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Organic Flow Battery Development

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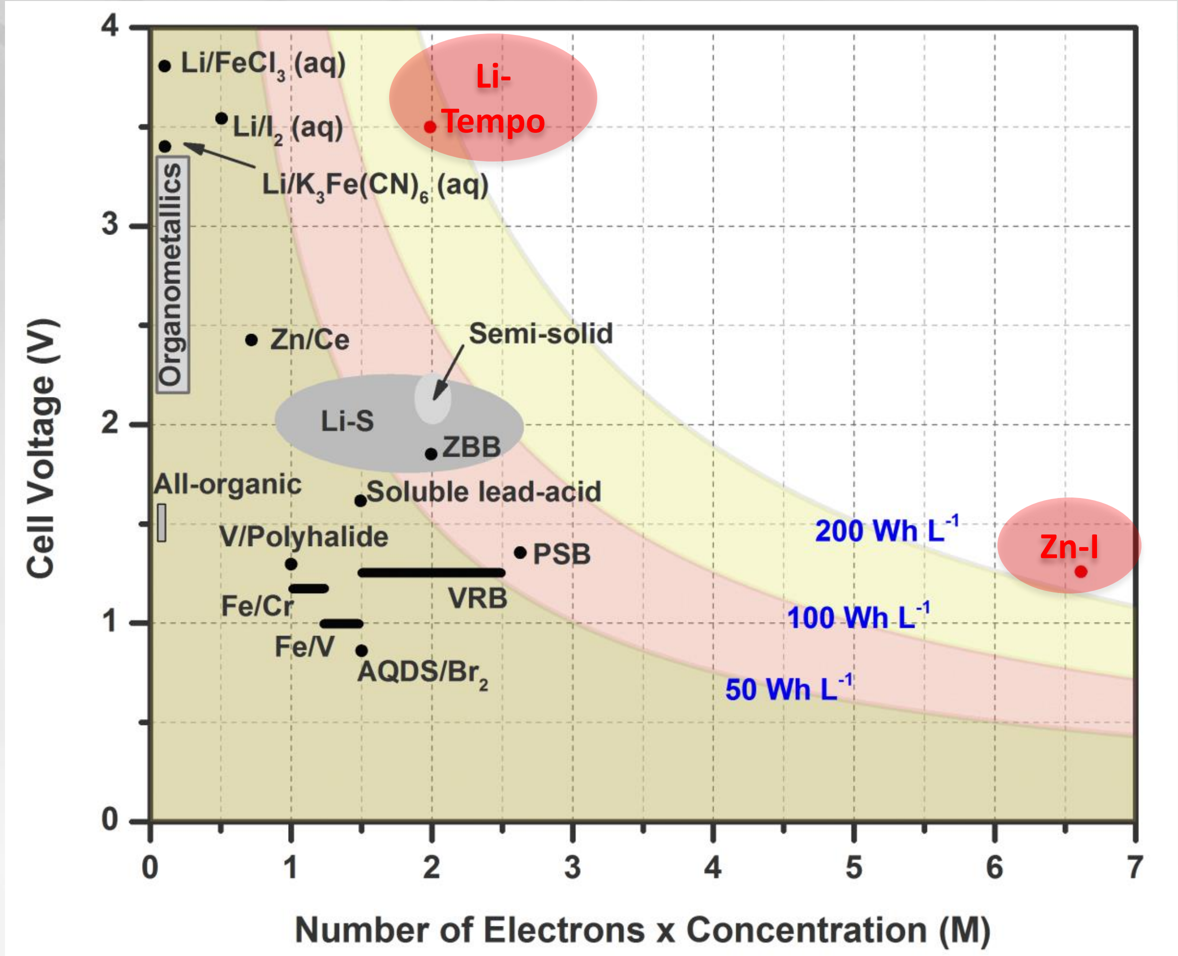
DOE Office of Electricity Energy Storage Program – Imre Gyuk Program Manager.

OE Energy Storage Systems Program Review

September 16-19th, 2014

Major challenge of the current RFBs



$$E = \frac{NC_a FV}{n}$$

- Increase C_a : Zn-I RFB
- Improve V: Nonaqueous RFB

Nonaqueous RFB Technology

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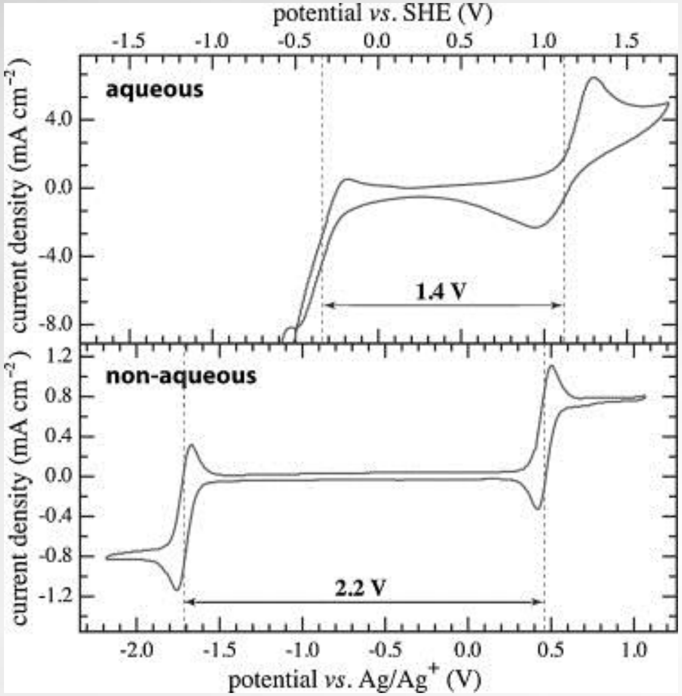
Advantages of Nonaqueous RFB

