DOE Office of Electricity Energy Storage Program
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Session 6: Flow Batteries
Presentation ID: 602

Recent Developments in Electrolytes and Membranes for Durable Redox Flow Batteries

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10/25/2023

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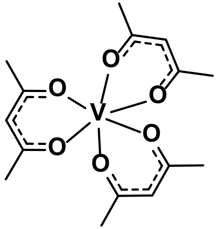
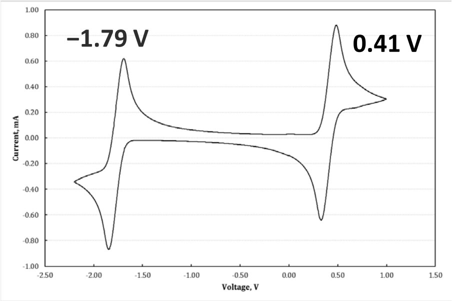
Outline

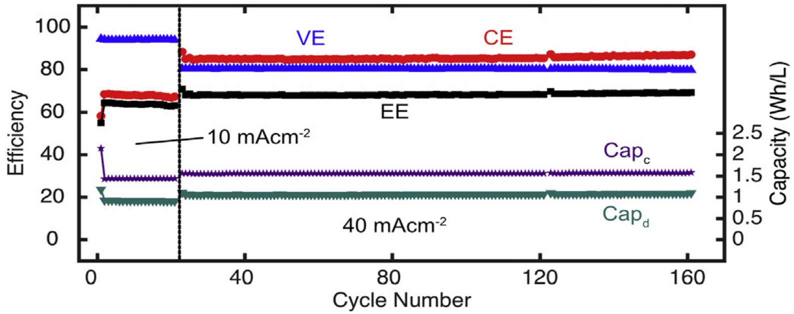
- Redox active materials development for non-aqueous redox flow batteries
  - Benzophenones derivatives
  - Degradation mechanism
  - Effect of bulky groups on flow cell performance
- Membrane development
  - Polybenzimidazole membranes as alternative to Nafion
  - Effects of additives on flow cell performance
- Conclusions

Motivation - $V(acac)_3$ as a carrier in non-aqueous RFBs





0.1 M $V(acac)_3$ / 0.5 M $TEABF_4$ / ACN



Low solubility and/or limited redox stability

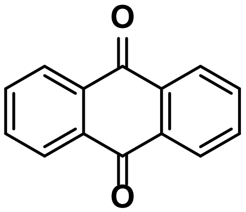
$$E_{vol} = n\, V_{cell}\, F\, C_{active}$$

- **The non-aqueous medium does not strictly limit power; non-aqueous flow cells can tolerate a current density of 100 mA cm^{-2} or higher.**
- **Stringent control of moisture and impurities is necessary to realize the full potential of redox chemistries.**
- **However, low solubility and limited redox stability still pose challenges to viability.**

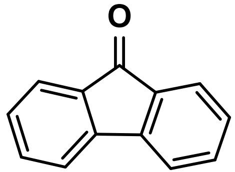
Saraidaridis, J. D.; Monroe, C. W. *J. Power Souces* **2019**, *412*, 384–390

Organic carriers in RFBs

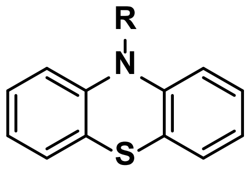
Anolyte/Negolyte



[1]Wu, M., et. al., *J. Mater. Chem. A* **2021**, *47*.
[2] Lantz, A. W., et. al., P. G. *Appl. Energy Mater.* **2019**, *2*, 7893–7902.
[3] Wu, M., et. al.,. *Batter. Supercaps* **2022**, 1–7.

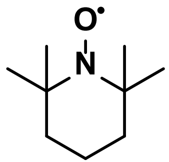


Feng, Ruozhu, et. al., *Science*. **2021**. *372,* 836-840.

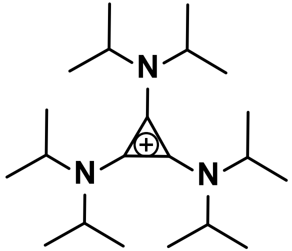


Attanayake, N. H., et. al., *Chem. Mater.* **2019**, *31* (12), 4353–4363.

