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High-Performance Nonaqueous Li-Organic Hybrid Redox Flow Batteries: A Pursuit of High Energy Density

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Pacific Northwest National Laboratory, Richland, WA 99354

Third International Conference and Exhibition on Materials Science & Engineering

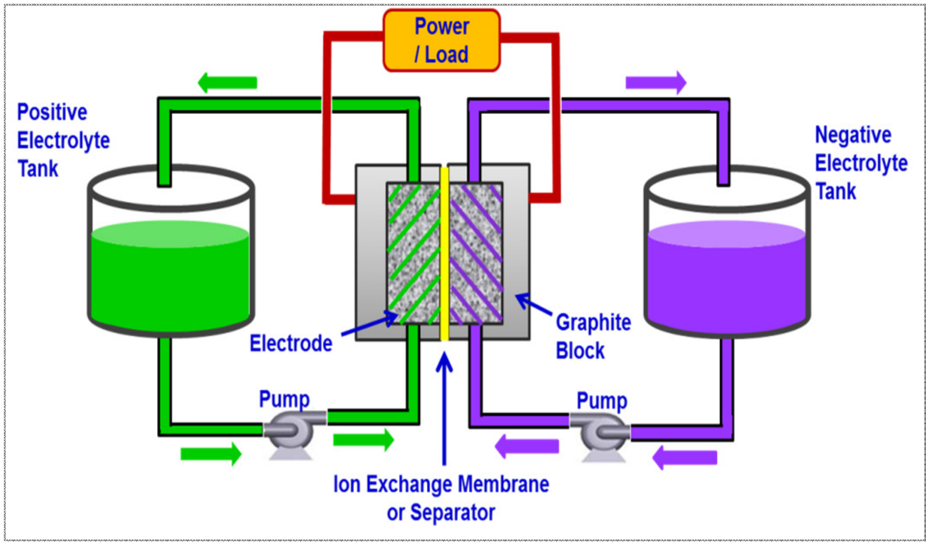
San Antonio, USA

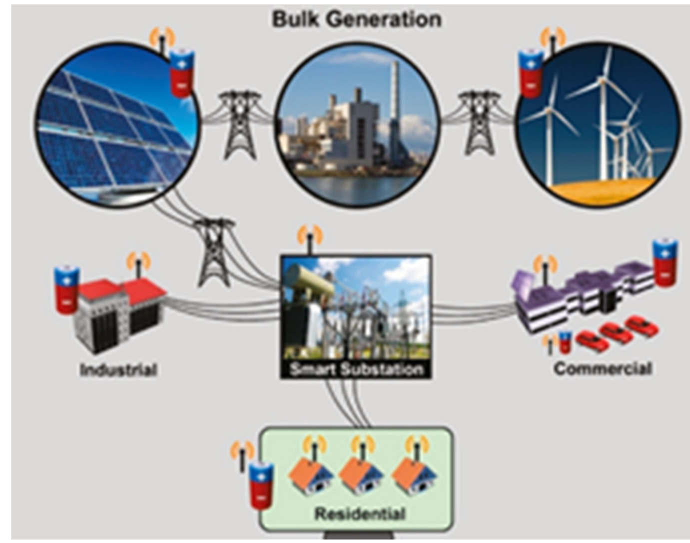
October 06, 2014

Outline of This Talk

- Background of redox flow battery
  - Aqueous vs non-aqueous
  - Our Strategy
- Flow cell performance and analysis
- Conclusion and future work