- High voltage
- Multi-electron reaction
- Potential high energy/power density



CV of vanadium ions in aqueous (0.01 M $VOSO_4$ and 2 M H_2SO_4 solution) and nonaqueous (0.01 M $V(acac)_3$ and 0.1 M $TEABF_4$ in CH_3CN) supporting electrolytes.

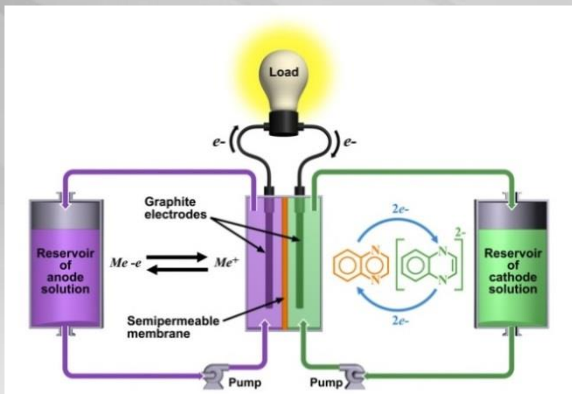
Current nonaqueous RFB Chemistries

- **Metal coordinated redox couple**
  - Metal coordination complexes (UMich)
  - Metal-based ionic liquids (Sandia)
- **Total organic redox flow battery** (ANL)
- **Hybrid non-aqueous RFBs**
  - Semi-solid lithium flow battery (MIT)
  - Li-redox flow battery (UTexas/JAIST)
  - Li-S flow battery (Stanford/MIT/PNNL)
  - Metal-organic hybrid RFB (PNNL)

- Low solubility
- Limited electrolyte stability
- Capacity decay during cycling
- Cost

Shinkle, et al. *JPS*, 2012, 206, 490

Metal-Organic Redox Flow Battery (MORFB)



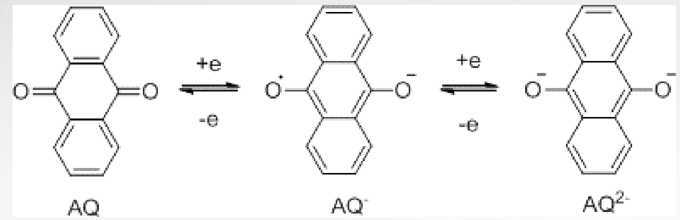
Metal-organic hybrid redox flow battery

- Anode/anolyte: metal or metal ions redox couple (Li/Li^+)
- Catholyte: organic redox active agent

Advantage:

- Flexibility with a designable voltage window
- Flexibility in structure and redox center design
- Natural abundance in resource.

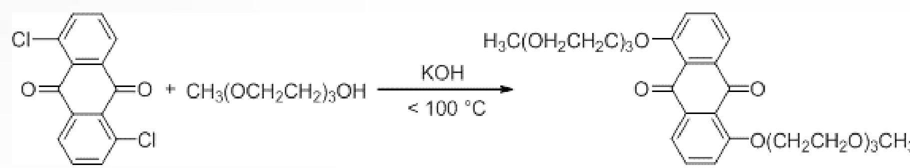
Anthraquinone based nonaqeuous electrolyte

