



Investigation of Iron-and Organic-based Bipolar Redox Molecules for Non-aqueous Flow Batteries

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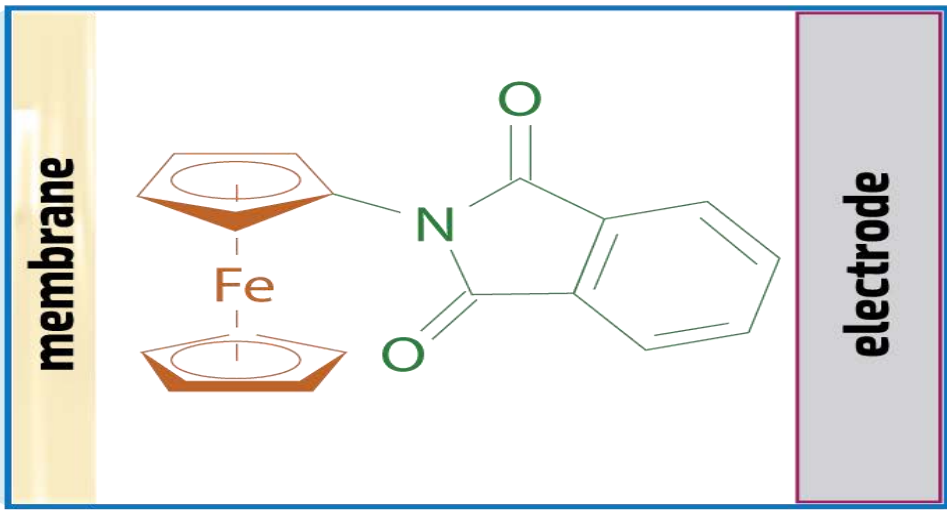
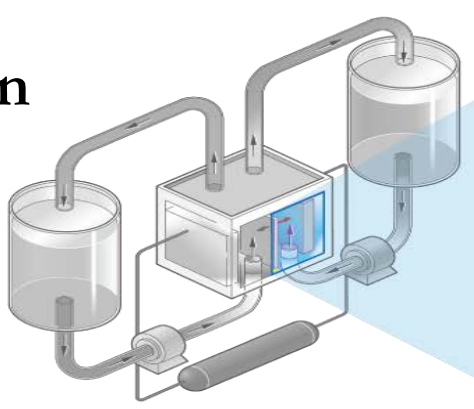
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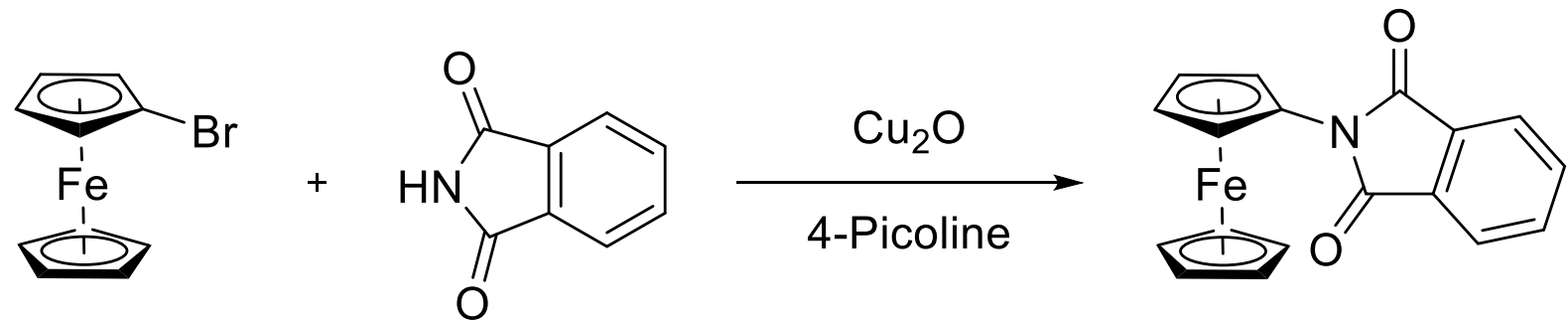
Scope of Project

Previous work has shown ferrocenylphthalimide (FcPI) to perform well in charge/discharge cycling using static H cells. However, in this work, FcPI is used as a single redox couple to further investigate its performance by employing it in a flow cell battery. This poster displays the results from various conditions of flow battery testing in an attempt to optimize or discredit its ability to perform under flow conditions. The variables tested are as follows:

