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Design and Applications of Redox Active Materials for Advanced Redox Flow Batteries

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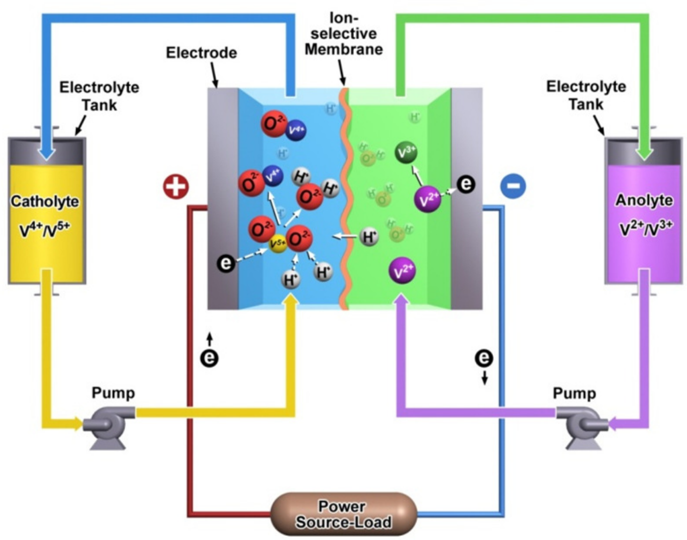
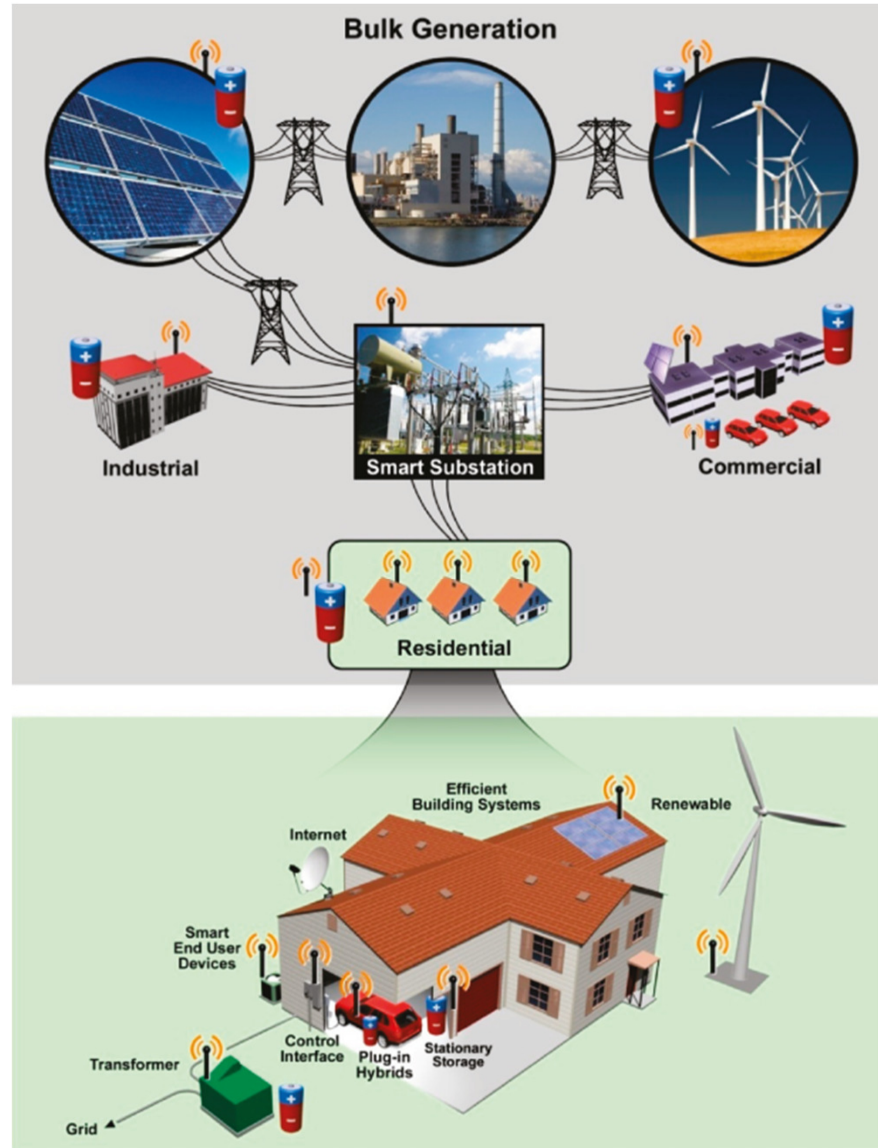
Redox flow batteries (RFB)

Flow Cell



Advantages:

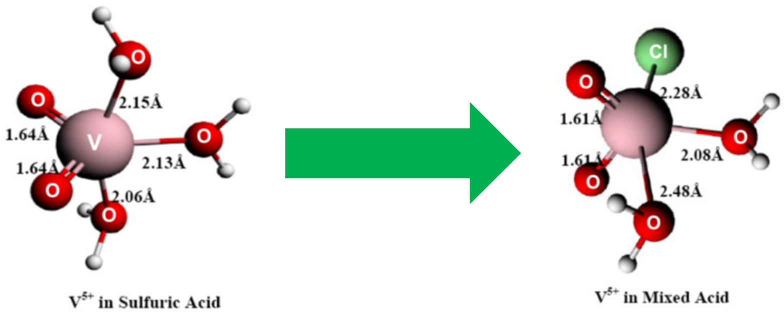
- ➢Separation of energy and power
- ➢Active heat management
- ➢ Safety
- ➢ Large scale energy storage (MWs/MWhs)
- ➢ Potential low cost
- ➢ Manufacture easiness (modular)



Zhenguo Yang, *et. al. Chemical Reviews,* **111**, 2011, 3577
Wei Wang, *et. al. AFM*, 2012,