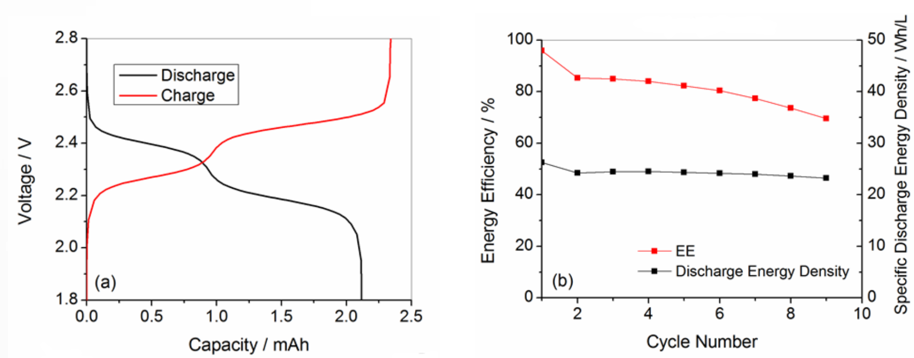


AQ redox reaction mechanism

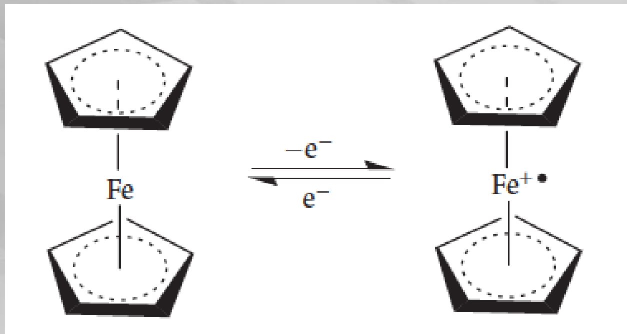
very low solubility (< 0.05 M) in most electrolytes of relatively high polarity

Structure modification to increase solubility 10X

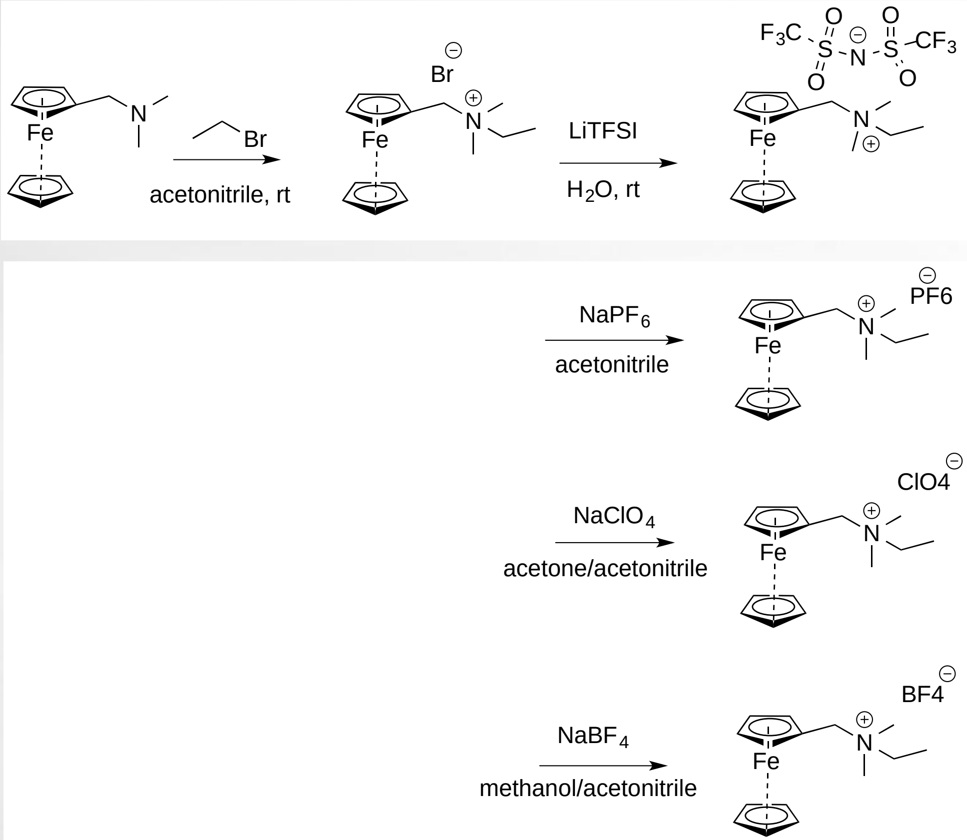




Ferrocene based redox active species



- Low solubility: 0.04M in EC/PC/EMC-1.2M LiTFSI
- Modified Ferrocene with an ionic charged tetraalkylammonium pendant arm with a TFSI- counter anion, resulting in a 20-fold increase in its solubility (0.85M in EC/PC/EMC-1.2M LiTFSI).