Redox Flow Battery

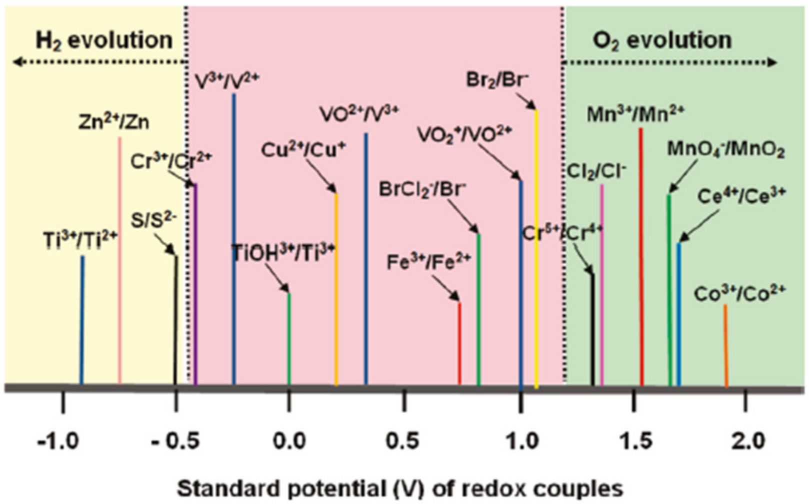




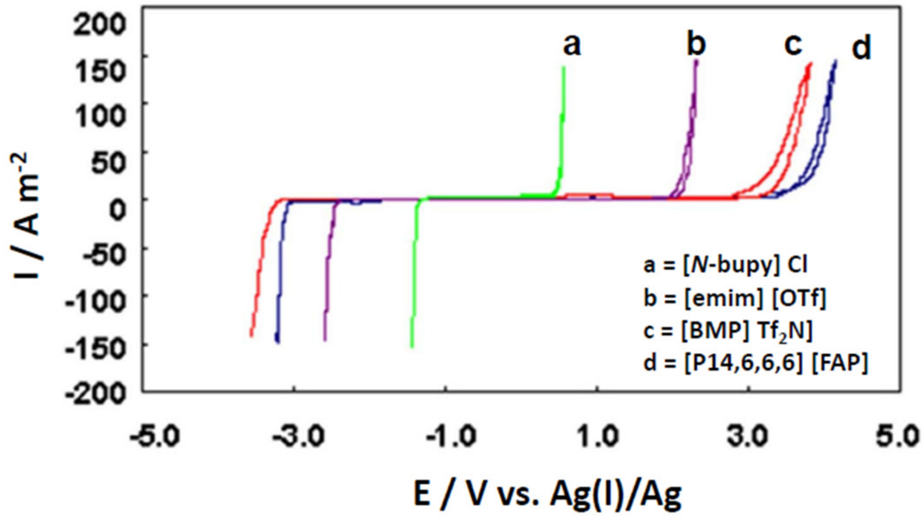
Wei et al *ECS Trans*. 2013, 45, 17-24
Yang et al *Chem. Rev.* 2011, 111, 3577-3613

- ❑ Separation of energy (electrolyte tank) and power (electrode)
- ❑ Excellent modularity and scalability
- ❑ Flexible design – Power/Energy ratio
- ❑ Active thermal management
- ❑ Stationary application – grid T&D stabilization and renewable integration

Electrolyte: Aqueous versus Non-aqueous



Yang et al *Chem. Rev.* 2011,111,3577-3613



http://aails.wikispaces.com/DSSC+Electrolyte+Requirements

- One of the most important parameters:

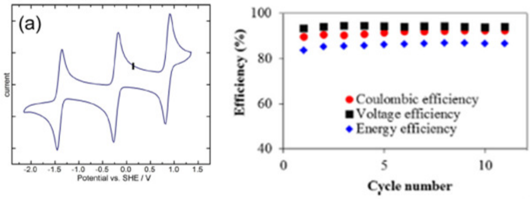
  Volumetric Energy density = n * Concentration * Voltage * F

- Conventional aqueous electrolytes are limited by narrow voltage window (usually <1.8V to avoid gas evolution)
- Non-aqueous electrolytes have wider electrochemically stable voltage window (2 – 6.5 V)
- Advantages: higher cell voltage, more redox couples available

Non-aqueous Redox Flow Batteries

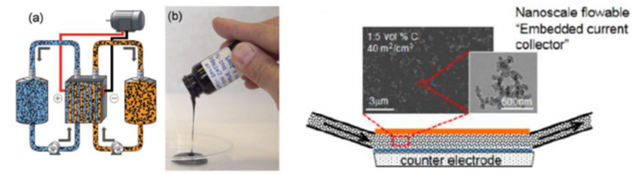
Non-aqueous redox flow batteries

Organometallics
(M=V,Cr,Mn,Co,Fe,Ni; L=acac,bpy,mnt)