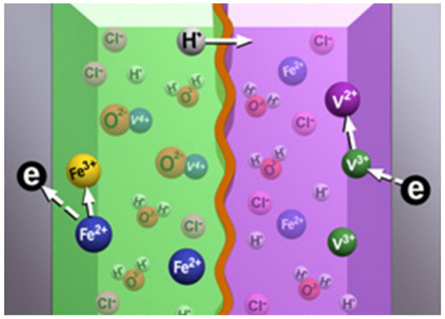
State-of-art aqueous RFB

Mixed-acid VRB



Double Energy Density
Extend temperature window

Fe/V RFB



Higher utilization, stable cycling
Low-cost membrane

2.5M,

- **Licensed to Unienergy Co. and other three**
- **2013 FLC Award**

Catholyte: VO^{2+} + Cl

Anolyte:

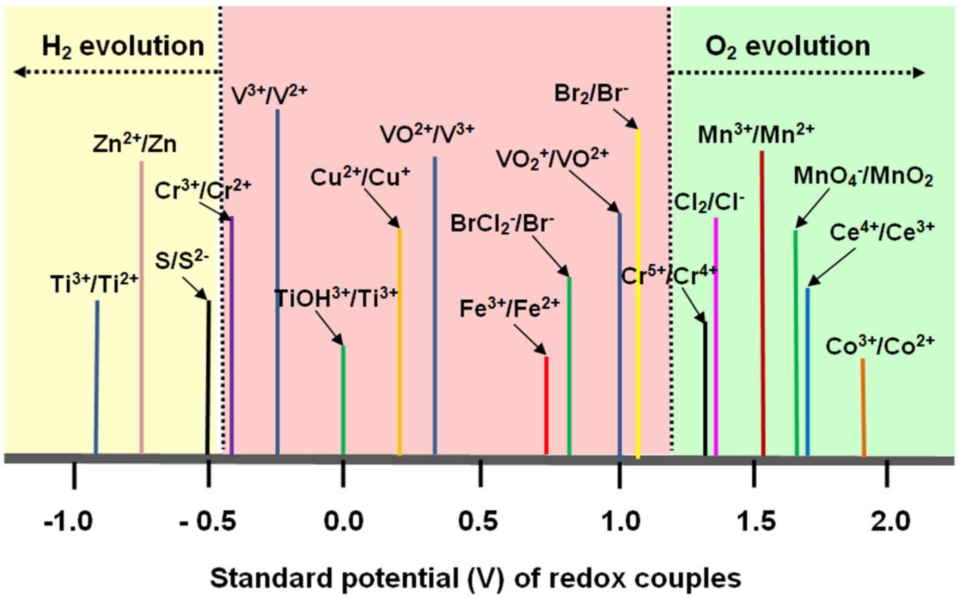
Negative: Discharge V

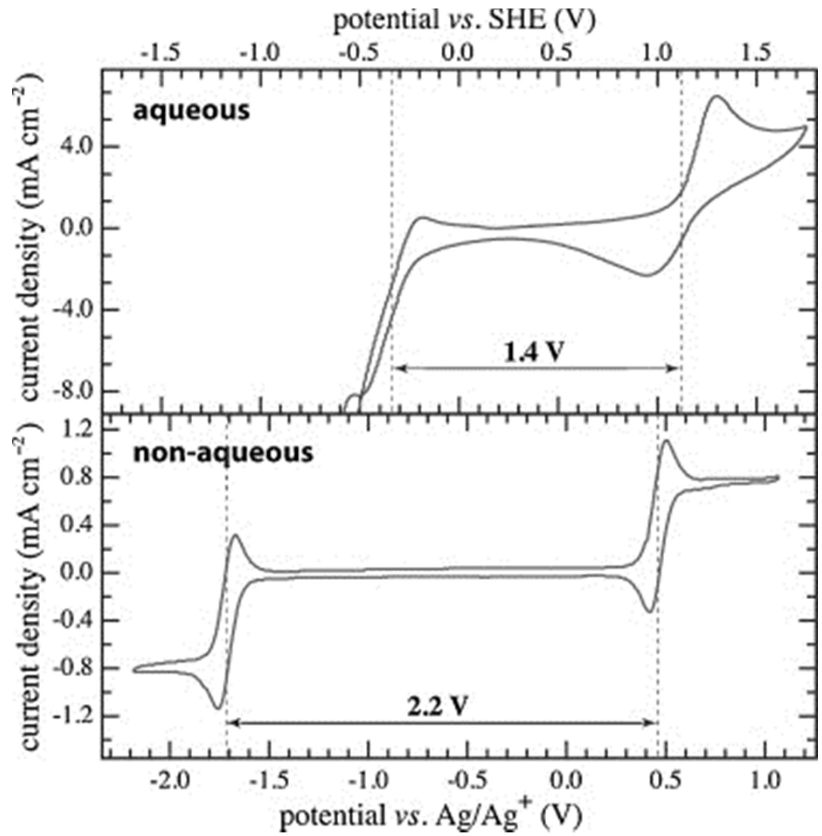
Overall: $VO^{2+} + Cl^- + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+ + V^{2+}$ E_o=1.25 V

Overall: $V^{3+} + Fe^{2+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+} + Fe^{3+}$ $E^o = 1.02\,V$

W. Wang, *et al*, *EES*, **4**, 4068, 2011
L. Li, *et al. AEM*, **1**, 394, 2011

Limitation of Aqueous RFB





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

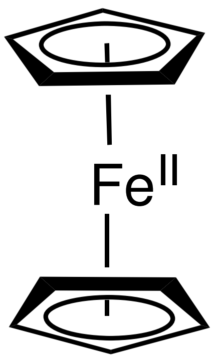
Limitation of aqueous RFB

- Low voltage (H_2/O_2 gas evolution)
- Expensive, > $500 kWh
- Low energy

Advantages of Nonaqueous RFB

- High voltage
- Potential high energy/power density
- Free from gas evolution
- Lower costs