Catholyte/Posolyte



Xing, X.; Huo, Y.; Wang, X.; Zhao, Y. *Int. J. Hydrogen Energy* **2017**, *42*, 17488–17494.



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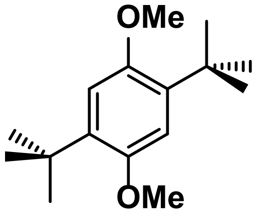
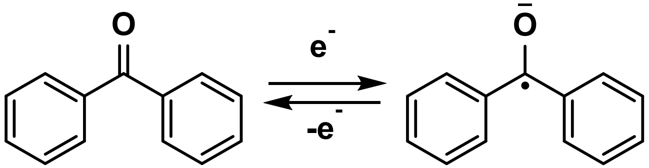
[2] Yan, Y., et. al., *J. Am. Chem. Soc.* **2019**, *141*, 15301-15306.
[3] Yan, Y., et. al., *J. Am. Chem. Soc.* **2021**



Wang, X., et. al., *Int. J. Electrochem. Sci.* **2018**, *13* (7), 6676–6683.

Benzophenone a promising candidate for negolytes



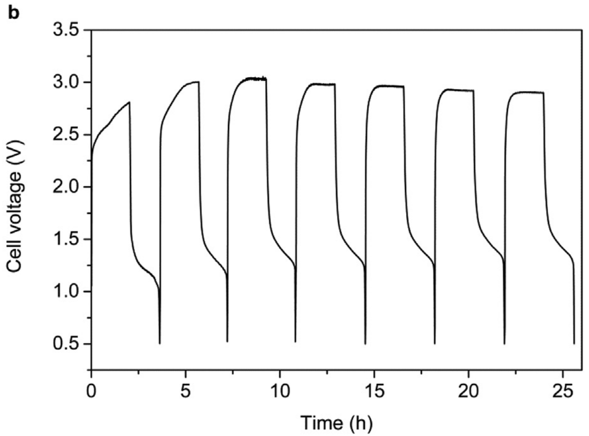
Highly soluble in MeCN (~ 4M in MeCN)

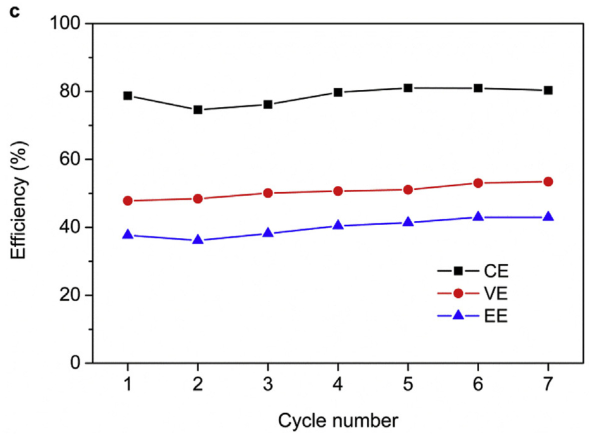
Reversible redox couple at -2.16 V vs. Ag/Ag^{+} in MeCN

Conjugated pi system allows for delocalization of spin and charge density in the radical anion

Highly modifiable on the aromatic rings

Downside: Not stable under extensive cycling





[1] Wang, X., et. al., *Int. J. Electrochem. Sci.* **2018**, *13* (7), 6676–6683.
[2] Xing, X.; Huo, Y.; Wang, X.; Zhao, Y. *Int. J. Hydrogen Energy* **2017**, *42*, 17488–17494
[3] Ouyang, J.; Na, B.; Xiong, G.; Xu, L.; Jin, T. *J. Chem. Eng. Data* **2018**, *63* (5), 1833–1840.