- Electrolyte choice and concentration
- Membrane/separator selection
- Active species concentration
- Pump speed

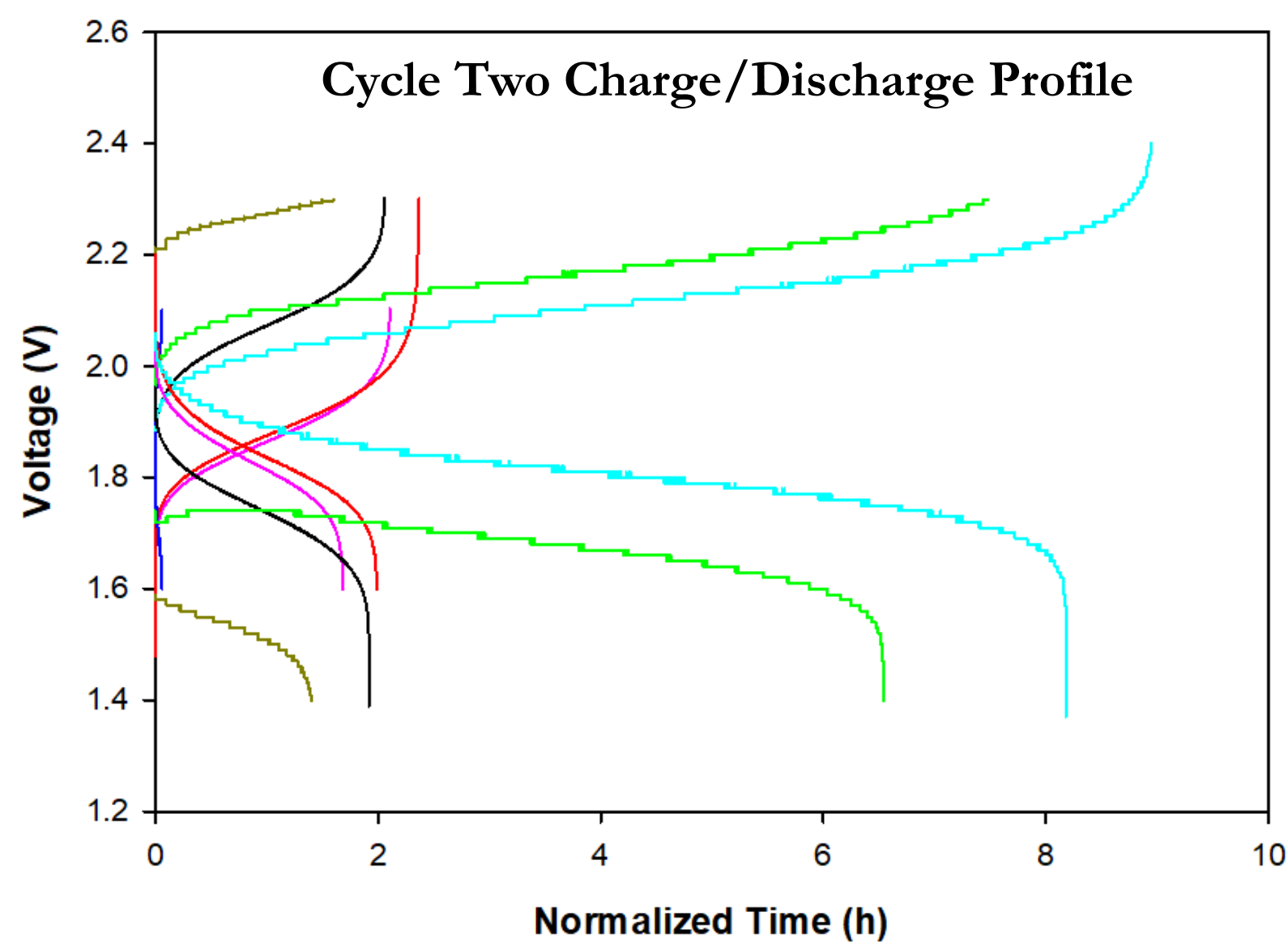
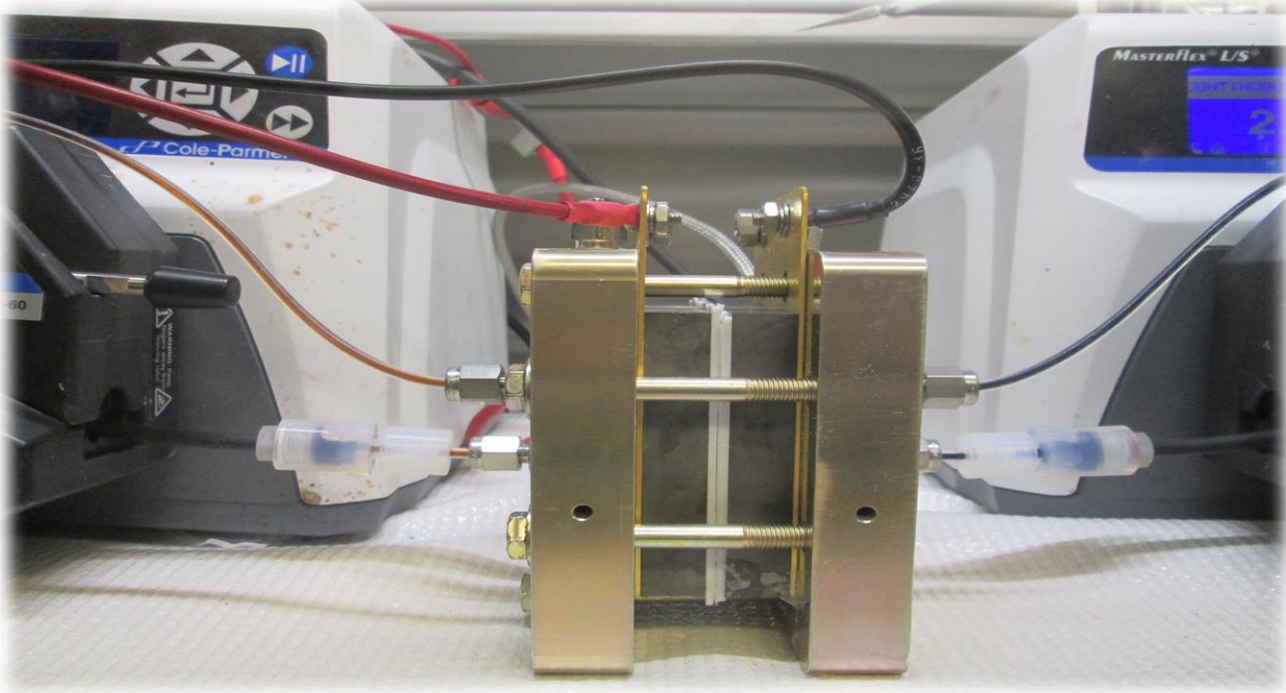
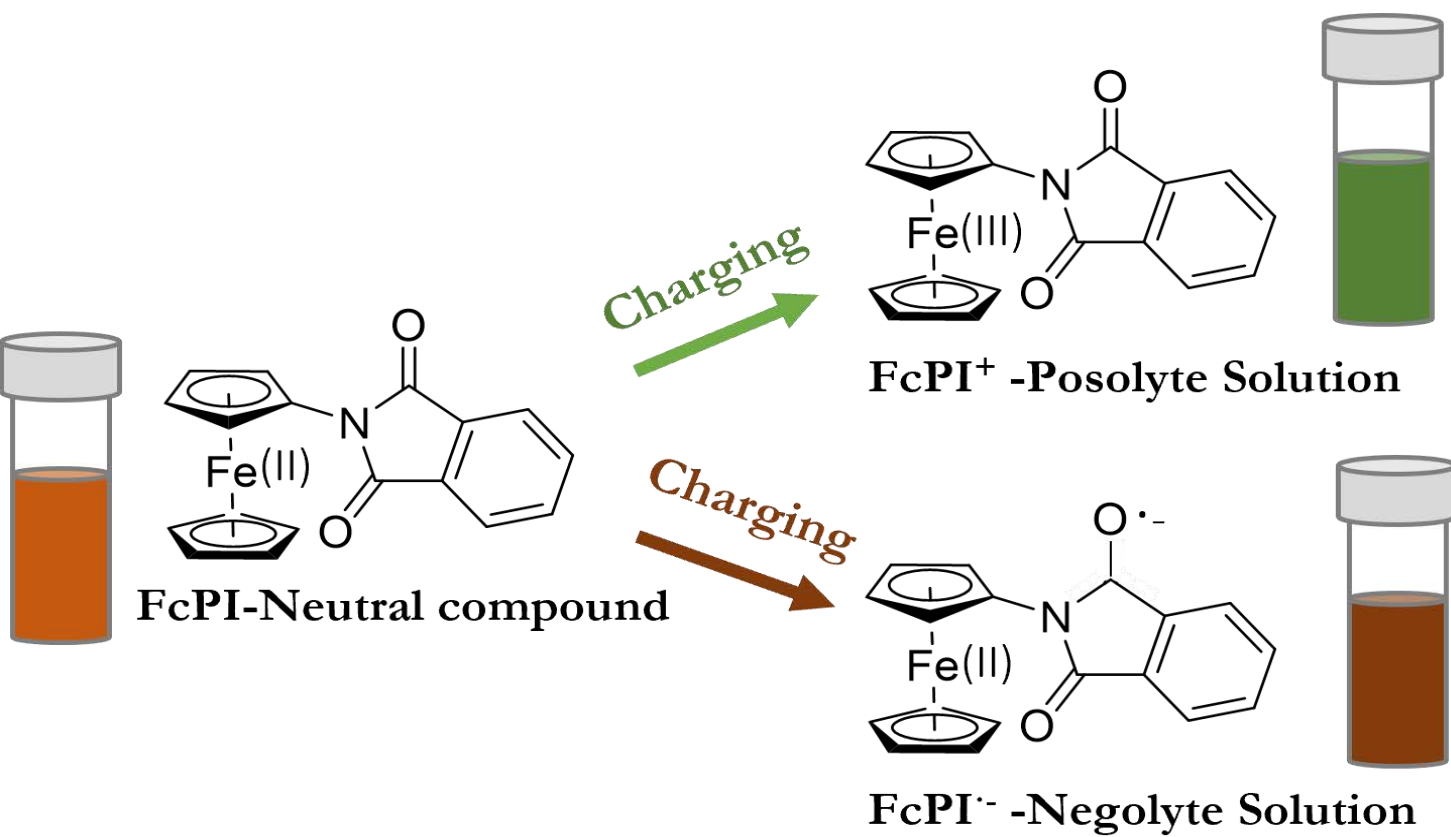