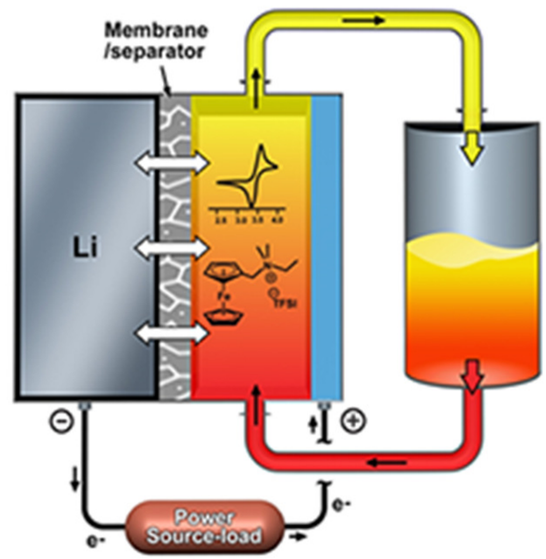
Background of Ferrocene (Fc)



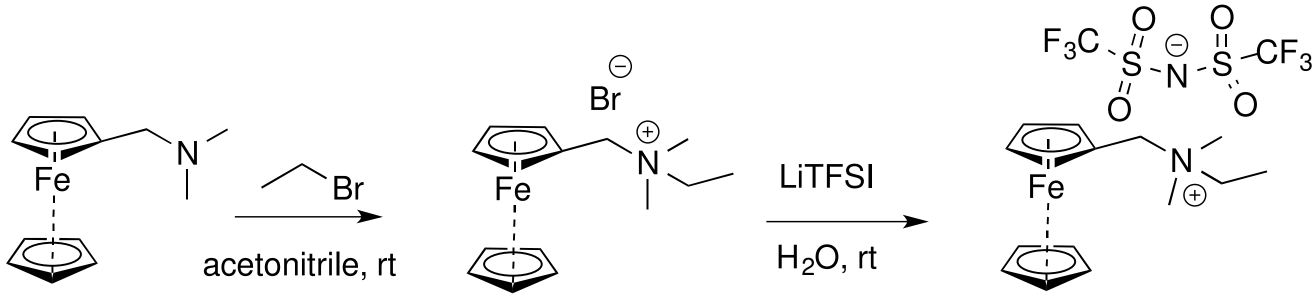
Versatile ferrocene

- A foundation complex for the field of Organometallic Chemistry (also a Noble prize compound for Wilkinson and Fisher in 1973)
- Fc and its derivatives widely used in synthesis, catalysis, medicine, electrochemistry and material chemistry
- Cathode materials for rechargeable Li ion batteries

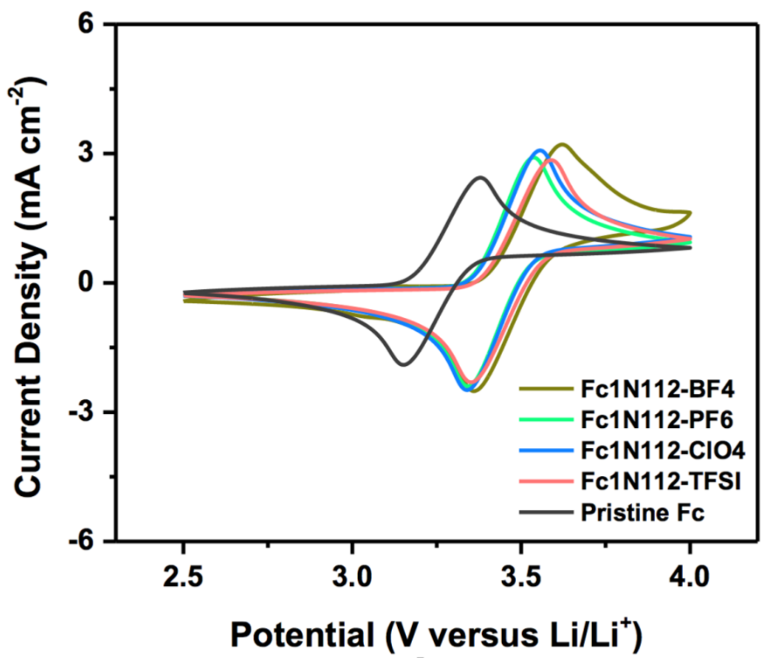
- Pristine Fc has poor solubility (ca. 0.2 M) in polar EC/PC/EMC and not good for NARFB (Li metal based semi-flow batteries).