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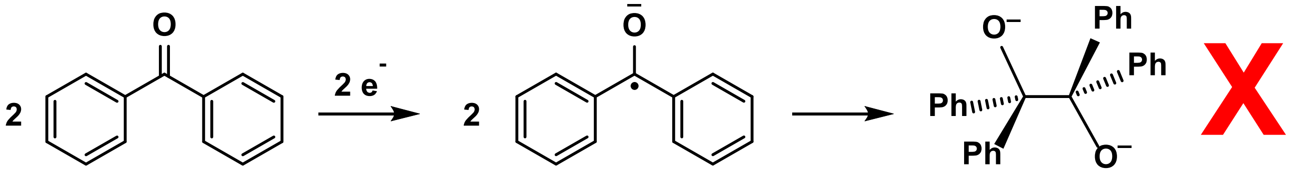
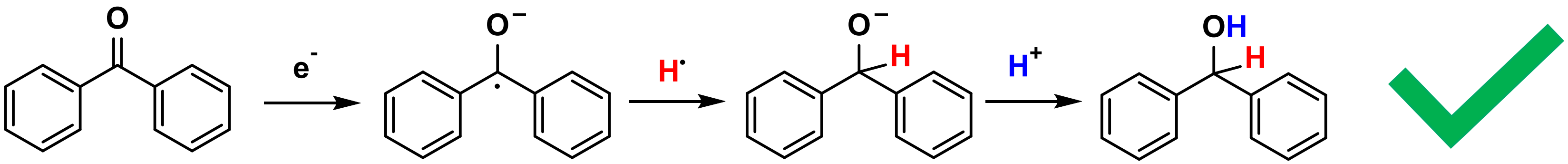
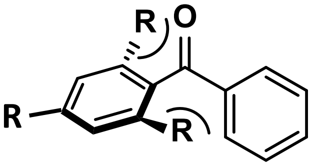
Degradation product and mechanism







R = ^{i}Pr, ^{t}Bu

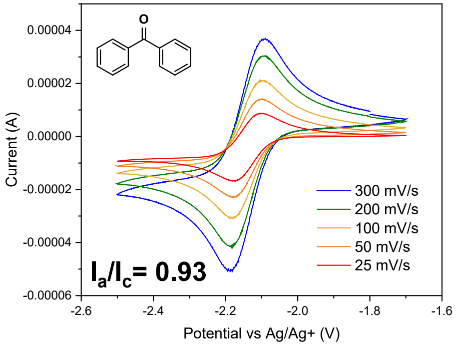
<u>Benefits of asymmetry</u>

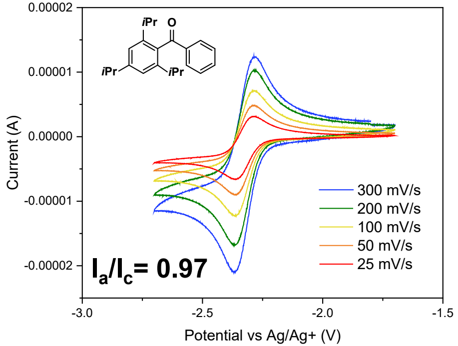
- Increased solubility over symmetric compounds
- Delocalization of charge and spin density onto phenyl ring
- Straightforward synthetic route

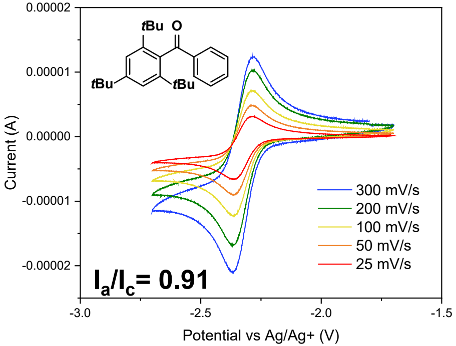
Reversibility of benzophenone derivatives