Methods and Materials



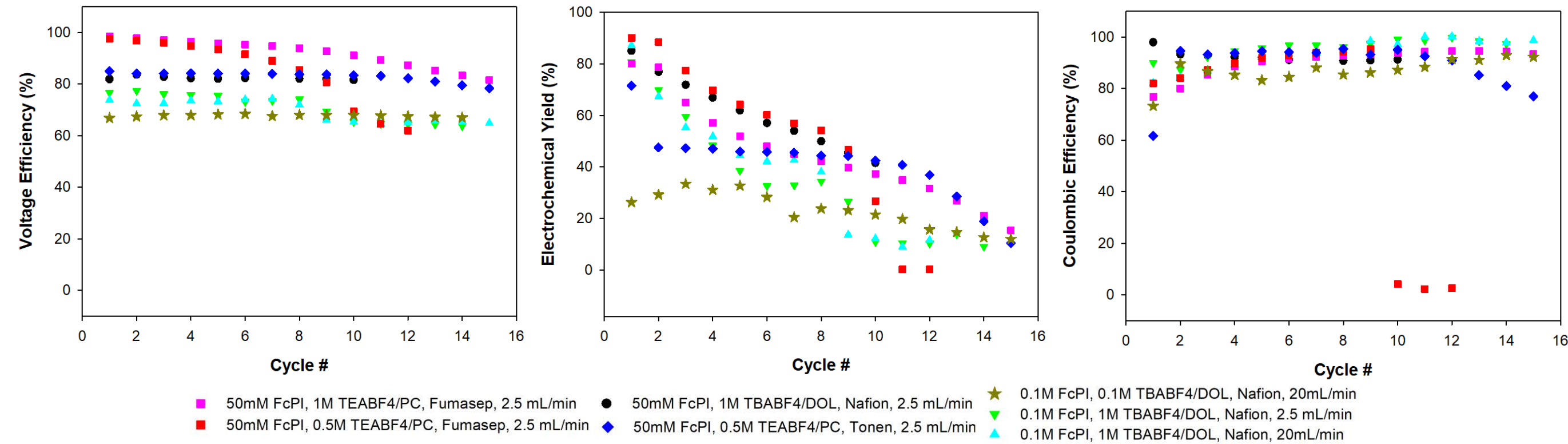
- N-Ferrocenylphthalimide was synthesized via the reaction mechanism shown above
- Cyclic voltammetry and bulk electrolysis were performed using a BASi Epsilon potentiostat
- Galvanic cycling on flow batteries was performed using a Solartron 1287 potentiostat
- Flow batteries built using:
 - 2.5" nominal thickness carbon felt, plasma treated on each side
 - Teflon gaskets and copper current collectors
 - Nafion 117 (pretreated w/ TBA-OH), Fumasep FAP 450, and Tonen membrane/separators
 - Serpentine graphite flow cells, 5 cm² active area
 - Peristaltic pumps with Norprene tubing and polypropylene reservoirs