Fc1N112-TFSI

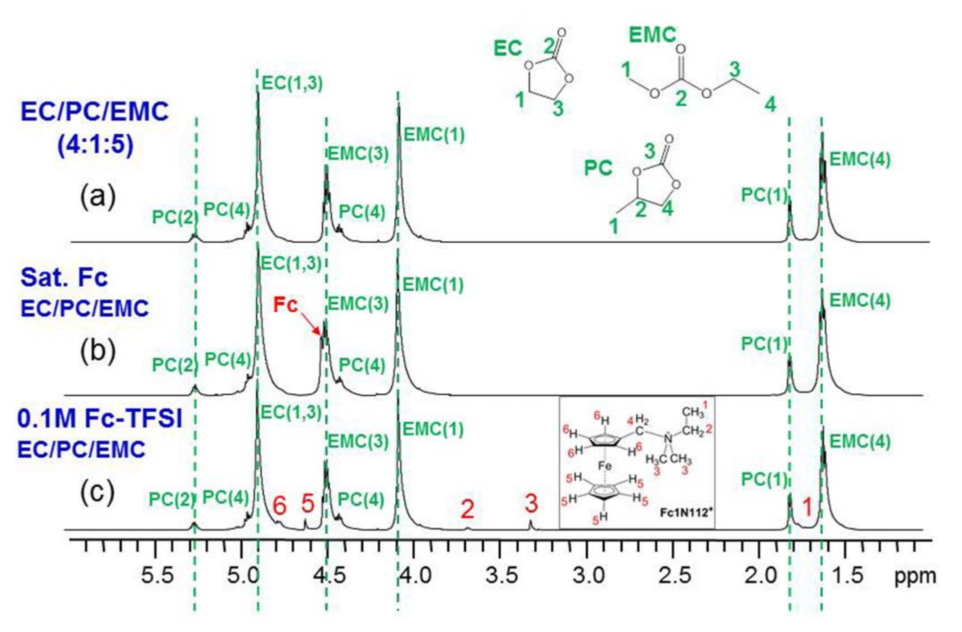
$Fc1N112\text{-}PF_6$

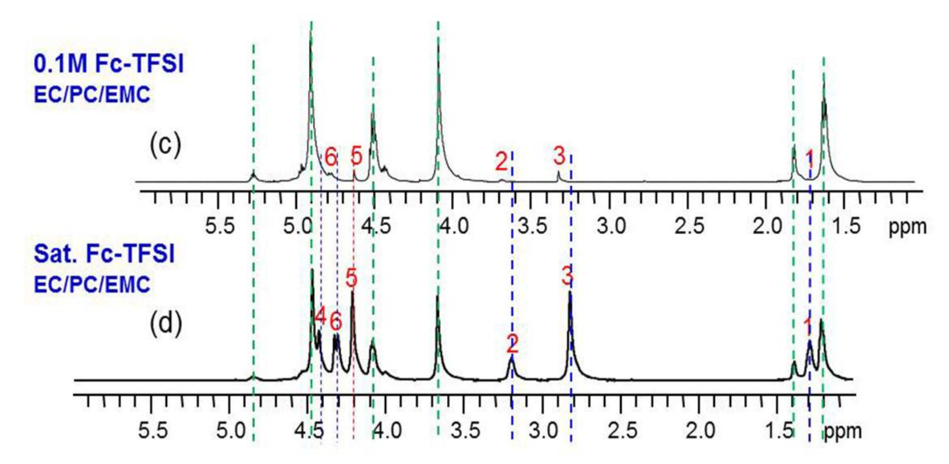
$Fc1N112\text{-}ClO_4$

$Fc1N112\text{-}BF_4$

Solubility

Solvation Chemistry of the FCN-TFSI

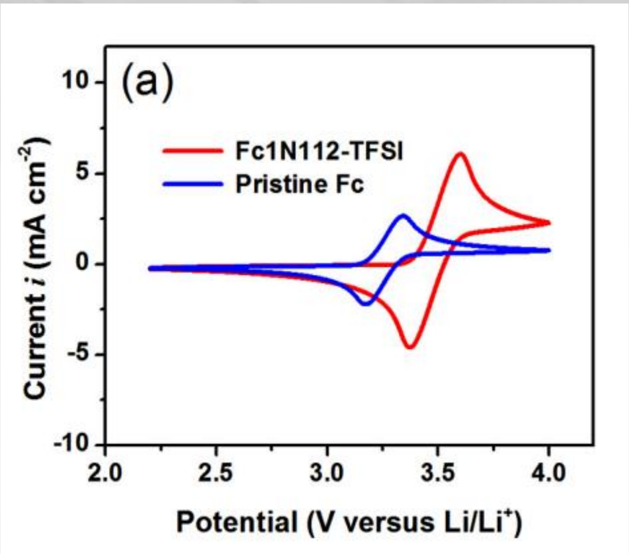


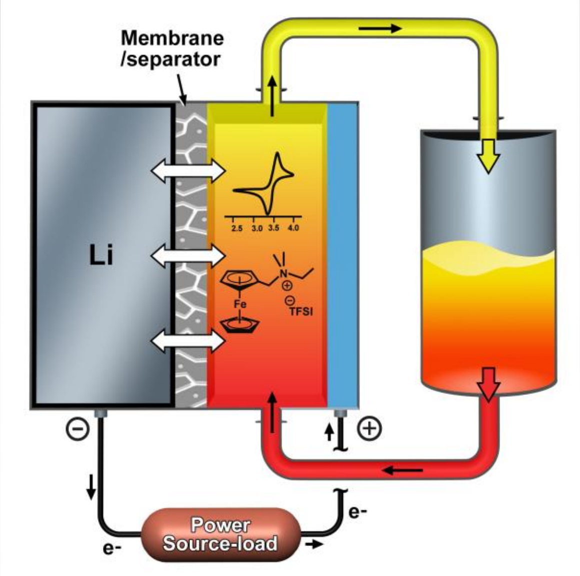


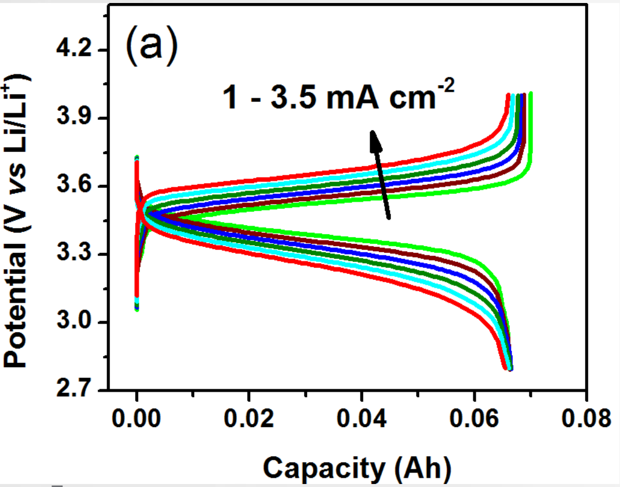
- No chemical shift change at low concentrations of either pristine ferrocene or Fc-TFSI

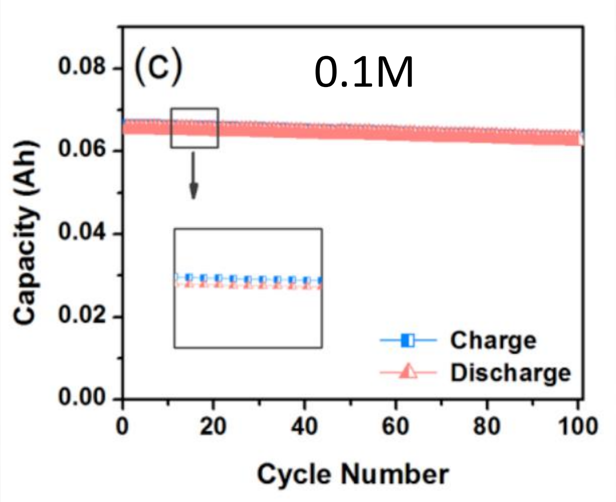