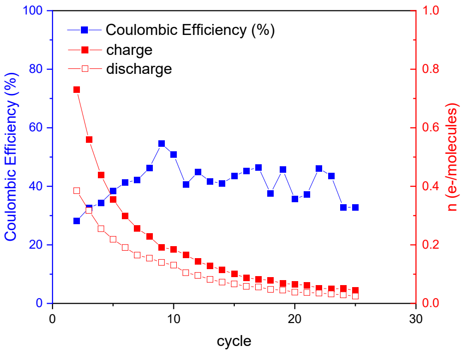
- CV and Bulk electrolysis

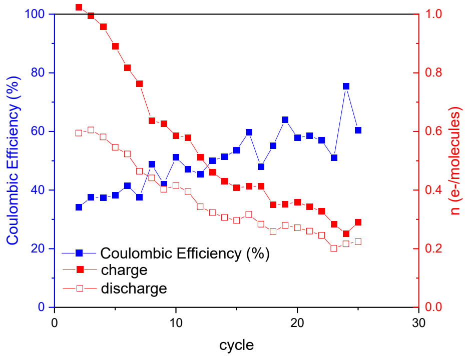
1 mM anolyte, 0.25 M, [TEA][BF_4], MeCN, 1 mA/cm^2

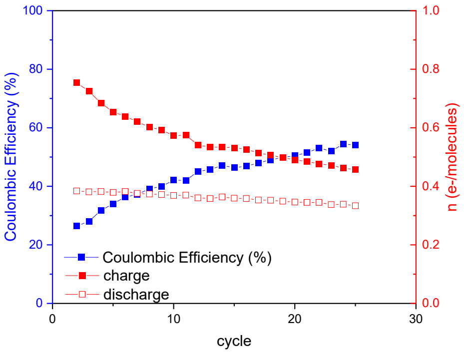






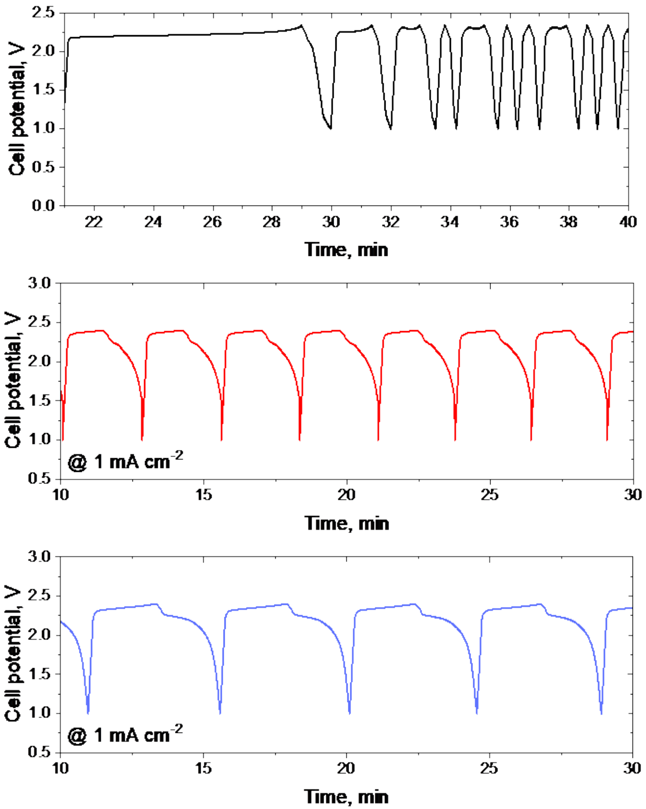


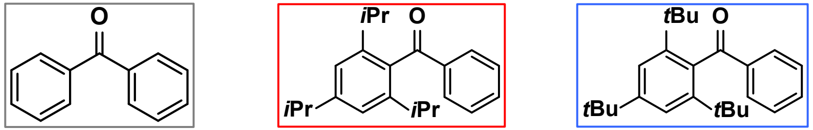




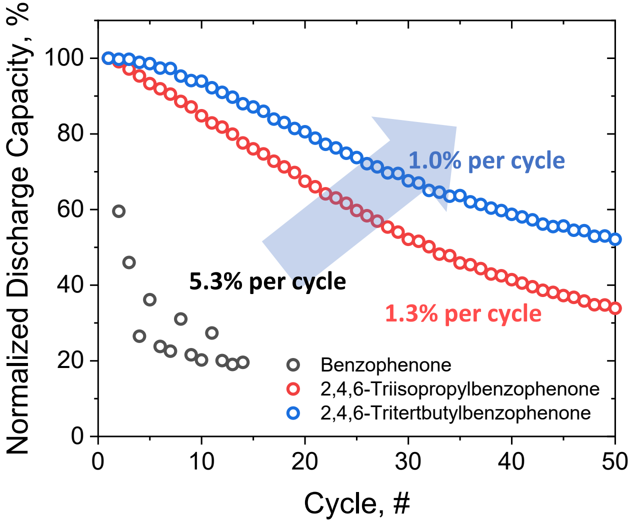
Jesse et al., In preparation (2023)

Benzophenone derivatives in a flow cell (vs Ferrocene)





10 mM   1 mM   1 mM



Future directions will look into increasing solubility and further sterically hindering protonation of the carbonyl.