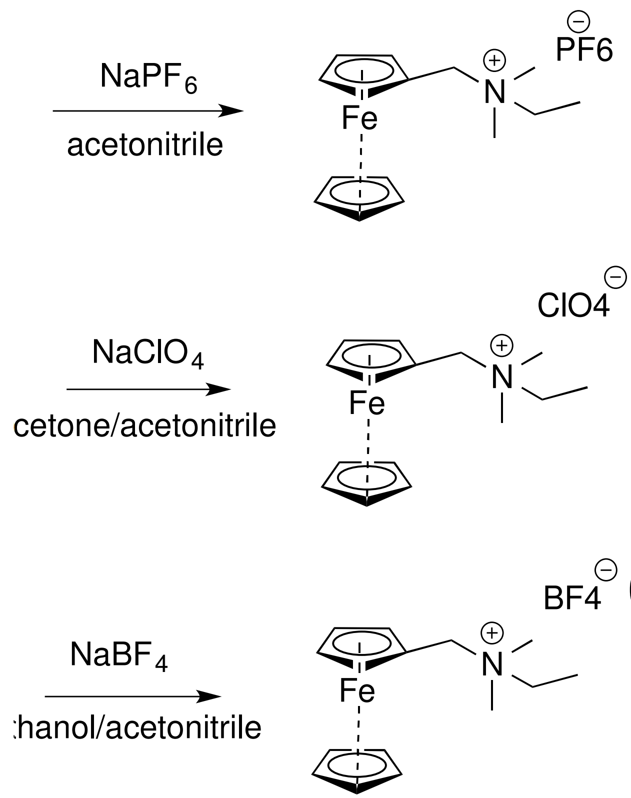


Functionalized Fc as Catholyte



1.73 M (79.5 Wh/L)
(EC/PC/EMC 4:5:1)
Fc1N112-TFSI





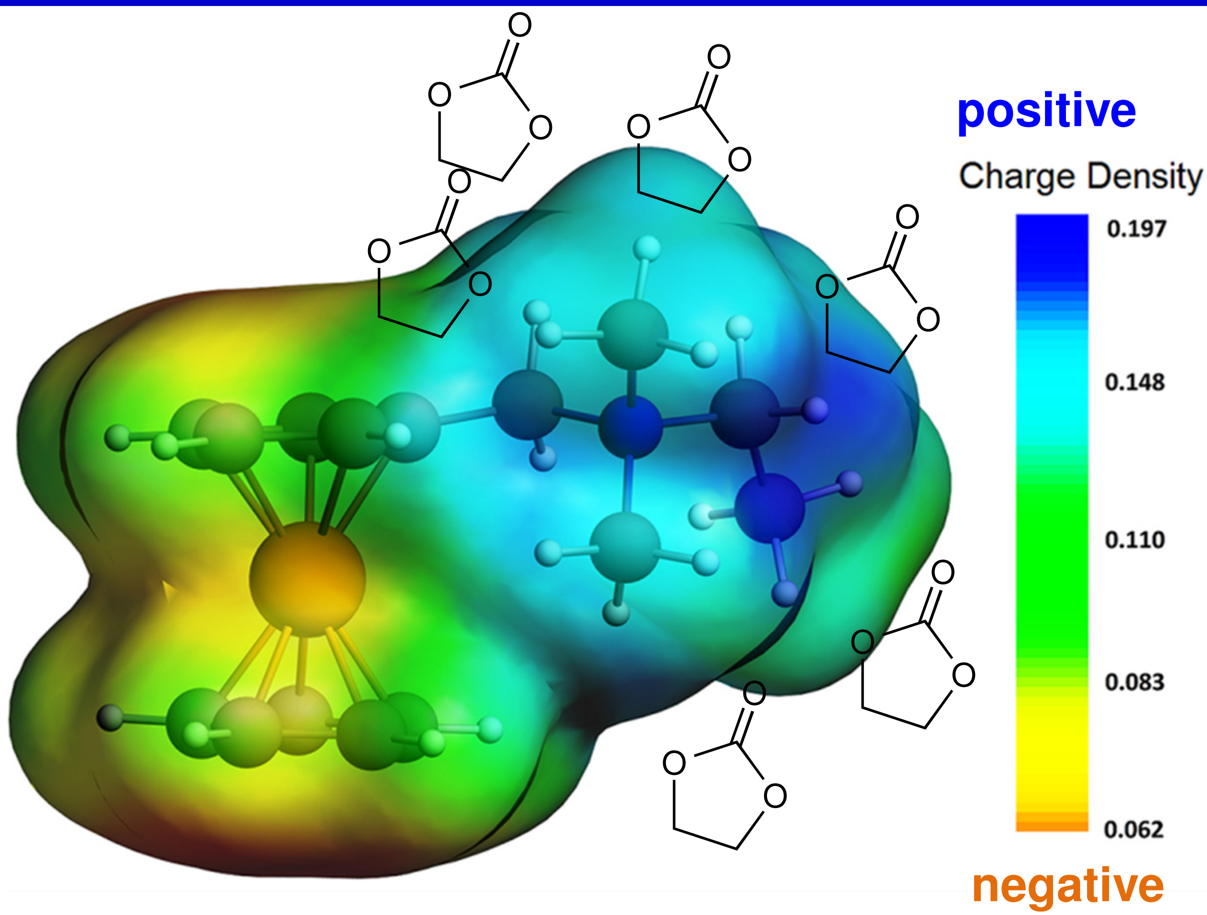
1.71 M
Fc1N112-PF_6

0.63 M
Fc1N112-ClO_4

0.40 M (30 Wh/L)
Fc1N112-BF_4

Understanding of Solvation Chemistry – DFT

❑ DFT calculation suggests the tetraalkylammonium cation improves the interactions with solvent molecules



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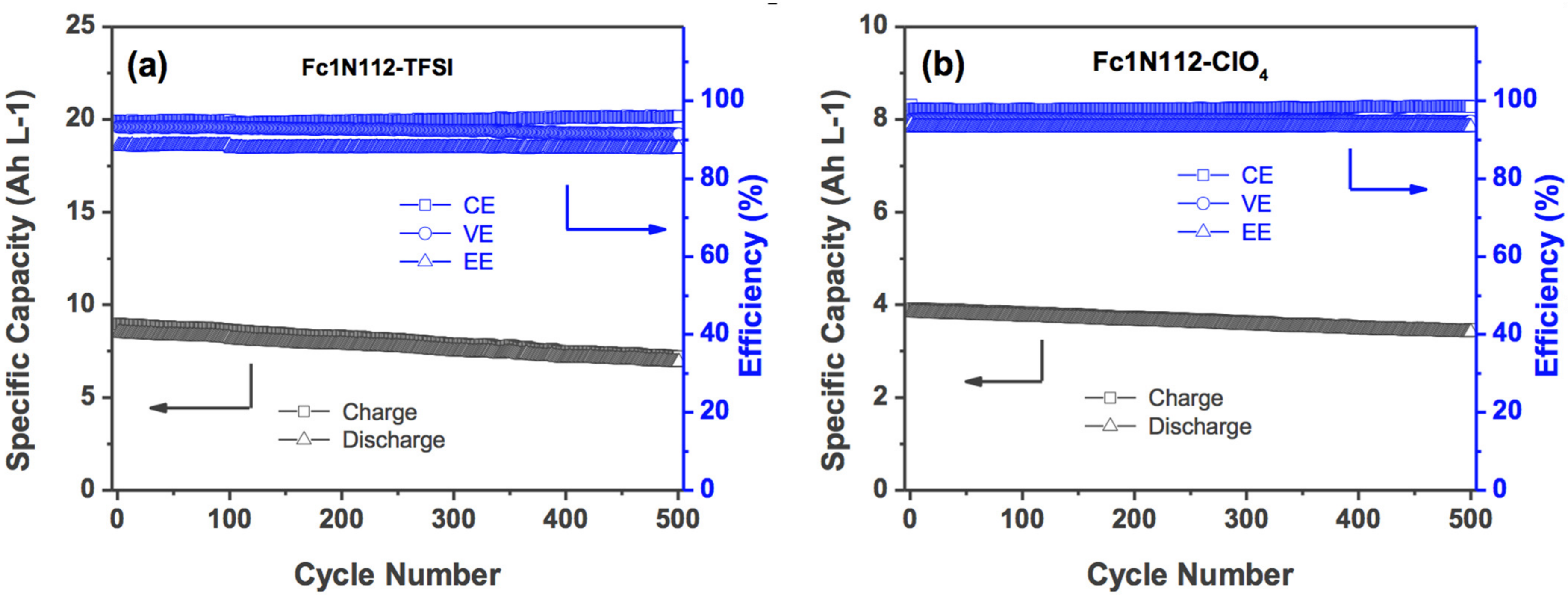
Static Cells of Functionalized Fc as Cathode