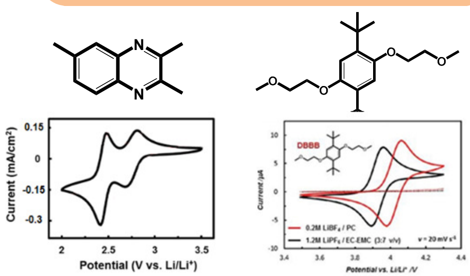
Anderson & Anstey et al *AEM* 2014, *4*, 1300566
Moon et al *J Power Sources 2014,* 255, 325-334

Semi-solid flow
LTO, LCO, LFP, Li-S



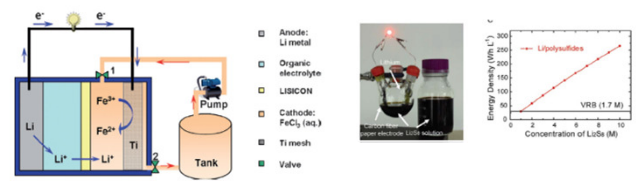
Chiang et al, *AEM* **2011**, *1*,511
Chiang et al, *Nano Lett* **2014**,*4*,14,2210–2218
Tarascon et al, *JECS* **2013**,*160(3)*,A516

All-organic flow



Brushett et al. *AEM 2012,2,1390-1396.*

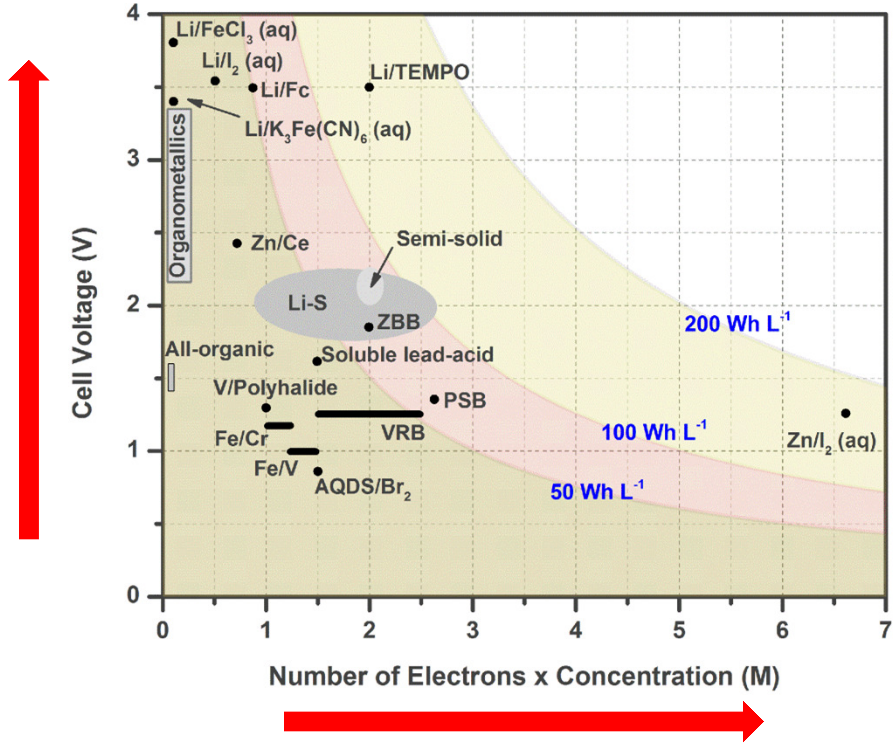
Hybrid Li-flow
Li-aqueous, Li-S



Zhou et al *ChemSusChem* 2011,4,1087-1090
Goodenough et al *J Mater Chem* 2011,21,10113-10117
Byon et al *AEM* 2013,3,1630-1635
Cui et al *EES* 2013,6,1552-1558

