

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

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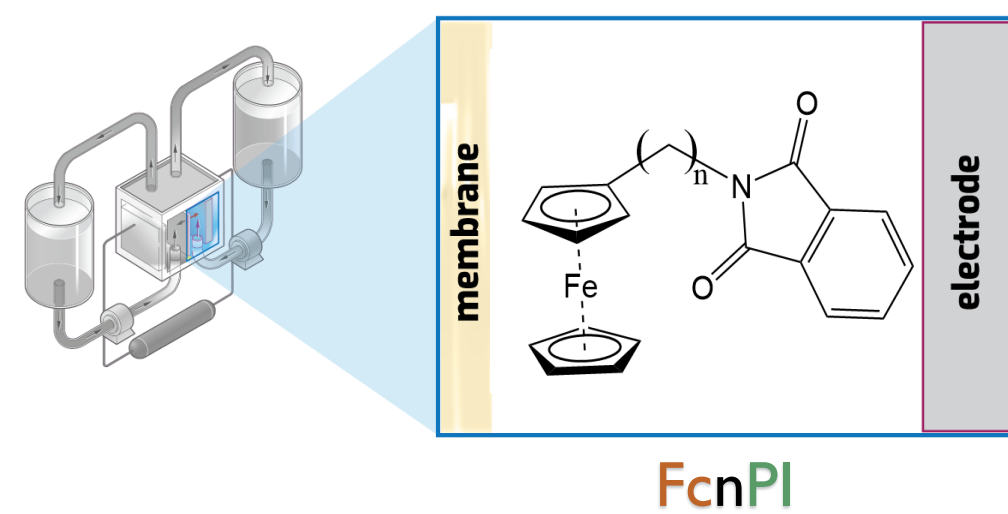
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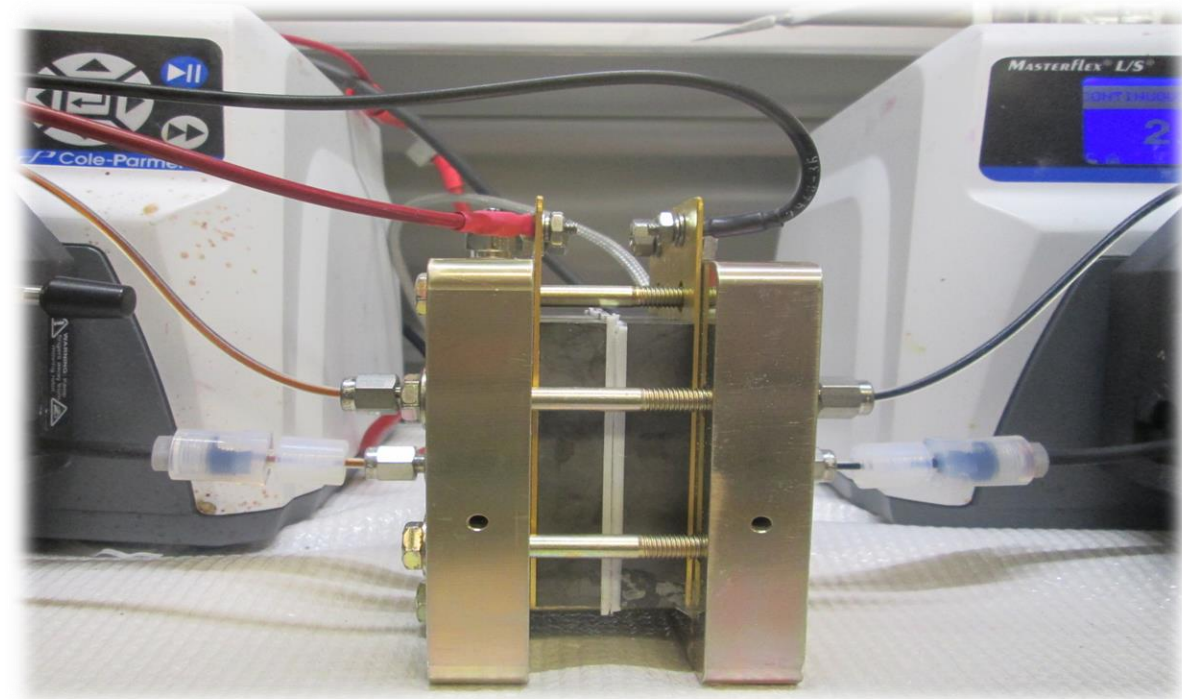
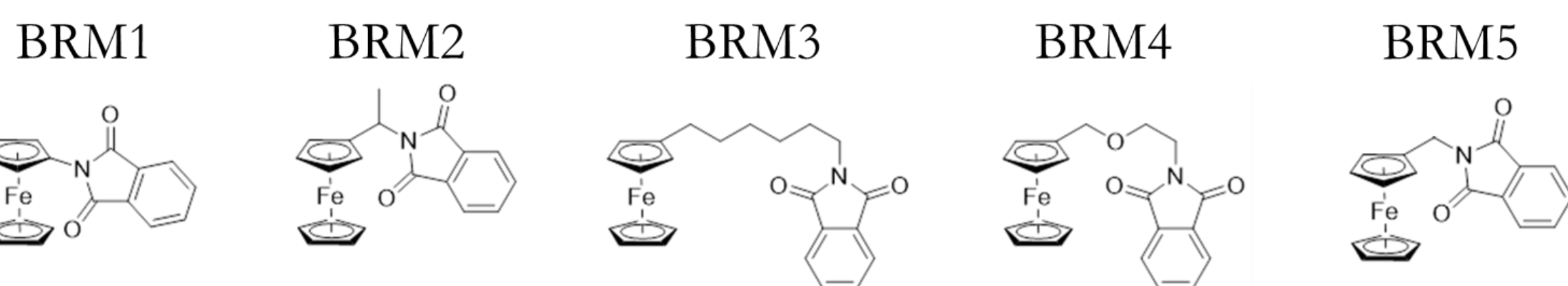
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Scope