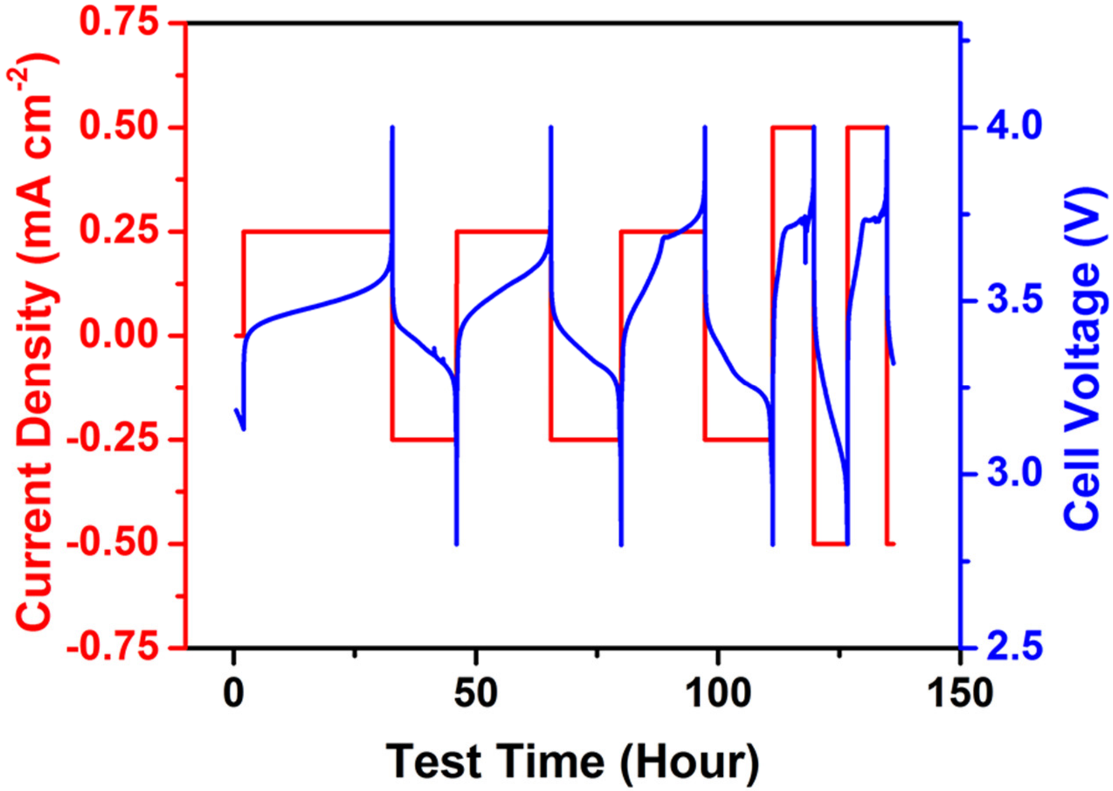
Model tests: Fc (cathode) / Li (anode) static cell configuration



- **High columbic efficiency (CE), voltaic efficiency (VE) and energy efficiency (EE), > 90%**
- **Good capacity retention due to SEI mitigated self-discharge**
- **Good candidates for RFB applications (FcTFSI-Li, 76 Wh/L)**

Flow Cell Cycling at High-Concentration Fc-TFSI

- Not successful with a Li metal anode even at 0.2M Fc-TFSI with 15wt% FEC
- The reason is **the excessive Li dendrite** with more redox species present.



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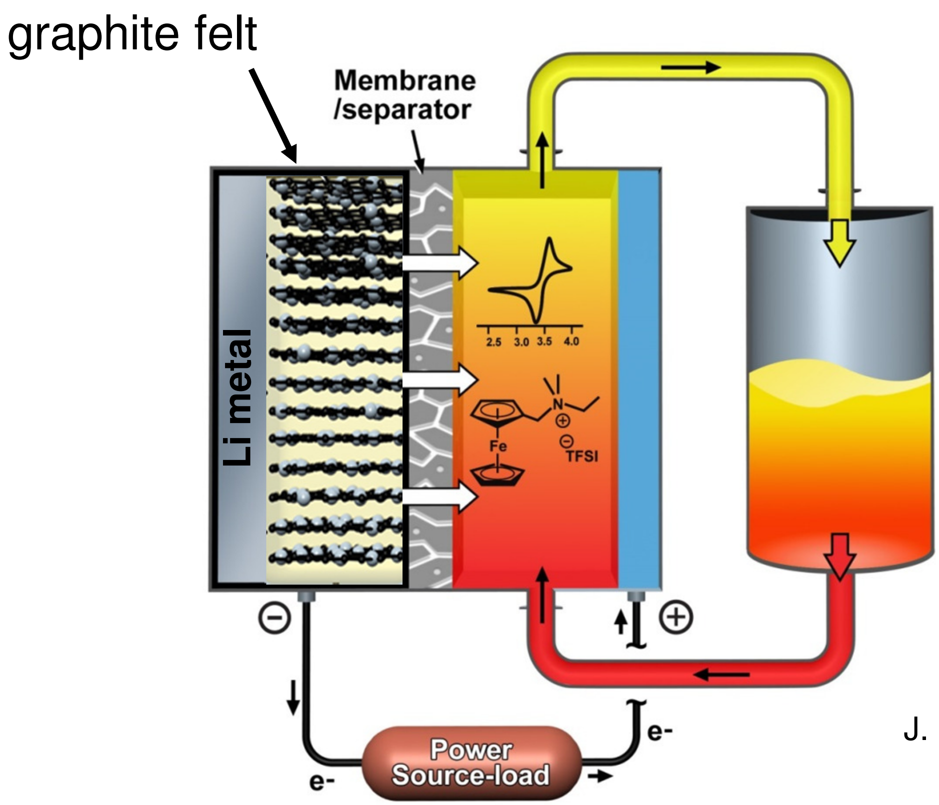
Hybrid Anode Assembly