Jesse et al., In preparation (2023)

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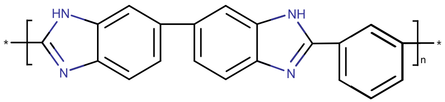
Ferrocene (2x concentration of anolyte), 0.25 M, [TEA][BF_4], MeCN,1 mA cm^{-2}, 2.40-1.00 V, Porous separator, Flow rate: 40 mL/min, Area: 10 cm^2

Membrane development for VRFBs

Polybenzimidazole membranes as alternative to Nafion

Effects of various additives on flow cell performance

Membrane fabrication, additives and VRFB conditions



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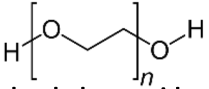
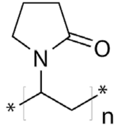
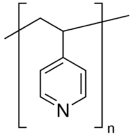
Common Membrane additives



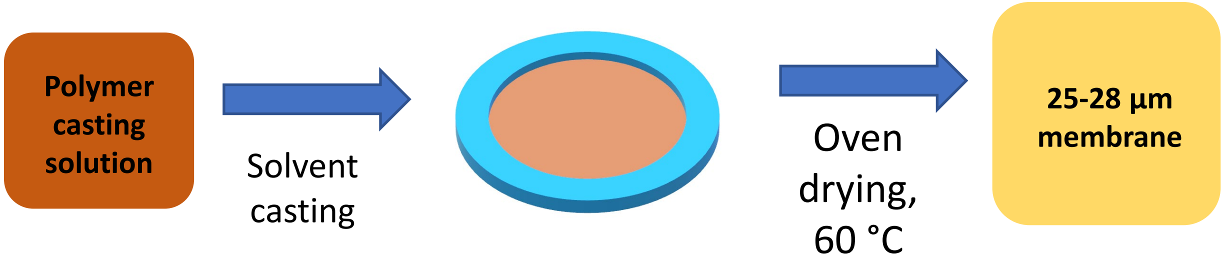
Polyethylene oxide



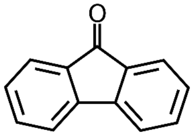
Polyvinylpyrrolidone



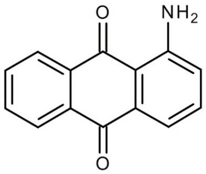
Polyvinylpyridine



Selected additives based on commonly used carriers in Aqueous organic flow batteries



Fluorenone



1-aminoanthraquinone

Flow Cell Test conditions:
Electrolyte:1 M $VOSO_4$ + 2.5 M H_2SO_4
(25 cm^2, No flow field, 60 mL electrolyte each side, 40 mL/min, activated graphite felt)
Current density range: 40 – 200 mA cm^{-2}
Cut-off voltage: 0.8 – 1.8 V
EIS: 100 MHz – 0.1 Hz, 100mV amplitude @50% SOC

