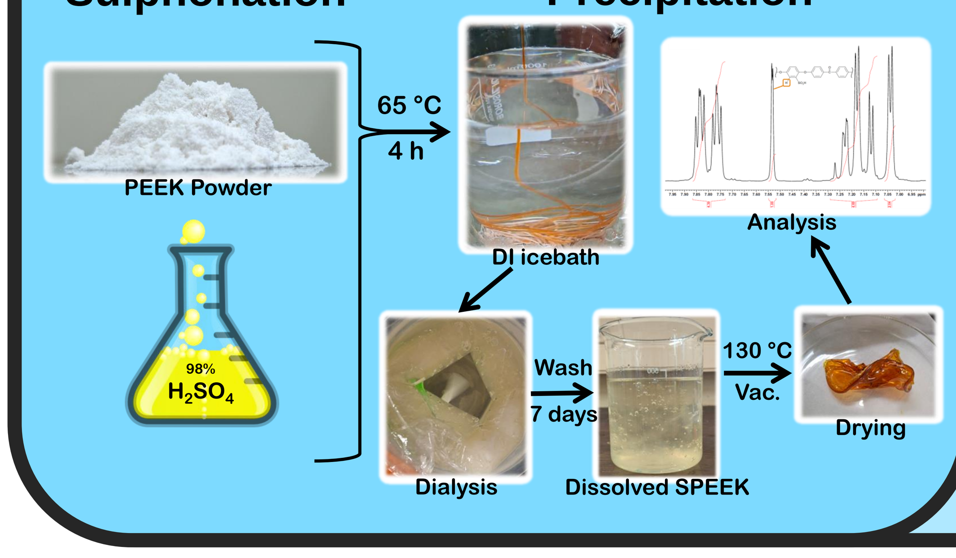


Figure 4: Illustration of SPEEK-OPBI crosslinked cation exchange membrane in ICFB.

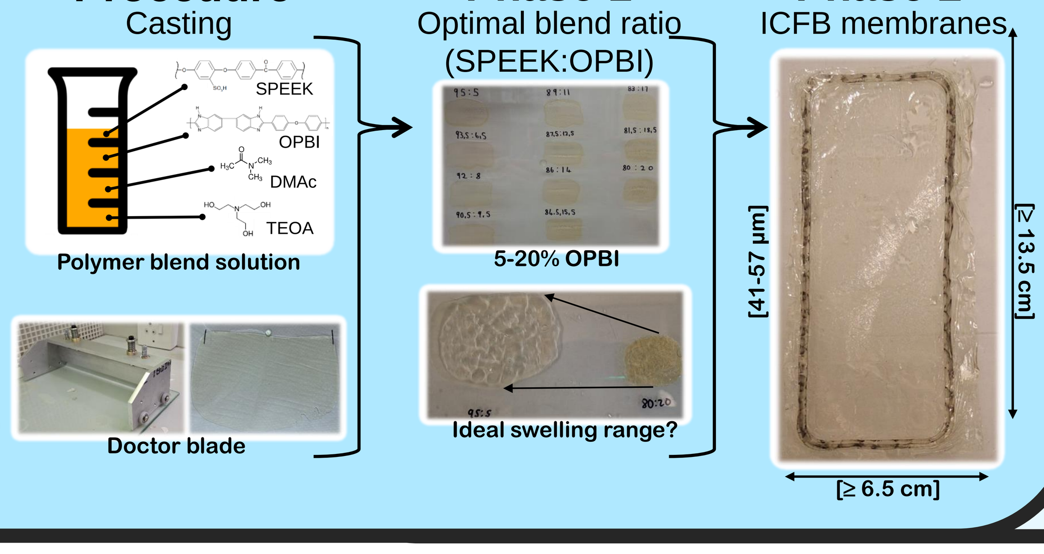
Highly sulphonated PEEK crosslinked with OPBI
Fully control selectivity & conductivity
(Thickness, IEC/DOS, dimensional stability, molecular pore size/swelling, flexibility)

Experimental

SPEEK Synthesis



Membrane casting



ICFB Tests

Performance
Electrolyte:
1,3 M Fe & Cr in 1 M HCl
100 mL @ 65 °C
Cycling up to 5 days

1. Potentiostat
2. Heating plate
3. Nitrogen supply
4. Peristaltic pump
5. Water circulator
6. Temperature probe
7. RFB cell
8. Electrolyte heaters
9. Water circulating pipes

Table 1: ICFB efficiency equations.