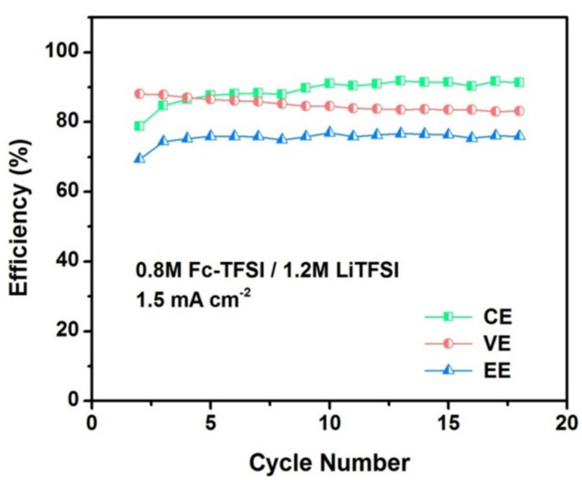


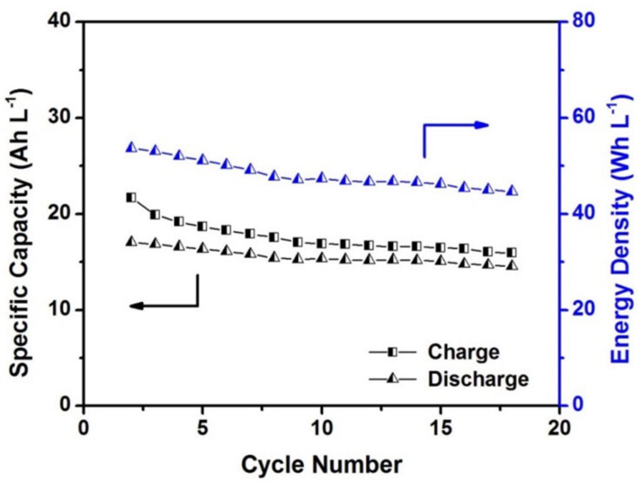
J. Liu et al *Nat Commun.* 2014,5,3015

- Change Li deposition/stripping chemistry to Li^+ ion intercalation → decreased involving of Li metal deposition
- Anode side is a shortened cell → not sacrificing cell potential

Hybrid Anode Enables High Concentration Cycling

- 0.8M Fc-TFSI / 1.2M LiTFSI / EC-PC-EMC / 15wt% FEC
- 2.8 – 4.0 V, 1.5 mA/cm^2





- CE: 85 – 91%, VE: 87 – 83%, EE: ~76%
- Energy density delivery ~ 50 Wh L^{-1}
- Moderate capacity retention

Conclusions

- We have successfully demonstrated a hybrid Lithium-organic redox flow battery using ferrocene as the catholyte redox material.
- Structural modification increases the ferrocene solubility by 20 times.
- Li metal anode works at low Fc-TFSI concentration, while a hybrid anode enables decent cycling at high Fc-TFSI concentrations up to 0.8M.
- Flow cell tests produce stable cyclability with EE >75% and energy density of 50 Wh L^{-1}.
- Key challenge is long-term anode protection.

Acknowledgements

- Financial Support from financial support from the U.S. DOE’s Office of Electricity Delivery & Energy Reliability (OE, Dr. Imre Gyuk).

- Colleagues: Lelia Cosimbescu, Vincent Sprenkle, Wei Wang, Wu Xu, Jun Liu, M. Vijayakumar, Bin Li.

- Professor C. Austen Angell (Arizona State University) for helpful discussions and comments.