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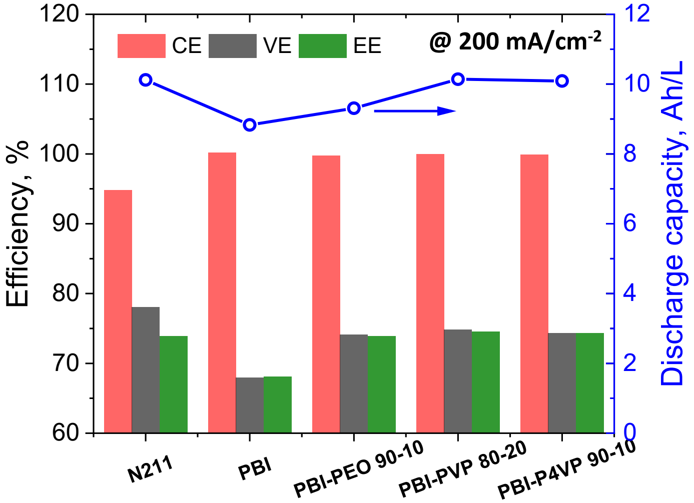
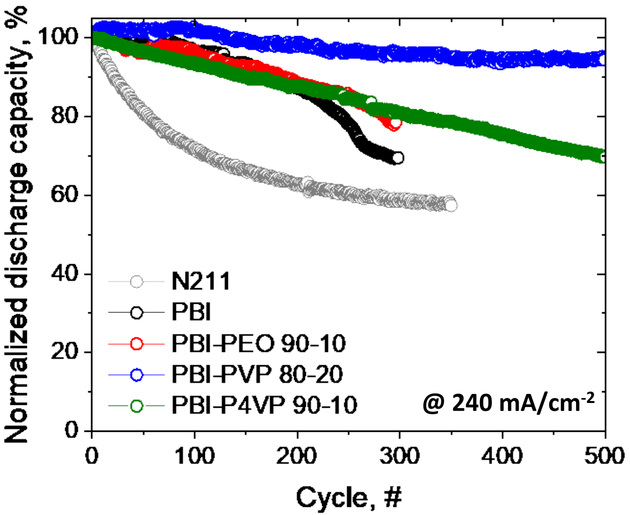
Superiority of PBI composite membranes in VRFBs





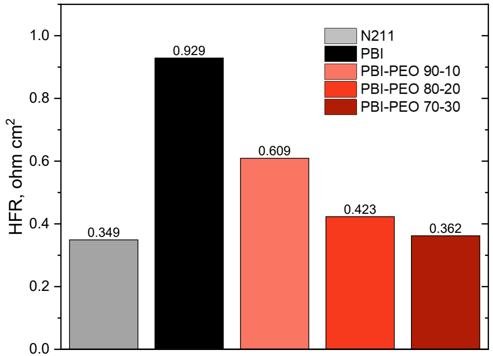
	Resistance Ohm-cm²	Capacity decay % per cycle
N211	**0.35**	**0.13**
PBI	0.929	0.10
PBI-PEO 90 -10	0.609	0.07
PBI-PVP 80-20	**0.653**	**0.011**
PBI-P4VP 90-10	0.622	0.06

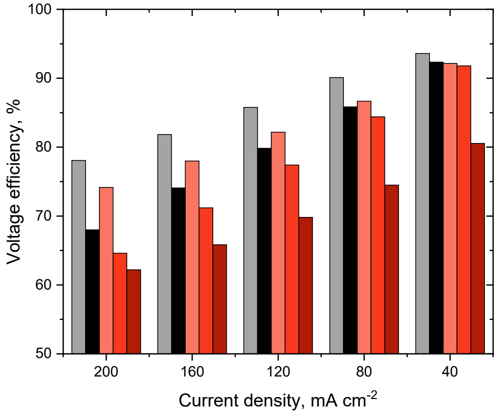
- PBI composite membrane (PBI-PVP 80-20) exhibits slowest capacity decay during 500 cycles.
- No significant water imbalance is observed in PBI membranes.

Diaz-Abad et al., In preparation (2023)

Simulating the effect of membrane additives

❖ **How additives affect the voltage efficiency?**

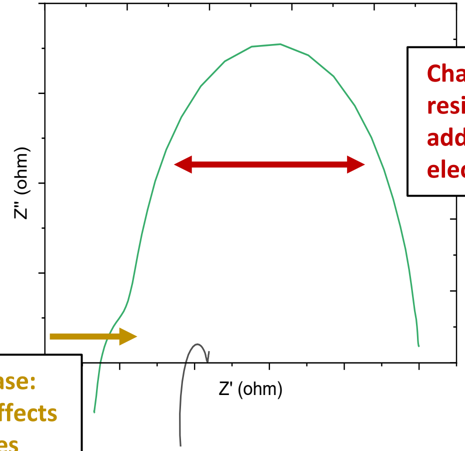




The VRFB cell with PBI-PEO 80-20 has lower voltage efficiency than 90-10 even when HFR is 30% less.