Parameter	Equation
Coulombic Efficiency (%)	$CE = \frac{A \times h_{(Discharge)}}{A \times h_{(Charge)}} \times 100\%$
A = current (A) and h = time of each charge or discharge cycle (h)	
Voltage Efficiency (%)	$VE = \frac{\bar{V}_{(Discharge)}}{\bar{V}_{(Charge)}} \times 100\%$
$\bar{V}$ = average voltage (V) for the charge or discharge cycle	
Energy Efficiency (%)	$EE = CE \times VE$

Figure 5: In-house built lab-scale ICFB test station.[3]

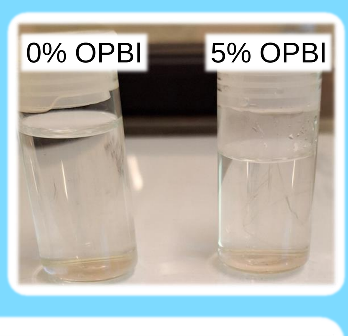
Results

Phase 1

Optimal blend ratio

Pure highly sulphonated SPEEK-95 (0% OPBI) polymer dissolves in water

Minimum crosslinker for aqueous stability = 5% OPBI



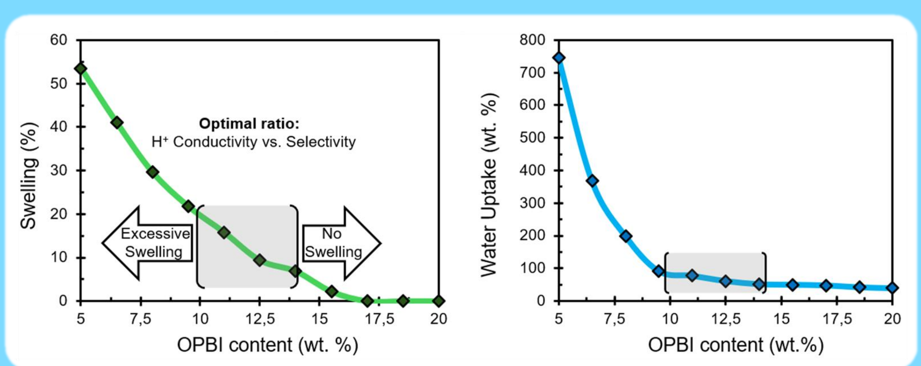


Figure 6: Dimensional swelling of different SPEEK-95:OPBI blend ratios.

Manufacturing and investigation of 11 membranes revealed that blending **10-13% OPBI** with highly sulphonated SPEEK-95 yielded suitable swelling range for aqueous systems

Phase 2

Membrane properties

Table 2: Physical and chemical properties of cation exchange membranes

Membrane	Wet thickness (µm)	Tensile strength (Mpa)	IEC (mmol g^{-1})	Water Uptake (%)	Electrolyte Imbalance (%)	Capacity decay (% h^{-1})
SPEEK-95:OPBI (90:10)	57	57	1,57	36,2	80	1,36
SPEEK-95:OPBI (89:11)	55	60	1,55	26,1	4	1,94
SPEEK-95:OPBI (88:12)	47	64	1,52	24,4	0	1,92
SPEEK-95:OPBI (87:13)	41	72	1,40	22,4	0	4,74
SPEEK-57	26	58	1,62	36,3	50	0,70
Nafion-212	58	23	0,98	14,5	35	0,42