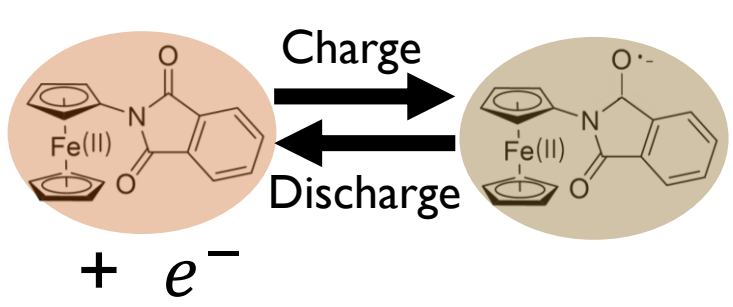
Previous work has shown ferrocenylphthalimide (FcPI) to perform well in symmetric redox flow cells. FcPI is considered to be a bipolar redox-active molecule (BRM) because it contains both a reduction- and oxidation-capable moiety covalently bound together. The two species can be connected directly or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



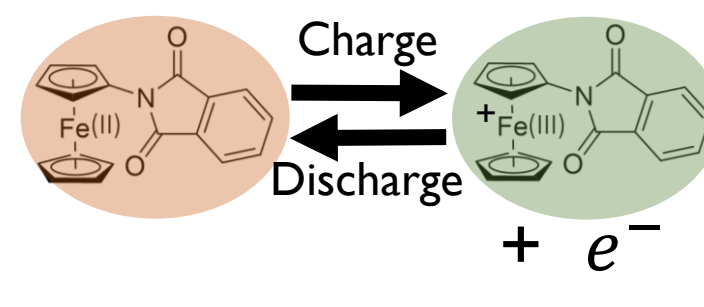
Molecules and Methods



Negolyte