- Constant spacing between solvent peaks → no cation-solvent chemical binding
- Only protons on substituted rings shift → solvation primarily on the cation

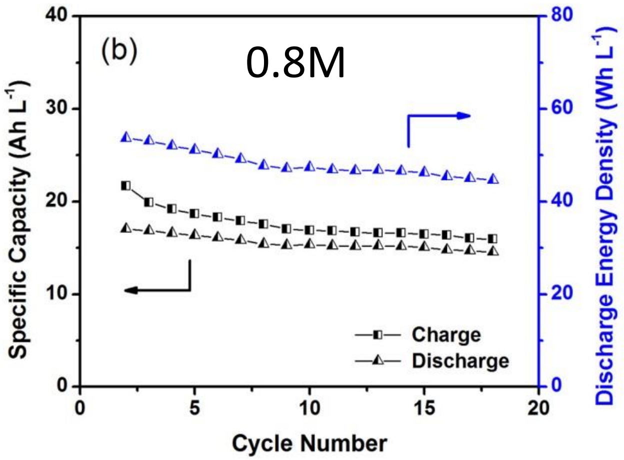
Electrochemical performance of the FCN-TFSI











X. Wei, *et. al. submitted*

High energy density Li-TEMPO NRFB

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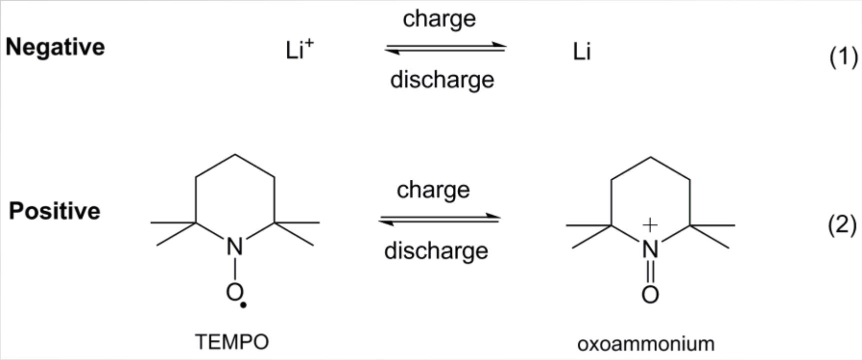
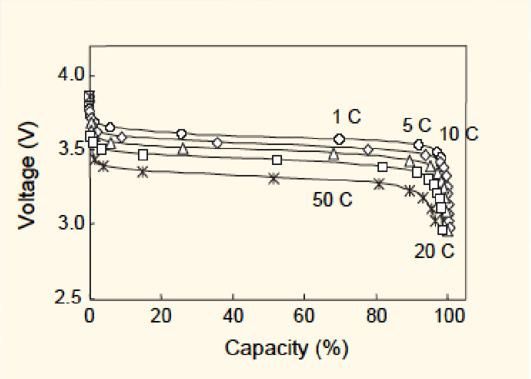
High voltage TEMPO based electrolyte