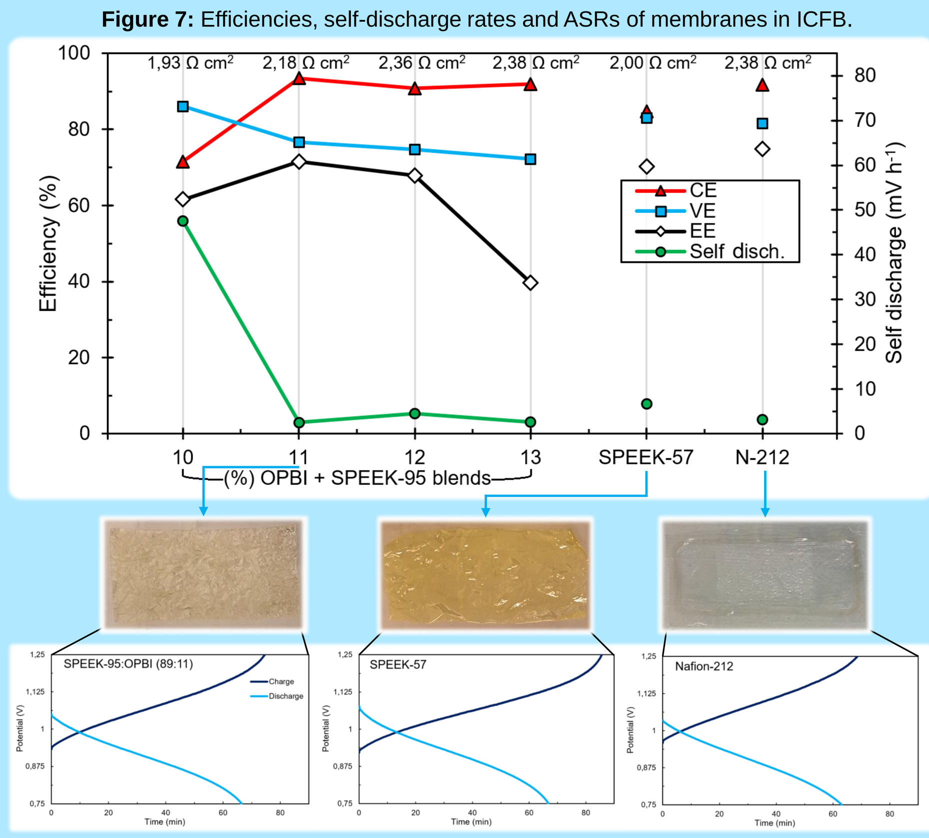
Electrolyte imbalance effectively reduced with 11-13% OPBI blends

Tensile strength of SPEEK membranes higher than PFSA

SPEEK membranes obtained significantly higher IEC than Nafion-212, while SPEEK-57 had slightly higher IEC than crosslinked membranes

Membrane efficiencies

Figure 7: Efficiencies, self-discharge rates and ASRs of membranes in ICFB.



Conclusions

Summary

Ionically crosslinked SPEEK-95:OPBI
Cost-effective, chemically stable and fluorine-free membranes synthesised and successfully applied in ICFB for 30 cycles with 100 mL electrolyte

Ideal swelling degree was found with blends of 10-13% OPBI with SPEEK-95

Performance parameters showed an optimal blend ratio of 89:11, obtaining 1.1% higher EE than SPEEK-57 & 3.3% lower than Nafion-212

Using an 89:11 blend in a lab-scale ICFB showed improved selectivity over Nafion benchmark and pure SPEEK, obtaining the highest CE (93.5%) and lowest self discharge (2.53 mV h^{-1})

Crosslinking of highly sulfonated SPEEK enhanced membrane tensile strength, while enlarging H^+ transfer channels, allowing the use of thicker membranes and effectively reducing osmotic drag and electrolyte imbalance

Challenges

Increasing ASR
Despite 100% IEC retention, operational increases in ASR of crosslinked and pure SPEEK membranes were observed

Reduced swelling during cycling caused elevated capacity decay (especially for crosslinked membranes)

Future work
Investigate swelling reduction that caused a narrowing of H^+ transfer channels, likely linked to water retention after washing

Produce a SPEEK-OPBI blend membrane that can perform long-term operation with a rebalance cell equipped ICFB

Acknowledgements

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References

[1] Y. K. Zeng, T. S. Zhao, L. An, X. L. Zhou, and L. Wei, "A comparative study of all-vanadium and iron-chromium redox flow batteries for large-scale energy storage," Journal of Power Sources, vol. 300, pp. 438-443, 2015/12/30/ 2015, doi: https://doi.org/10.1016/j.jpowsour.2015.09.100.
[2] C. Sun, Z. Huan, X.-D. Luo, and N. Chen, "A comparative study of Nafion and sulfonated poly(ether ether ketone) membrane performance for iron-chromium redox flow battery," *Ionics*, vol. 25, 23/04 2019, doi: 10.1007/s11581-019-02971-0.
[3] J. P. du Toit and H. M. Krieg, "The feasibility of microporous separators in iron-chromium flow batteries," *Journal of Energy Storage*, vol. 107, p. 115008, 30/01 2025, doi: https://doi.org/10.1016/j.est.2024.115008

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