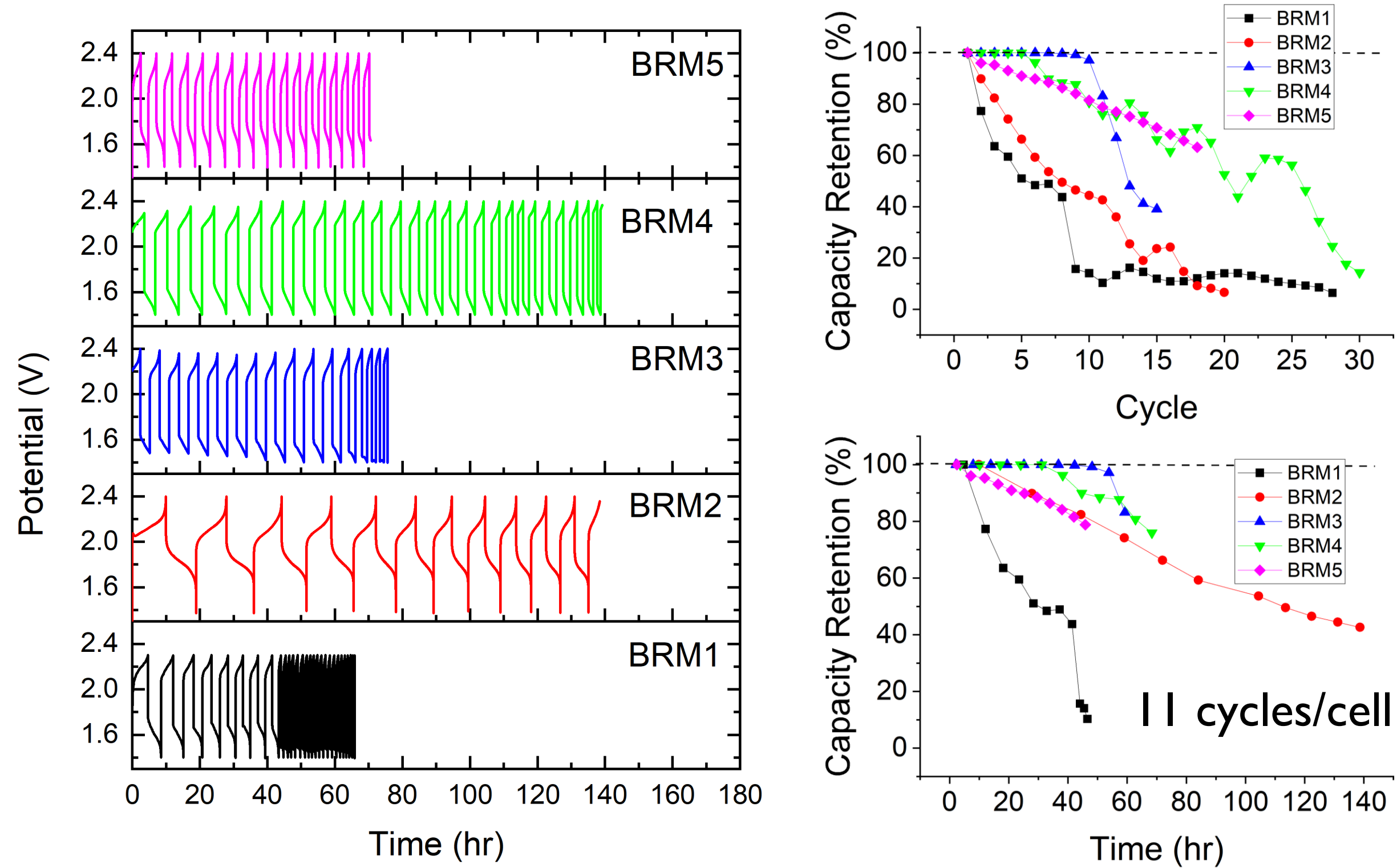


Posolyte

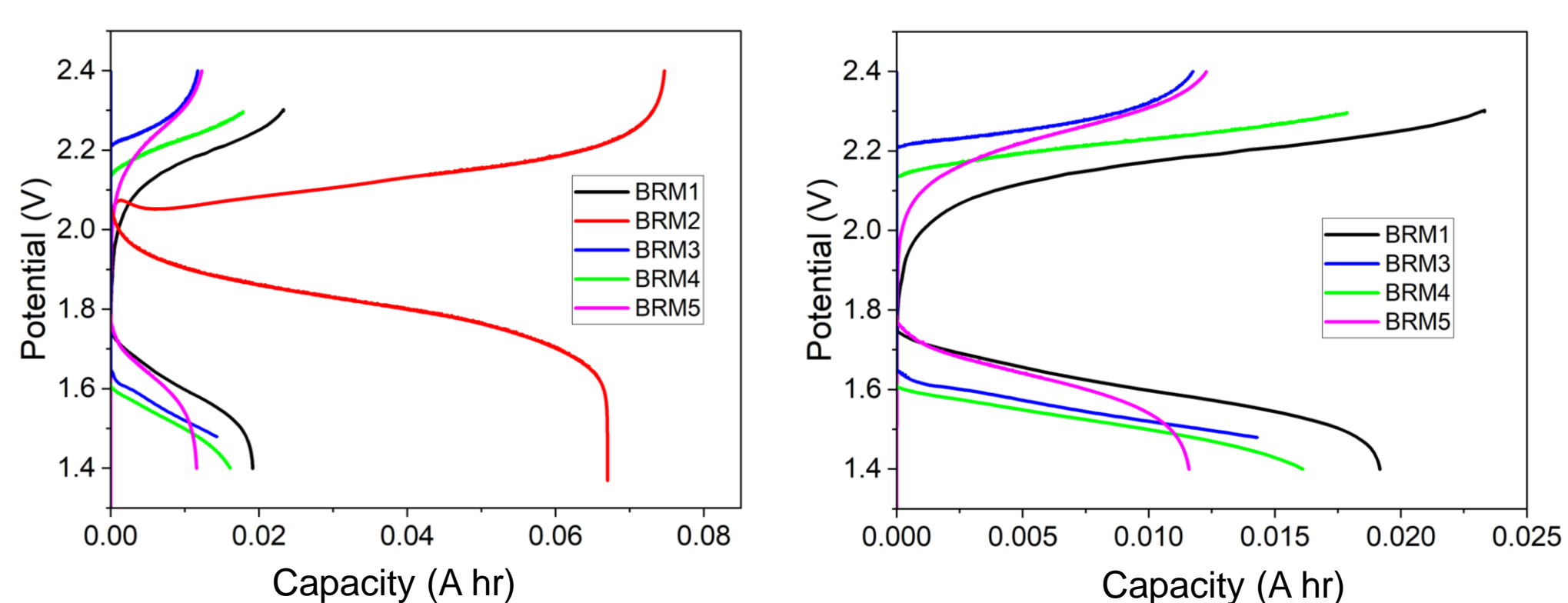


Flow batteries built using: 2.5 cm nominal thickness carbon felt plasma treated on each side, Teflon gaskets and copper current collectors, Nafion 117 (pretreated w/ TBA-OH) membrane, serpentine graphite flow cells, 5 cm² active area, and peristaltic pumps with Noreprene tubing and polypropylene reservoirs. Galvanic cycling performed with Solartron 1287 potentiostat.