Current effort: Redox chemistry development

Status Summary of Flow Batteries in Energy Density

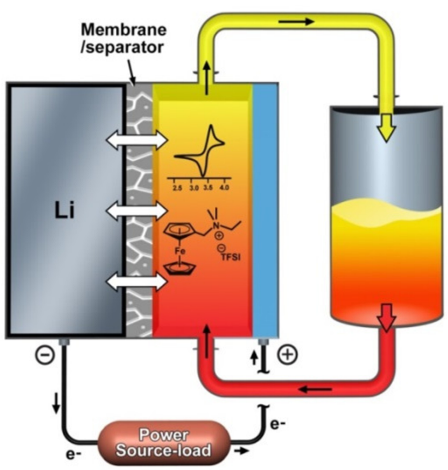


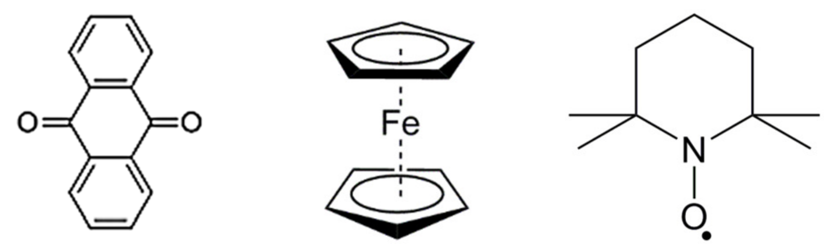
Challenges in current non-aqueous redox flow batteries

- **Demonstrated low energy density (~ 0.1M → < 10Wh/L)**
- **Side reactions of organic redox species**
- **Low current density (0.05 – 0.5 mA/cm²)**
- **No flow cell test data in many systems**

Our Strategy – Hybrid Lithium/Organic Flow Battery

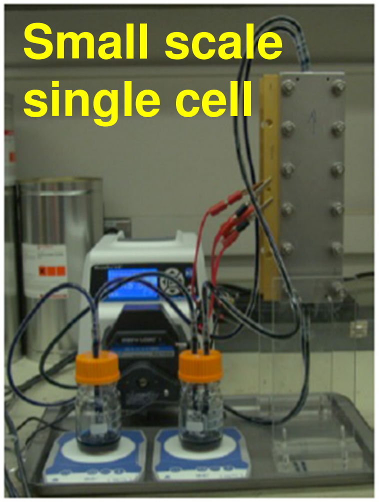
- ❑ **Cell voltage**
  - ➢ Li metal anode to push down anode redox potential
  - ➢ High redox potential electroactive organic compound
- ❑ **Concentration of electroactive materials**
  - ➢ Highly soluble organic compounds
  - ➢ Rational molecular engineering to increase solubility
  - ➢ Anthraquinone, Ferrocene, TEMPO
- ❑ **Hybrid Li/organic nonaqueous redox flow battery**
- ➢ Membrane – free cell design → high conductivity
- ➢ SEI to reduce self-discharge



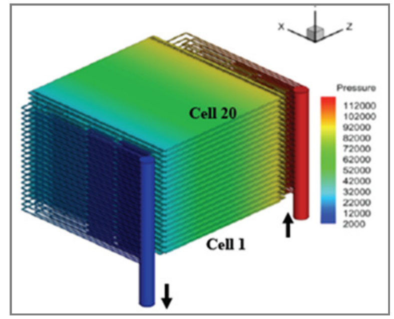


W. Wang et al *Chem. Common.* 2012, 6669.
X. Wei et al *Adv. Energy Mater.* 2014, online.
X. Wei et al *Adv. Mater.* 2014, accepted.