2,2,6,6-tetramethylpiperidine-1-oxyl



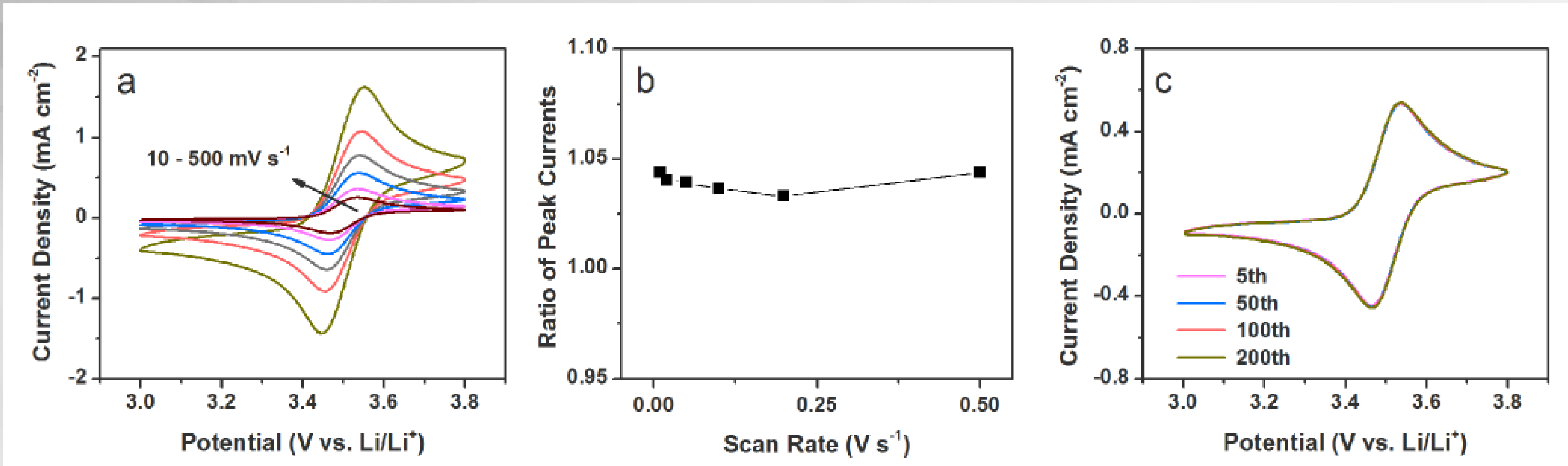


Example of the TEMPO discharge curve

High concentration TEMPO electrolyte

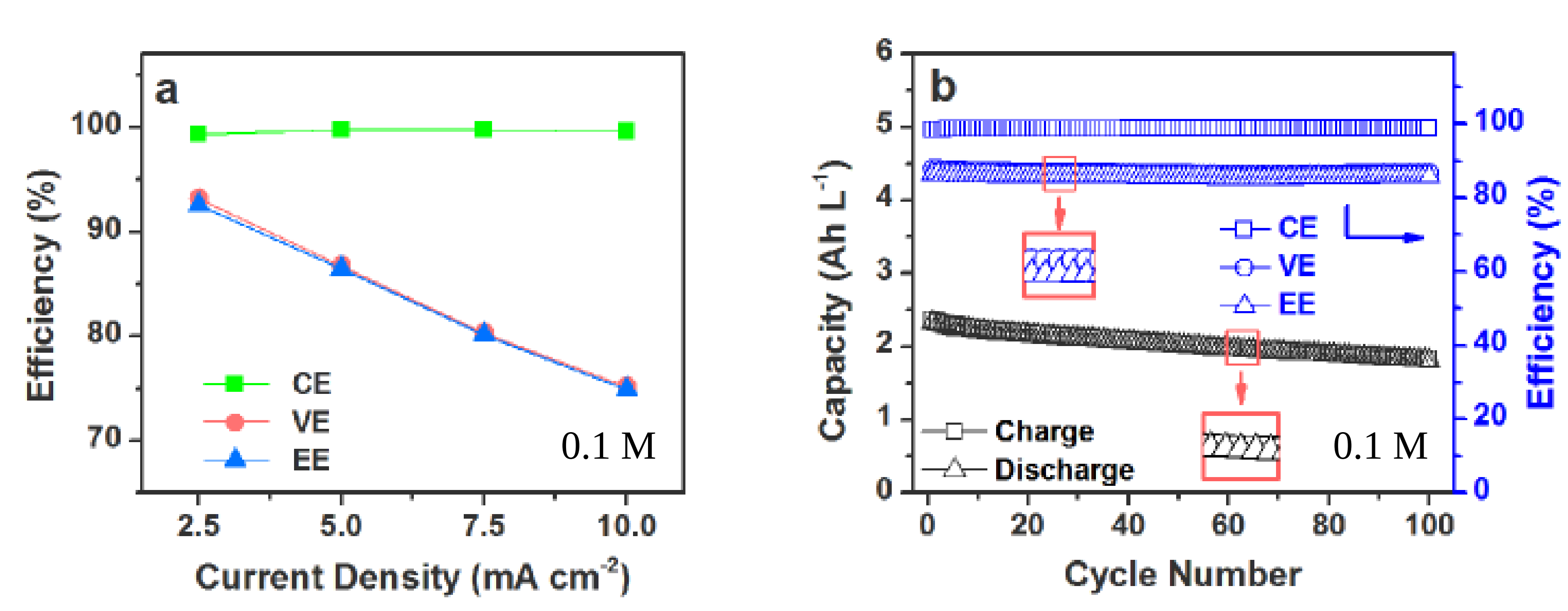
- Solubility > 5 M in EC/PC/EMC
- 2.0 M TEMPO in 2.3 M $LiPF_6$ in EC/PC/EMC with theoretical energy density of 187Wh/L