Flow Battery Testing

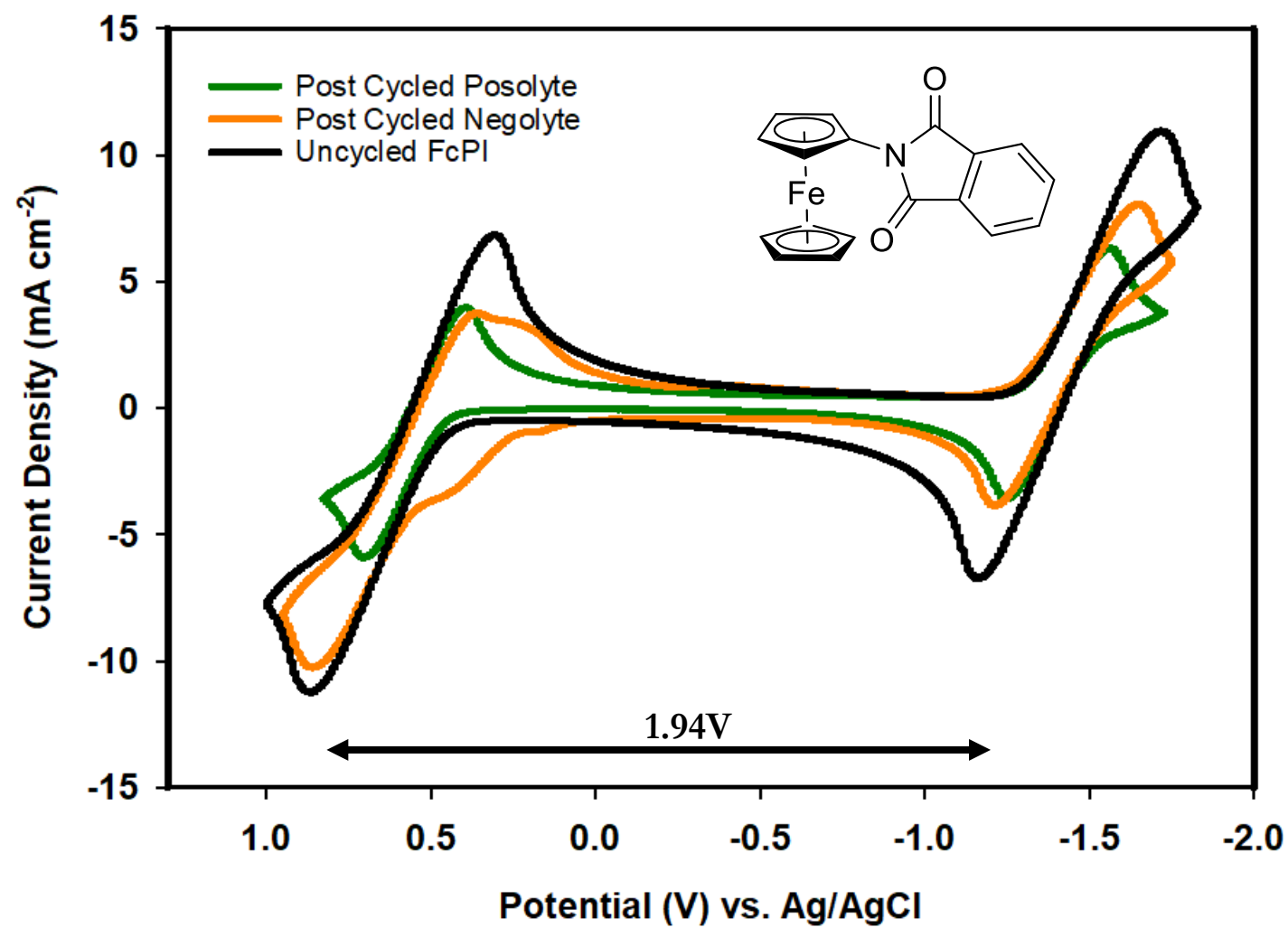


★ 500uA/cm² Charge/Discharge Rate

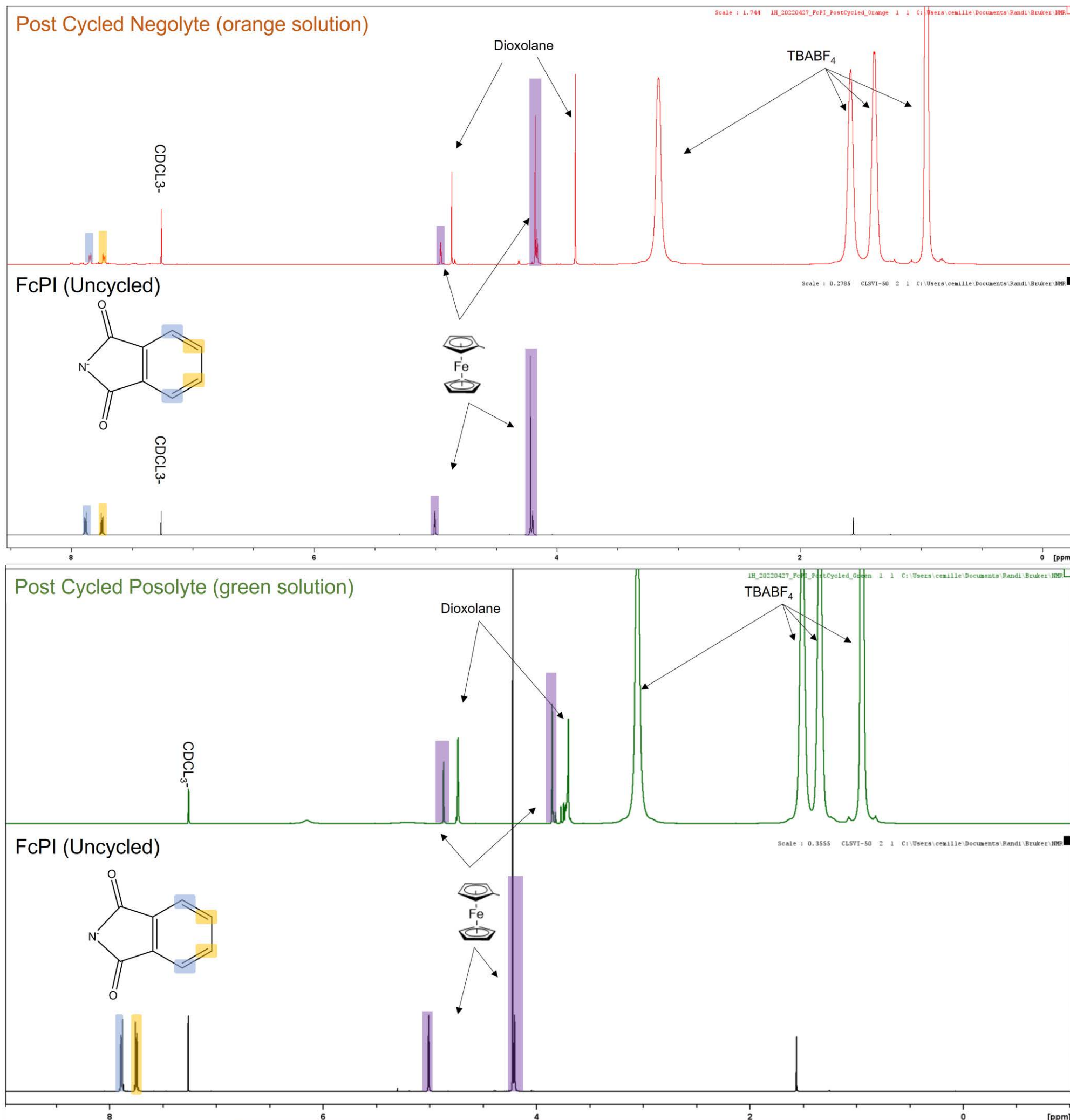
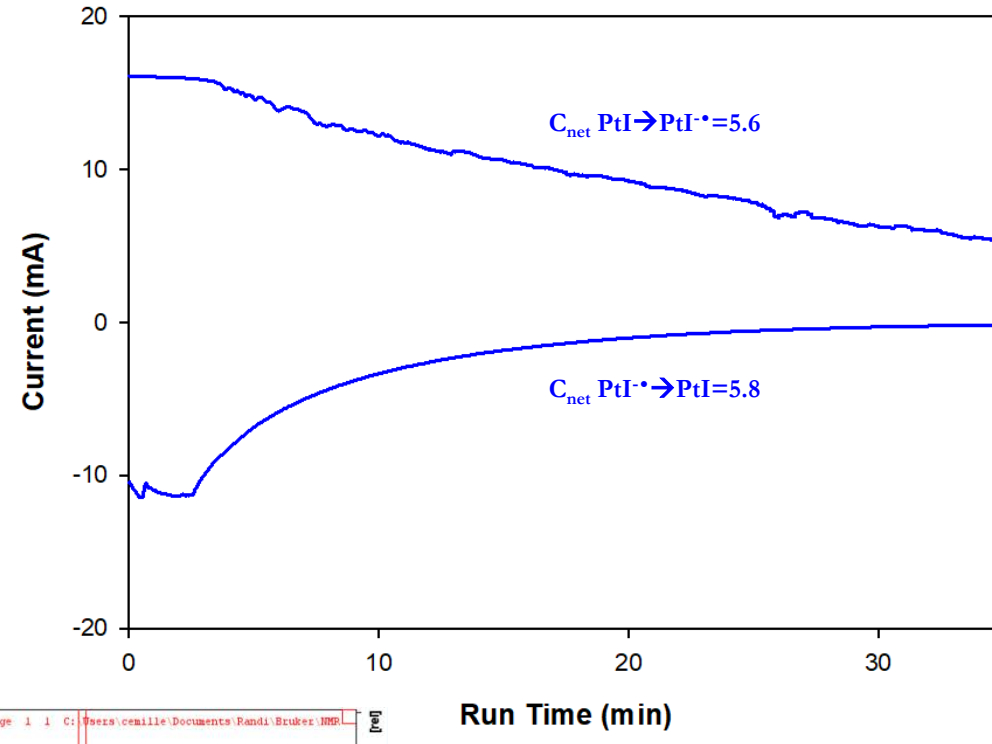
