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Influence of Linker Group on Bipolar Redox-Active Molecule (BRM) Performance in Non-Aqueous Flow Batteries

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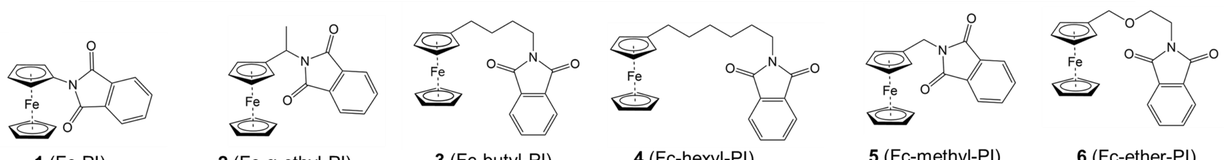
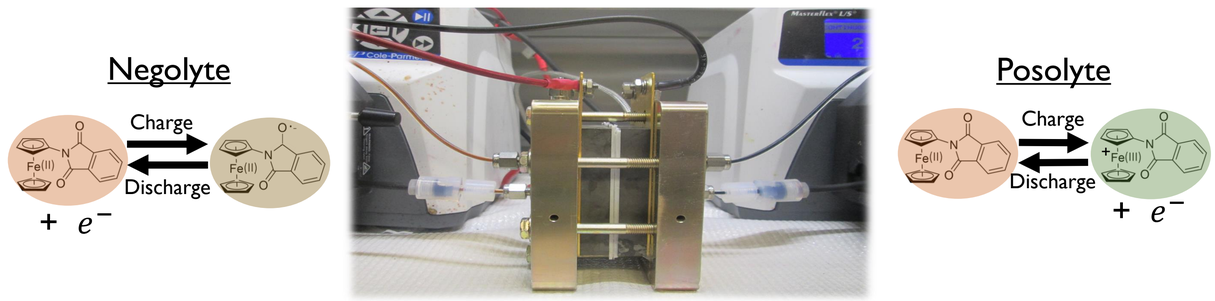
Abstract

Previous work has shown ferrocenylphthalimide (FcPI) to perform well in symmetric redox flow cells. FcPI is considered to be a bipolar redox-active molecule (BRM) because it contains both a reduction- and oxidation-capable moiety covalently bound together. The two species can be connected directly or via some linker group. This study focuses on the effect of the linker group on battery performance. Five derivatives of FcPI (BRM1) were synthesized with linkers of varying chain length and functional groups. The total six BRMs were studied electrochemically via charge/discharge cycling in symmetric flow cells and cyclic voltammetry before and after cycling.

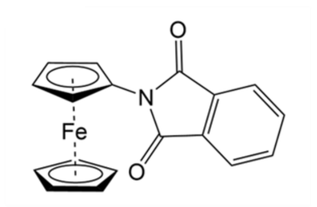
Molecules and Methods



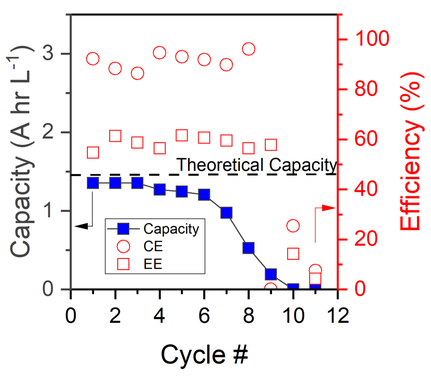


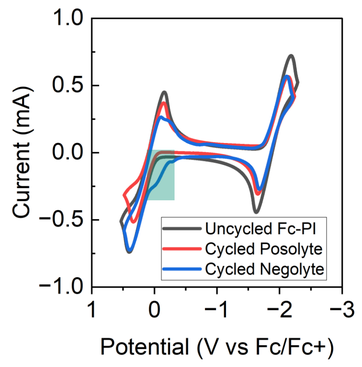
Flow batteries built using: 2.5 cm nominal thickness carbon felt plasma treated on each side, Teflon gaskets and copper current collectors, Nafion 117 (pretreated w/ TBA-OH) membrane, serpentine graphite flow cells, 5 cm^2 active area, and peristaltic pumps with Norprene tubing and polypropylene reservoirs. Galvanic cycling performed with Solartron 1287 potentiostat.