Electrochemical performance of the TEMPO



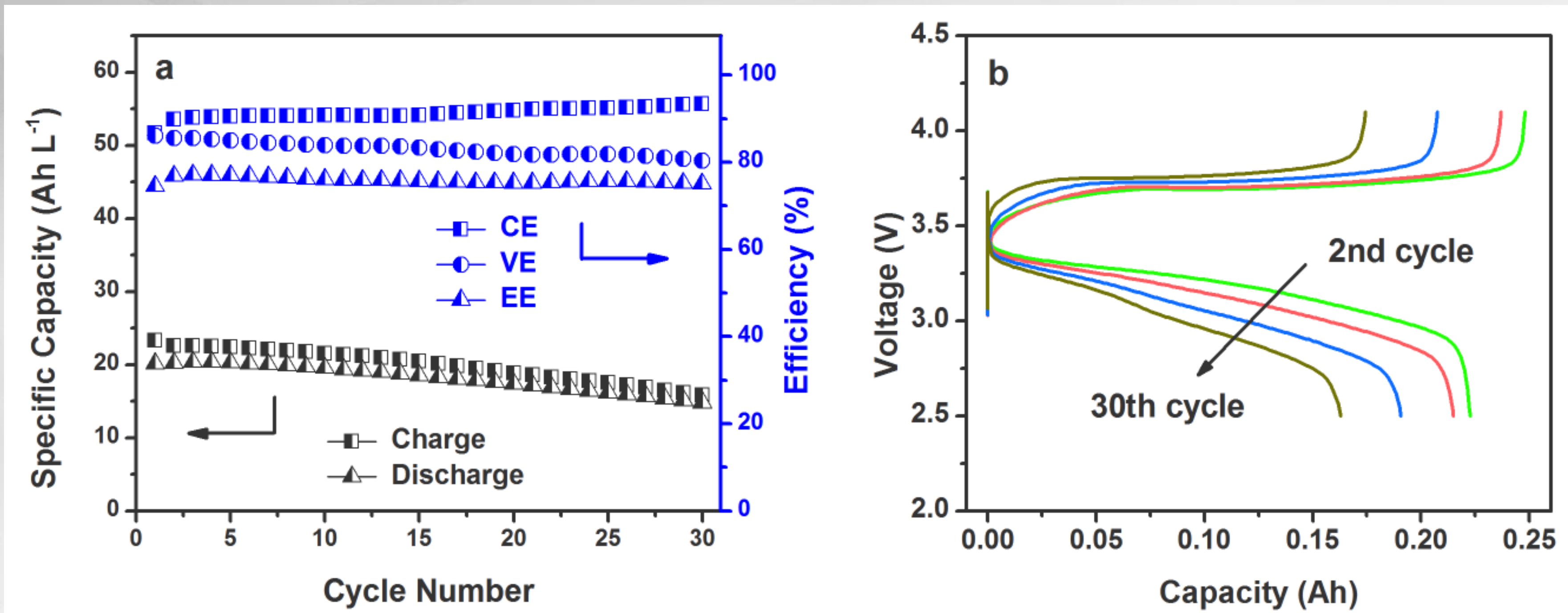
(a) CV curves of 0.005 M TEMPO in 1.0 M $LiPF_6$ on a glassy carbon electrode at scan rates ranging from 10–500 mV s^{-1}; (b) ratio of the oxidation and reduction peak currents with respect to scan rate; (c) CV curves for the 5th, 50th, 100th, and 200th cycles at 50 mV s^{-1}.

Cycling performance of Li-TEMPO NRFB at 0.1M



Electrochemical performance of the Li|TEMPO flow cells: (a) rate capability and (b) cycling efficiency and capacity at 0.1 M TEMPO in 1.0 M $LiPF_6$ with 15 wt% FEC and Li-graphite hybrid anode at 5.0 mA cm^{-2}.