VRFB with Nafion N211 membrane → **Performance EIS** → Additive (20 mg) added to the posolyte and Negolyte → **Performance EIS**

Nafion was used to confirm that all contributions are from additives

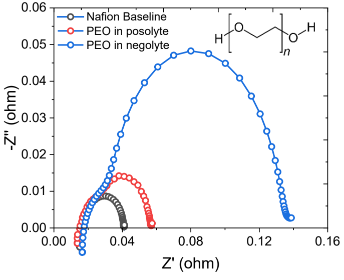


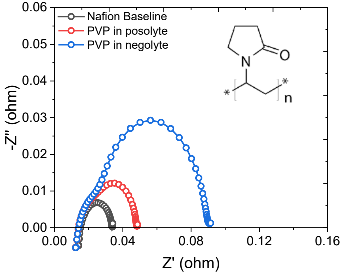
Charge transfer resistance increase: additive affects the electrodes

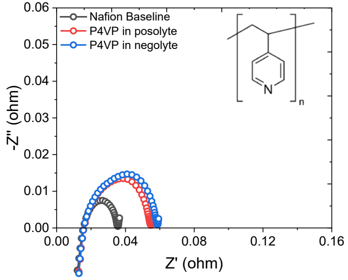
HFR increase: additive affects membranes

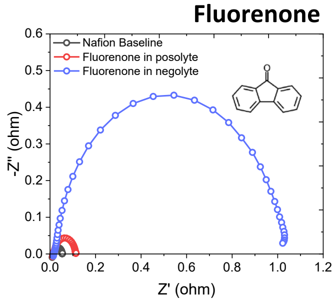
Diaz-Abad et al., In preparation (2023)

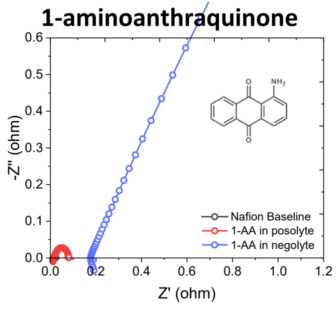
Effect of additives on electrode kinetics and VE

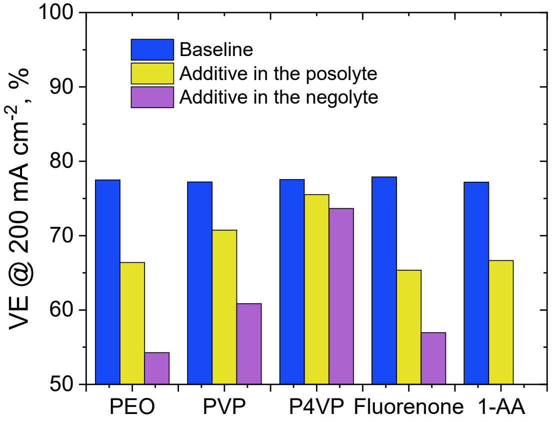












Significance

- Several redox molecules in aqueous organic flow batteries can influence electrode kinetics upon adsorption onto the electrode surface (examples are fluorenone and 1-aminoanthraquinone).

Limitation

- While this study was conducted in an acidic environment, we did not specifically investigate the effects of additives in an alkaline/Neutral medium. Nonetheless, additives may still impact kinetics even in alkaline or neutral media.