Flow Cell Cycling

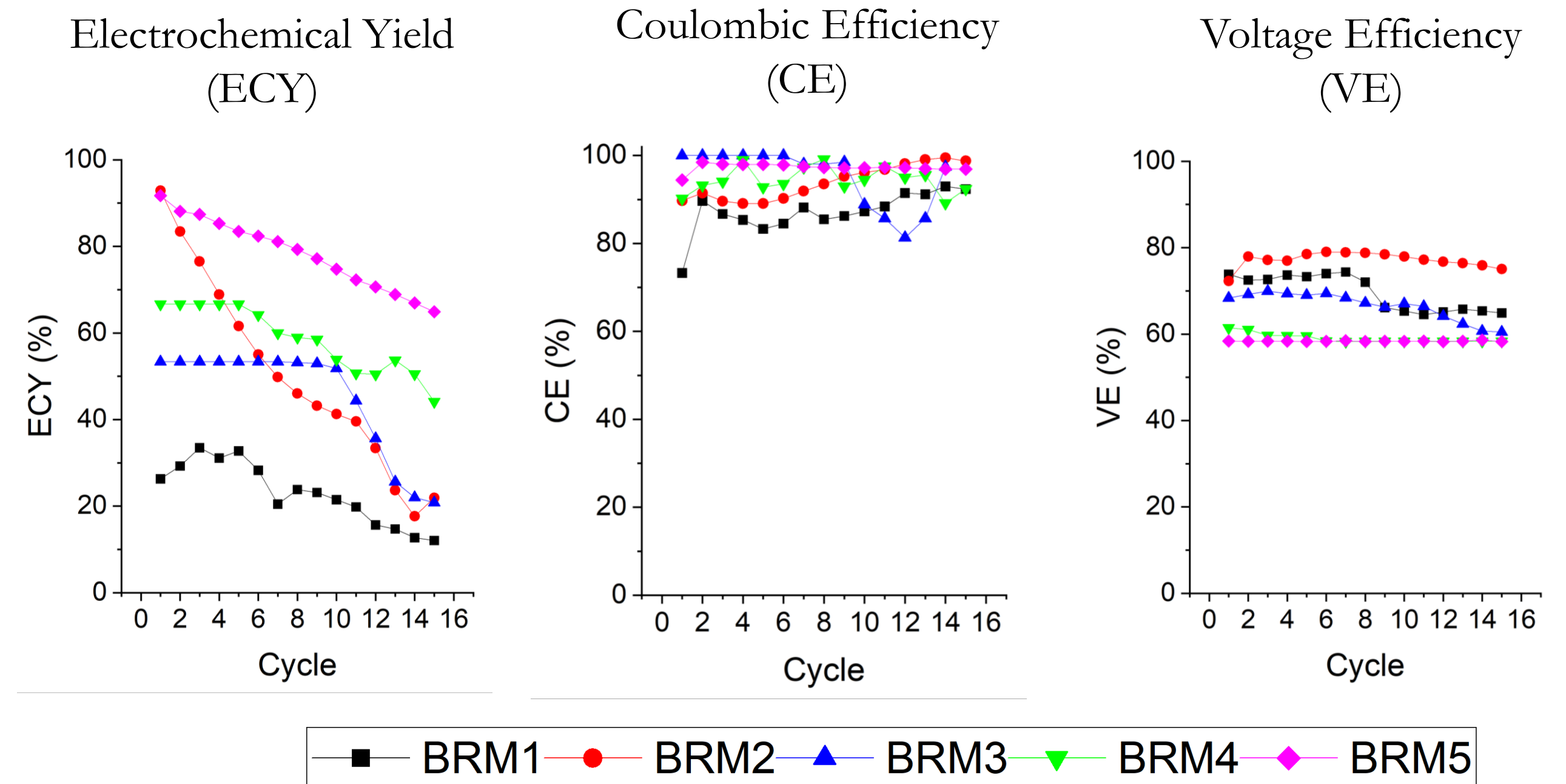


All BRM concentrations are 0.1 M with the exception of BRM5 which is 0.05 M, due to solubility constraints.