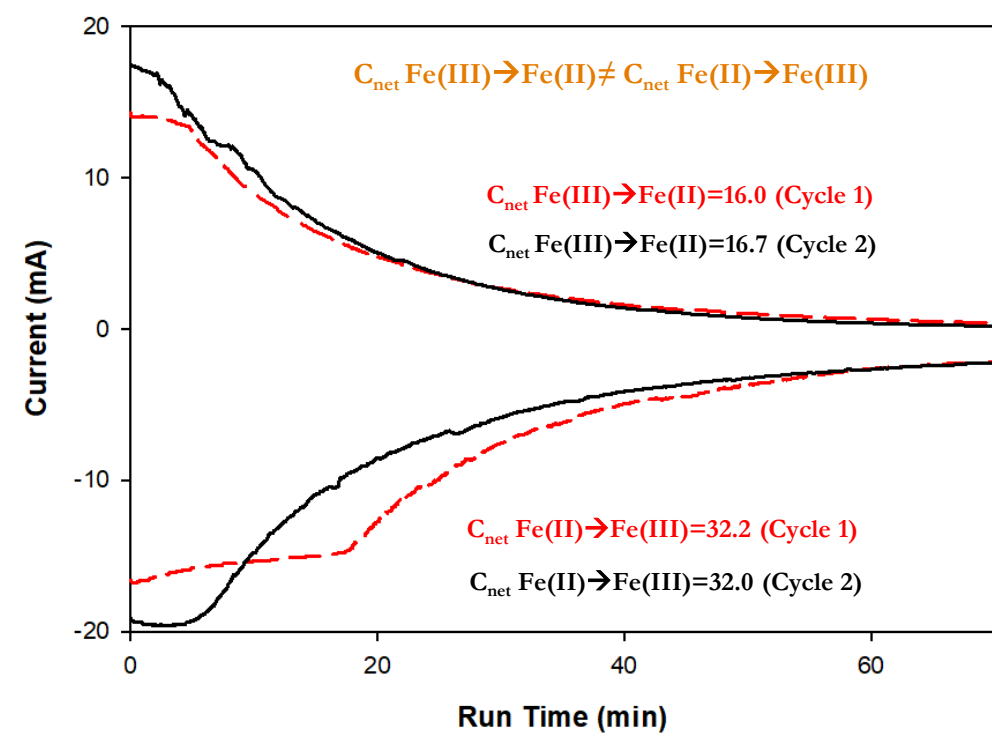
- 50mM FcPI, 0.5M TEABF₄/PC, Fumasep, 2.5mL/min
- 50mM FcPI, 1M TEABF₄/PC, Fumasep, 2.5mL/min
- 50mM FcPI, 1M TBABF₄/DOL, Nafion, 2.5mL/min
- 50mM FcPI, 0.5M TEABF₄/PC, Tonen, 2.5mL/min
- 0.1M FcPI, 0.1M TBABF₄/DOL, Nafion, 20mL/min
- 0.1M FcPI, 1M TBABF₄/DOL, Nafion, 2.5mL/min
- 0.1M FcPI, 1M TBABF₄/DOL, Nafion, 20mL/min