U.S. DEPARTMENT OF ENERGY

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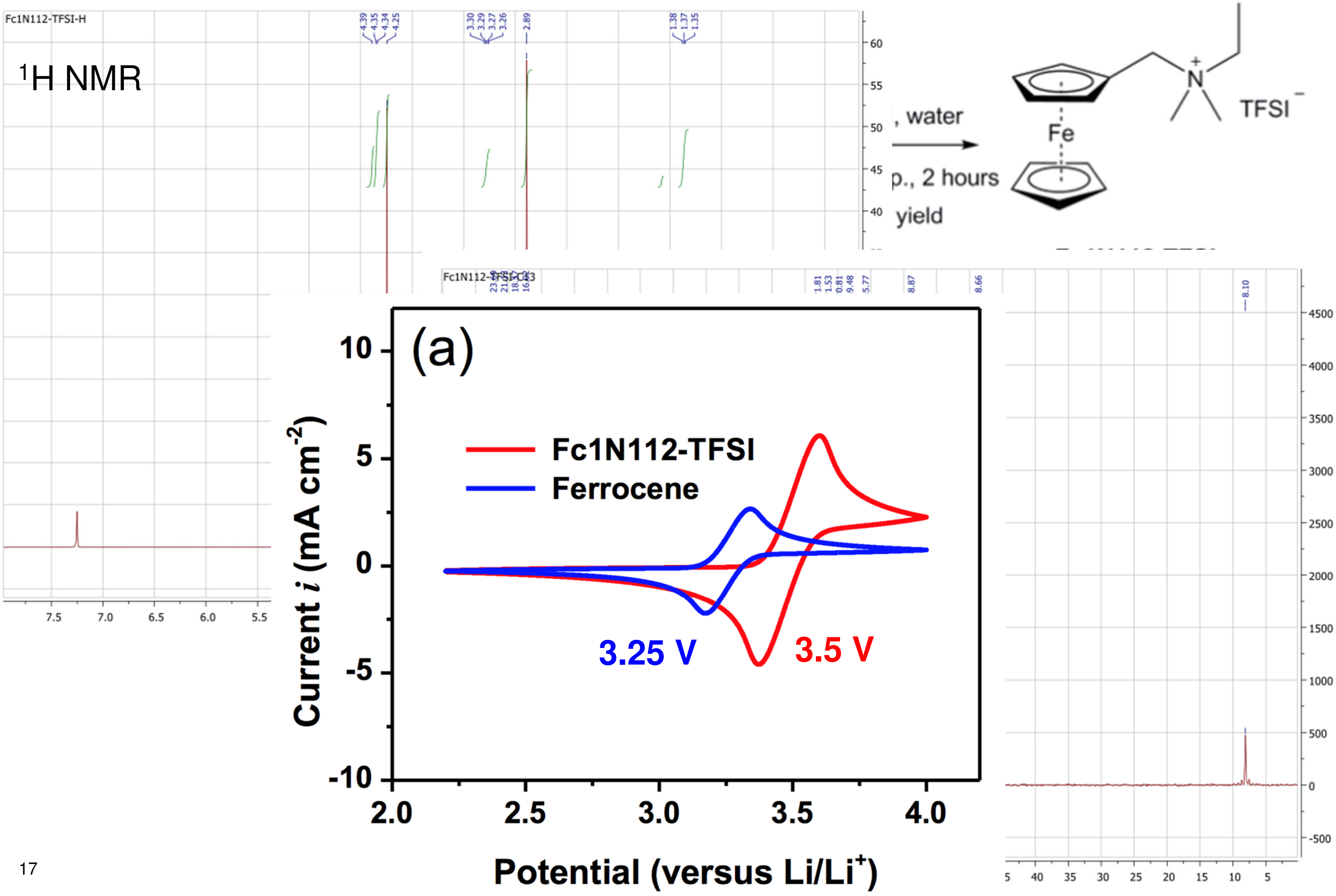
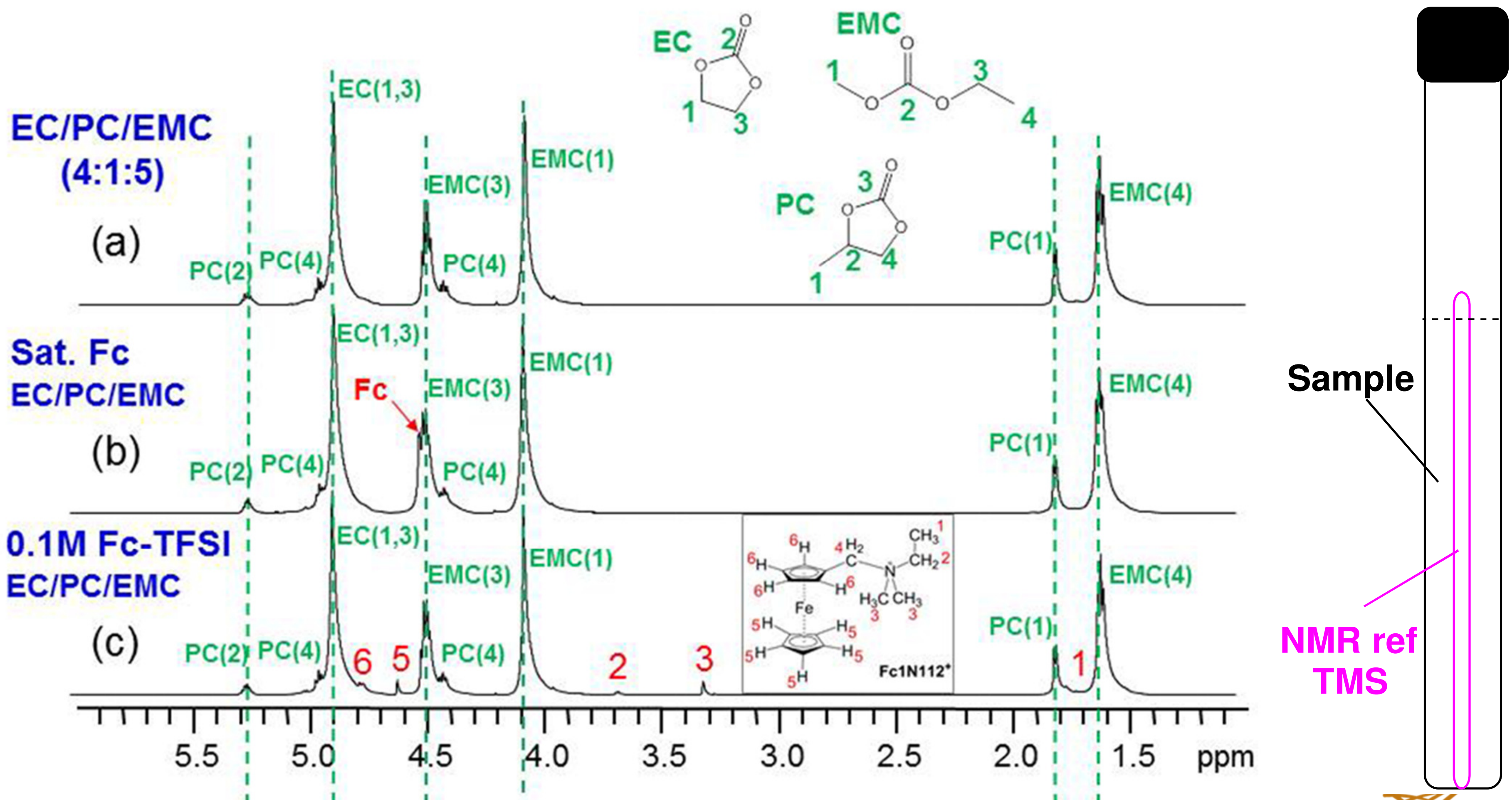
Thanks for your attention!