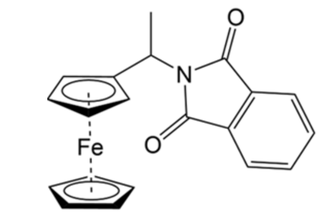
Flow Battery Performance



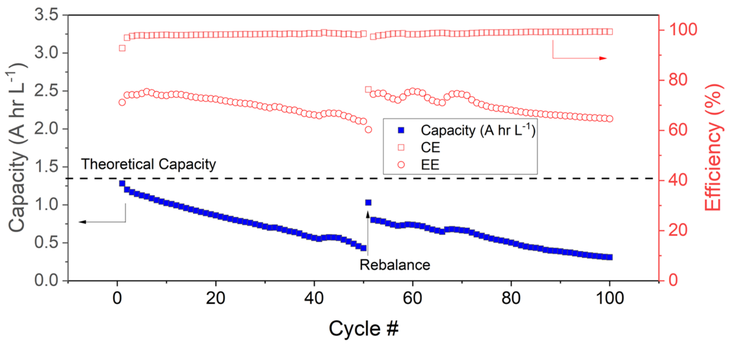
- Rapid failure
- Molecular degradation of the negolyte

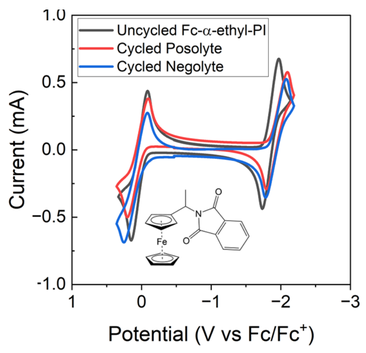


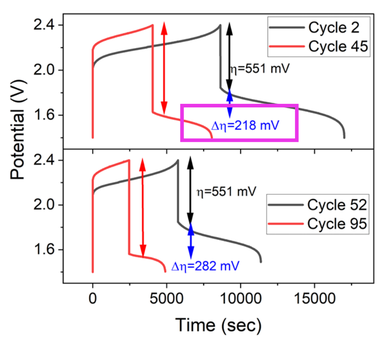


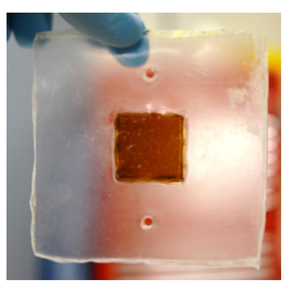


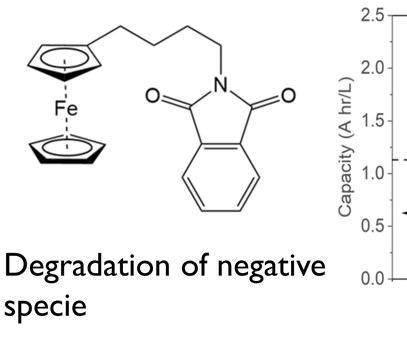
- Increased resistance & active material loss due to membrane fouling