Electrochemical Testing-CV and BE



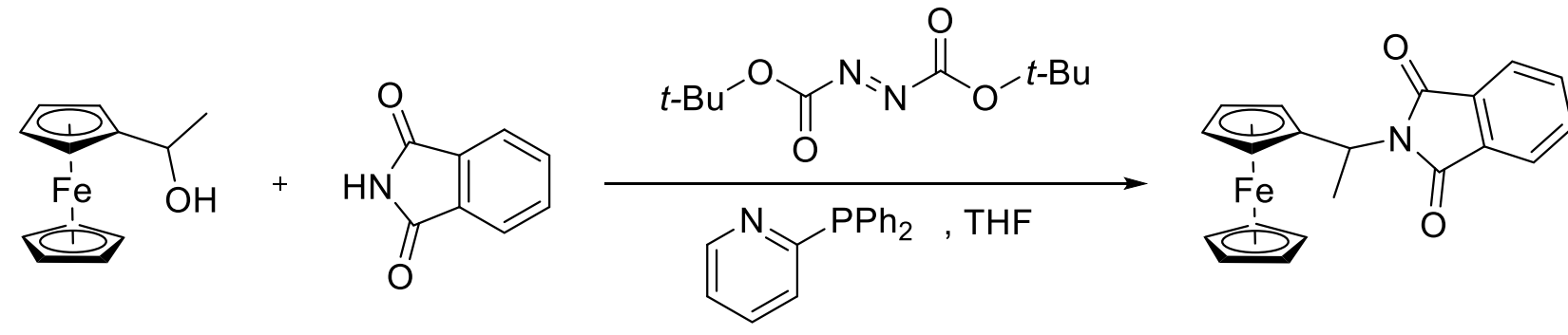
- Cyclic voltammetry run at 100 mV/second
- The posolyte and negolyte CVs were taken from the 0.1M FcPI in 1M TBABF₄ in DOL post-mortem flow battery
- Degradation noted in the post cycled negolyte solution needs to be further investigated using NMR
- The BE of the Fc moiety does not utilize equal charge in the forward and reverse directions



Proton NMR was performed using a Bruker Avance 500 instrument and calibrated to the CDCl₃ peak at $\delta=7.6$ ppm. The protons assigned to the ortho and meta protons of the phthalimide are not visible in the NMR taken from the post-cycled posolyte solution. The NMR also shows a significant shift of the protons involved in the ferrocene molecule that are directly attached to the nitrogen in the phthalimide moiety. The ¹H NMR of the post-cycled negolyte solution shows no shifts in signals from the uncycled solution.

Conclusions and Future Work

- ¹H NMR of the posolyte (green) solution shows the disappearance of the peaks for the PI moiety- this is suspected to be due to the Fe (III) in the Fe moiety. We believe that the Fe (II) \rightarrow Fe (III) reaction is possibly not fully reversible in this particular bipolar molecule.
- Bulk electrolysis of the green posolyte shows 32 net coulombs transferred for the Fe(II) \rightarrow Fe (III) reaction but only 16 net coulombs transferred for the reverse reaction which is consistent with the suspicion of the iron becoming "trapped" in the +3 oxidation state.
- The cyclic voltammogram of the post-cycled negolyte (orange) solution shows new peaks appearing in the Fc region (~ 0.75 V) even though it is the PI moiety that is electrochemically active in that solution. This is counterintuitive because the Fc is not active at this voltage.
- Collectively, the results show that the Fc is unstable whether it is participating in the electrochemical reaction of the battery or not.



The FcPI compound has been modified by inserting an α -methyl group between the ferrocenyl and the phthalimide moieties. This addition not only improves the solubility of the electroactive species in the TBABF₄/DOL electrolyte, but it also is suspected to stabilize the compound as it undergoes electrochemical testing. Furthermore, yet another modification has been made to N-ferrocenylphthalimide compound that could provide yet another source of stabilization. These two new compounds will be rigorously studied using the same techniques as described in this poster and will be presented at the MRS Fall meeting in Boston.