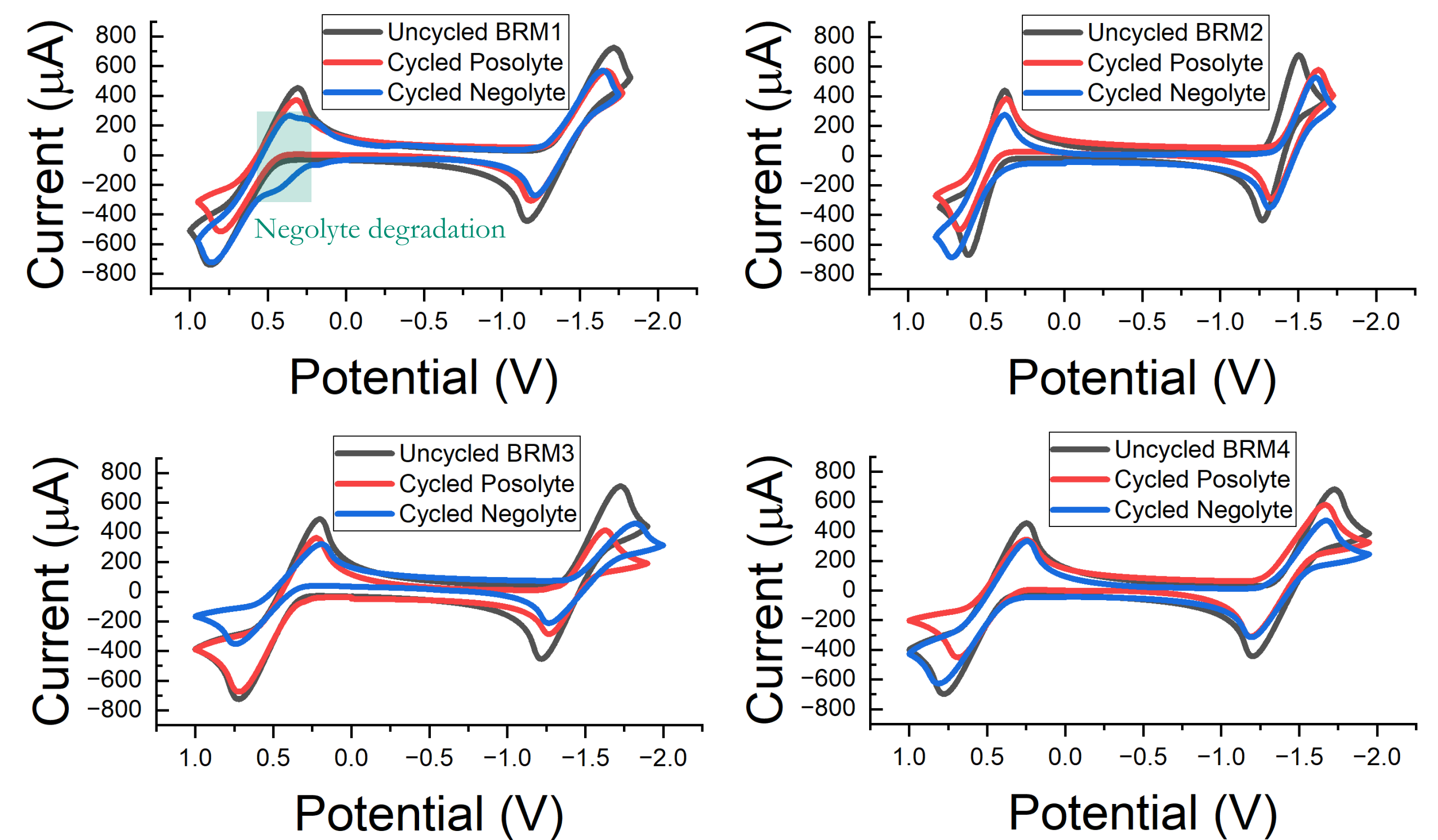


First charge and discharge cycle for BRMs with the right graph showing a zoomed-in plot of BRM1, BRM3, BRM4, and BRM5 for clarity.

Battery Efficiency



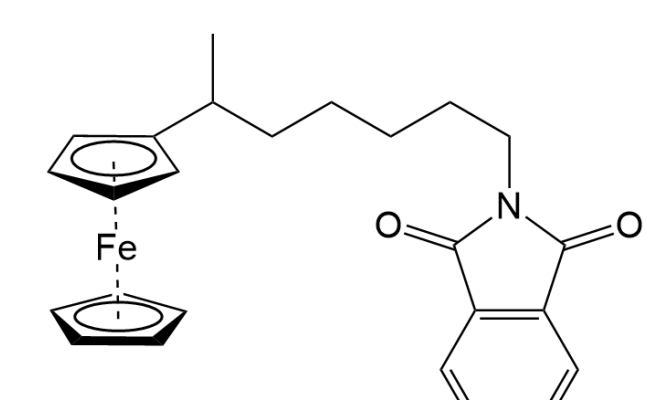
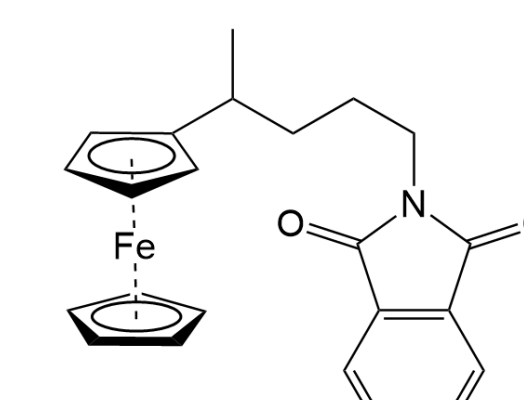
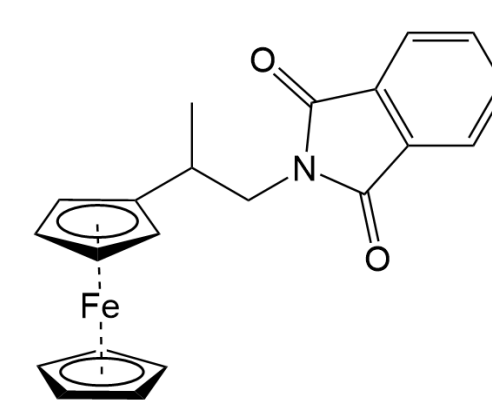
Cyclic Voltammetry



Cyclic voltammetry was performed using a BASi Epsilon potentiostat with Ag/Ag⁺ reference electrode and Pt counter electrode.

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.



The α -methyl group between the ferrocenyl and the phthalimide moieties in BRM2 is believed to provide optimal molecular conformation during battery operation, owing to its high initial capacity. Conversely, the long alkyl chain length of BRM3 provides superior stability while sacrificing some capacity. In the future we will synthesize an array of extended chain length α -methyl-substituted linker BRMs as shown above. In this way, we will be able to optimize both capacity and stability. Experiments are also ongoing to better understand the degradation pathway and products of BRM1 as well as how BRM solubility changes with varying linker group.