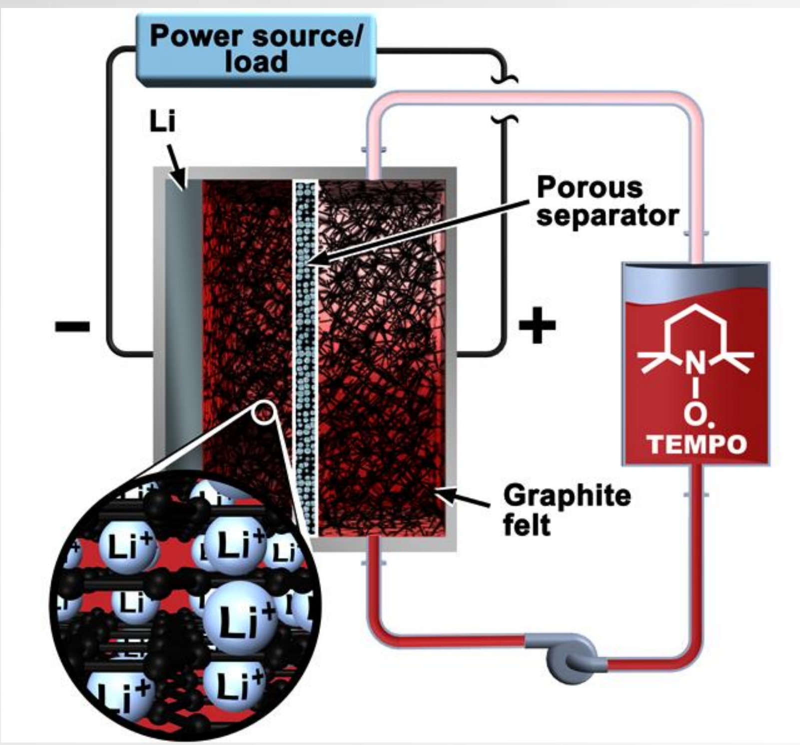
Cycling performance of Li-TEMPO NRFB at 0.8M

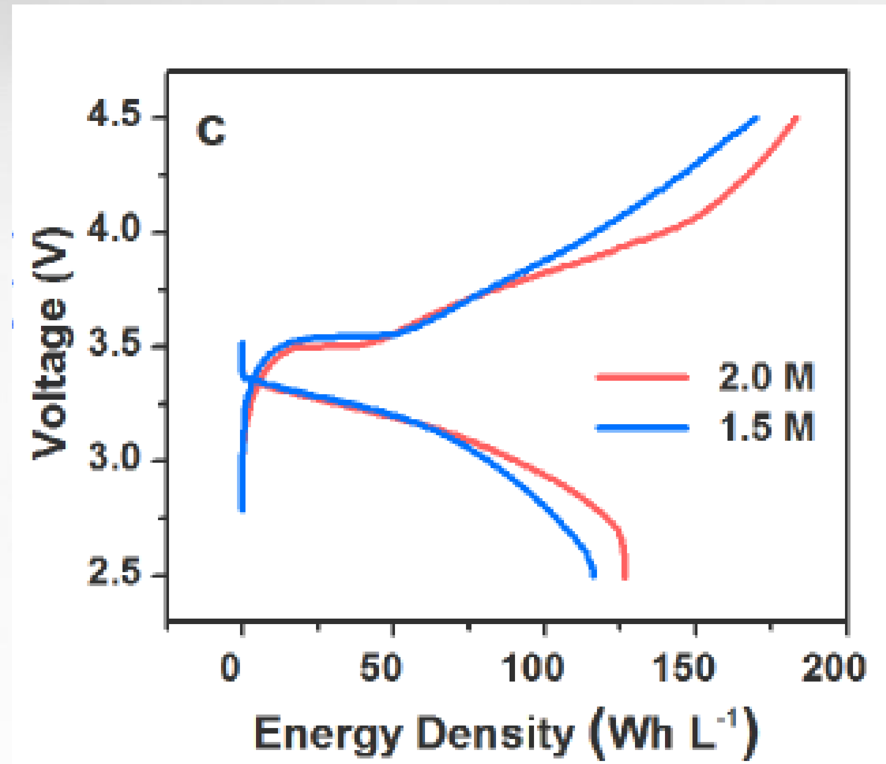


Cycling efficiencies and volumetric capacities of the 0.8 M Li|TEMPO flow cells at 5 mA cm^{-2}; (b) Voltage profiles of the 2nd, 10th, 20th, and 30th cycles for the Li|TEMPO flow cell at 0.8 M TEMPO, showing increased overpotential over cycling.

Cycling performance of Li-TEMPO NRFB at higher concentration

At high TEMPO concentration the severe lithium dendrite issue greatly limit the cycling. A hybrid anode is designed to enable the charge/discharge cycle.





Voltage curves with respect to energy density for the 1.5 M (using 2.5 mA cm^{-2}) and 2.0 M (using 1.0 mA cm^{-2}) Li|TEMPO flow cells.

Conclusions and future work

- We proposed to a new hybrid metal-organic redox flow battery.
- Molecular structure design and functionalization is a feasible strategy to increase the solubility and therefore energy density of the nonaqueous flwo battery.
- We demonstrated a high energy density Li-TEMPO nonaqueous RFB (>125Wh/L).
- Continue to investigate lithium dendrite growth and mitigation, develop new nonaqueous flow battery chemistries.

Acknowledgements

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