Functionalized Fc as Catholyte



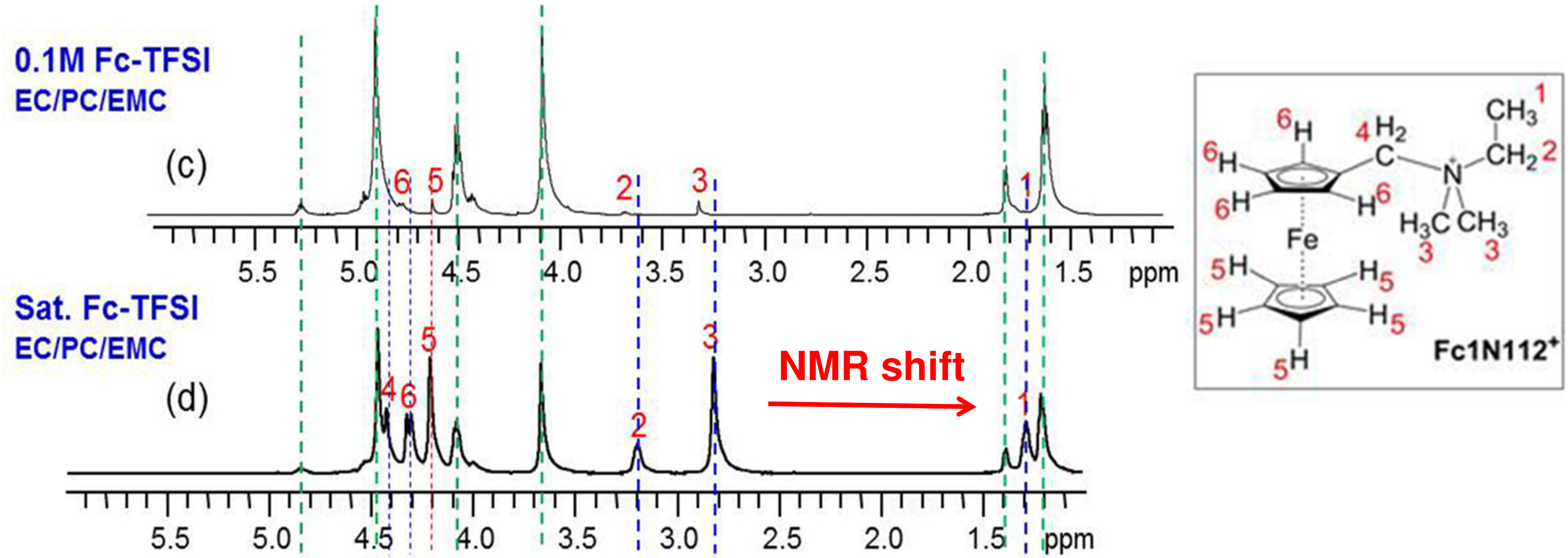
Understanding of Solvation Chemistry – NMR

❑ Co-axial NMR to investigate the cation – solvent interactions



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

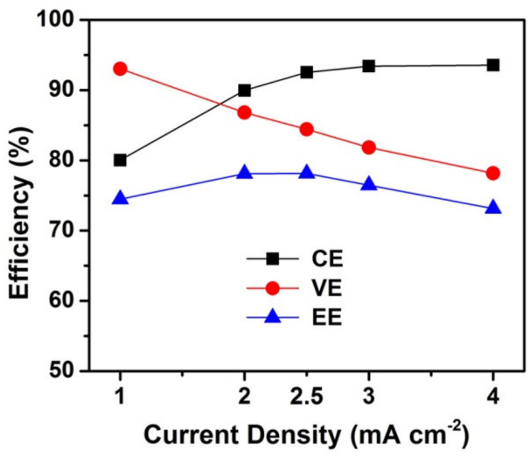
Understanding of Solvation Chemistry – NMR

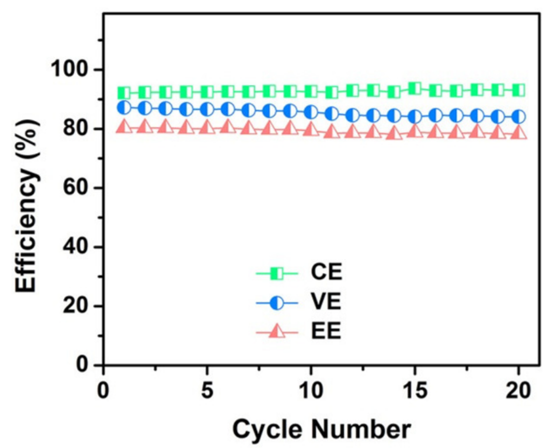


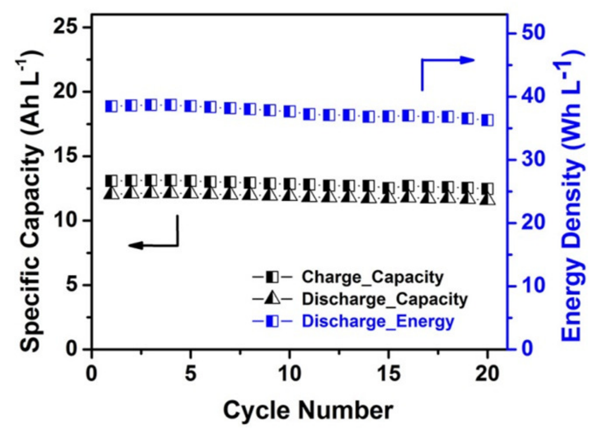
- ❑ Spacing between solvent peaks remain constant → no cation-solvent chemical binding
- ❑ Parallel upfield shift for both solvents and Fc-TFSI → enhanced solvation interactions
- ❑ Compared to solvent peaks, protons on unsubstituted ring remain unchanged while protons on substituted rings change significantly → solvation primarily on the cation
- ❑ Presence of the quaternary ammonium increases the solubility

Hybrid Anode Enables High Concentration Cycling

- ❑ 0.5M Fc-TFSI / 1.0M LiTFSI / EC-PC-EMC / 15wt% FEC
- ❑ 2.8 – 4.0 V, 2.5 mA/cm^2







- CE: 92%, VE: 87%, EE: 80%
- Energy density delivery ~ 38 Wh L^{-1}
- Remarkable capacity retention over 20 cycles

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