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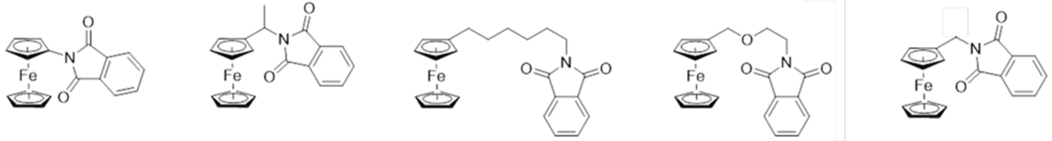
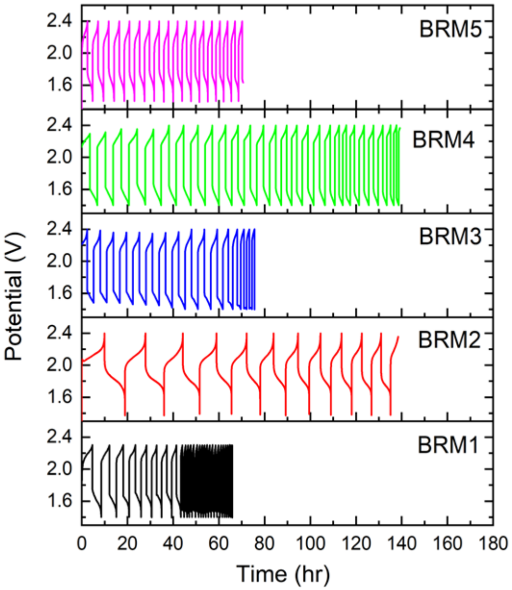
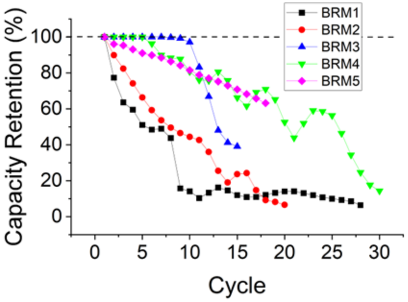
Diaz-Abad et al., In preparation (2023)

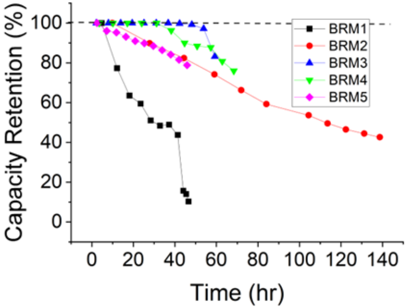
Sandia Bipolar Redox-Active Molecules (BRMs)—Flow Battery

BRM1 BRM2 BRM3 BRM4 BRM5









- A series of BRMs were synthesized with varying spacer groups.
- Flowing cell tests were conducted to assess BRM performance.
- BRM2 with α-methyl spacer showed the highest initial capacity and BRM3 with hexyl spacer had the best longevity.

Conclusions

- The degradation product and mechanism for Benzophenone were identified, and bulky groups were introduced to increase the electrochemical stability of Benzophenone derivatives.

- PBI membranes are a promising alternative to Nafion membranes, and their HFR/conductivity can be easily tailored.

- The interaction of membrane additives / redox-active organic molecules with electrodes can impact electrode kinetics and add additional resistance to charge transport processes.

Publication List

- Sandip Maurya, Sergio Diaz Abad, Eun Joo Park, Kannan Ramaiyan, Yu Seung Kim, Benjamin L Davis, Rangachary Mukundan, Phosphoric acid pre-treatment to tailor polybenzimidazole membranes for vanadium redox flow batteries, ***Journal of Membrane Science* 668 (2023) 121233**.
- Kate A. Jesse, Sergio Diaz Abad, Chad Studvick, Gabriel A. Andrade, Sandip Maurya, Brian L. Scott, Rangachary Mukundan, Ivan A. Popov, and Benjamin L. Davis, Impact of Pendent Ammonium Groups on Solubility and Cycling Charge Carrier Performance in Nonaqueous Redox Flow Batteries, ***Inorganic Chemistry*, Accepted (2023)**.
- Stracensky, Thomas, Rangachary Mukundan, Sandip Maurya, Sanjeev Mukerjee, Relating solvent parameters to electrochemical properties to predict the electrochemical performance of Vanadium acetylacetonate for non-aqueous redox flow batteries, **In communication (2023), *Journal of Electrochemical Society***.
- Sergio Diaz-Abad, Benjamin L Davis, Rangachary Mukundan, and Sandip Maurya, Effects of various additives on the electrode performance in all vanadium redox flow batteries, **To be submitted (2023)**.

Acknowledgements

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- Dr Kate Ashley Jesse and Dr. Adolfo Romo Barros : LANL post docs
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- Cy Fujimoto for membrane related discussions