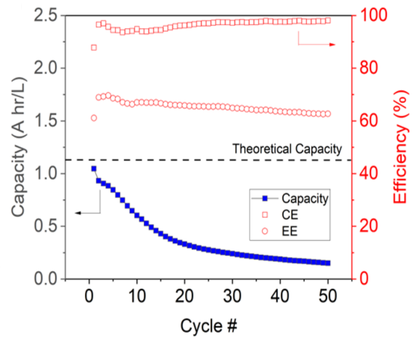


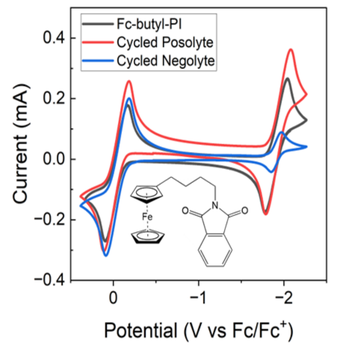






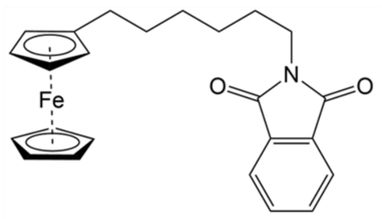




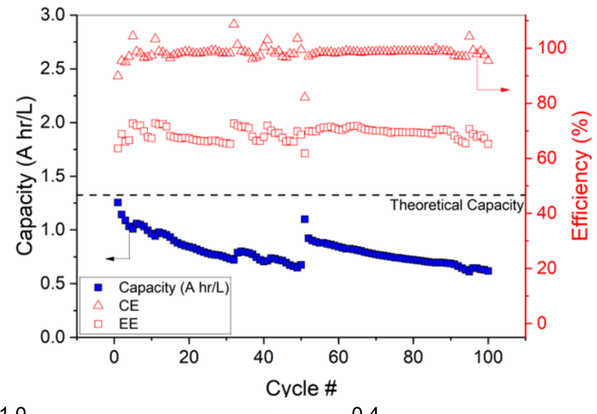


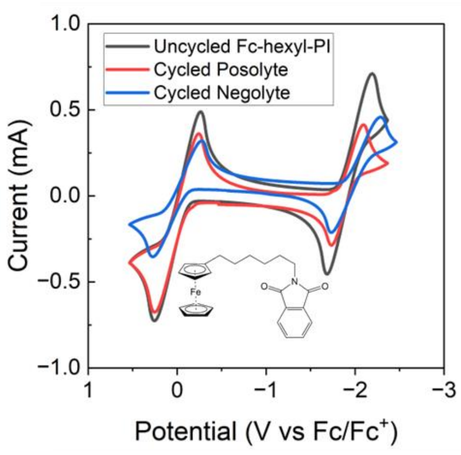
- Degradation of negative specie

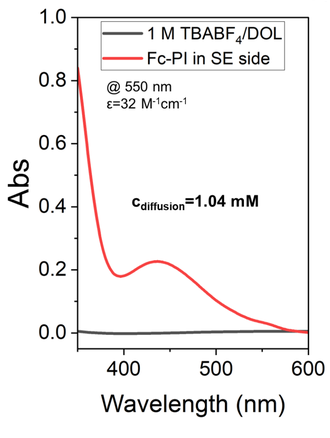
Optimized BRM

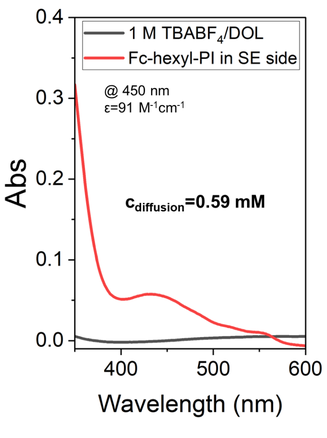


- Long linker allows:
  - Increased stability
  - Less crossover

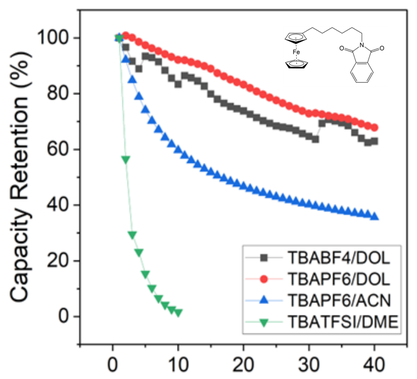


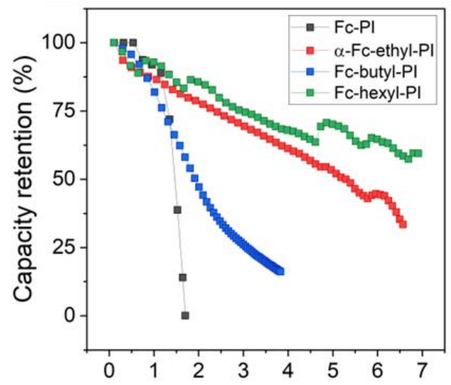




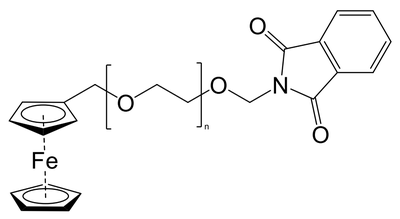


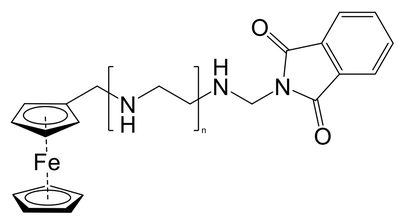
Conclusions and Future Work





- The linker group plays a key role in flow battery performance in terms of both capacity and stability.
- The direct linkage of ferrocene and phthalimide (BRM1) is highly unstable due to degradation of the negolyte during charging, likely due to radical reaction(s).
- As the chain length of the linker increases, the stability increases, due to adequate charge separation of the two moieties.
- Introduction of the α-methyl ethyl group as a linker dramatically increases the capacity of the cell with moderate capacity losses over time. It is hypothesized that this group limits molecular rotation and introduces asymmetry, leading to an optimal conformation for oxidation/reduction at the electrode surface.





- Water soluble BRM derivatives are being investigated by introduction of polar groups to the linker.
- These aqueous BRMs will allow for increased current loading (greater conductivity of water) and potentially increased working solubilities.

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[1] Seunghae, H., Kim, H., Ryu, J., Oh, S., (2018). N-ferrocenylphthalimide; A single redox couple formed by attaching a ferrocene moiety to phthalimide for non-aqueous flow batterires. J of Power Sources 395, 60-65.
[2] Seunghae, H., Kim, H., Ryu, J., Oh, S., (2019). N-(α-ferrocenyl)ethylphthalimide as a single redox couple for non-aqueous flow batteries. J. Power Sources 421, 1-5.

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