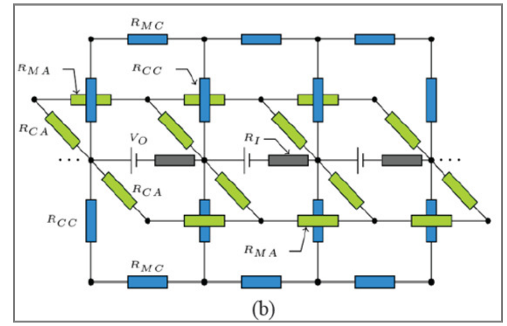
R&D Capabilities at Pacific Northwest National Lab

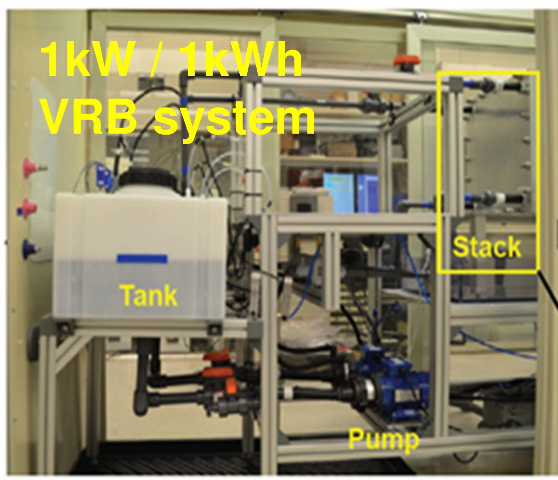


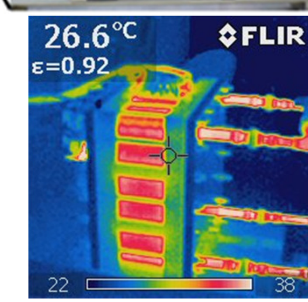
Flow field model



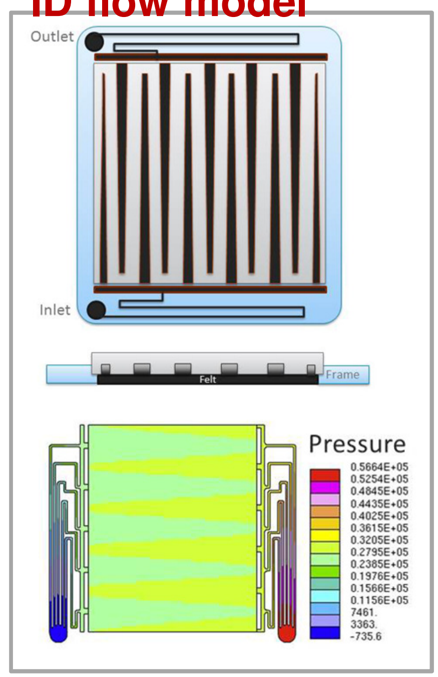
Shunt current model



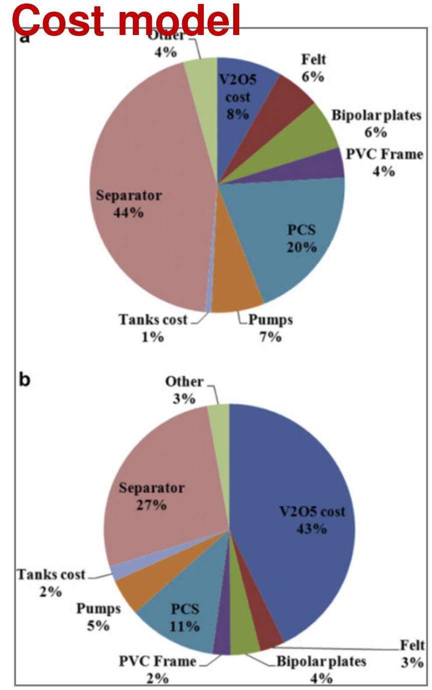




ID flow model

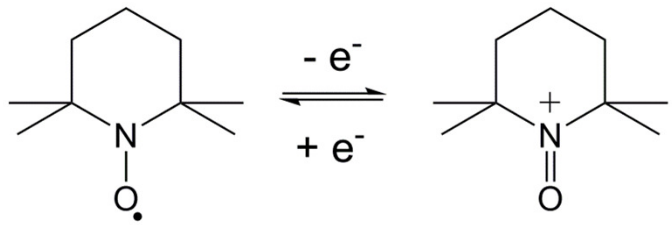


Cost model



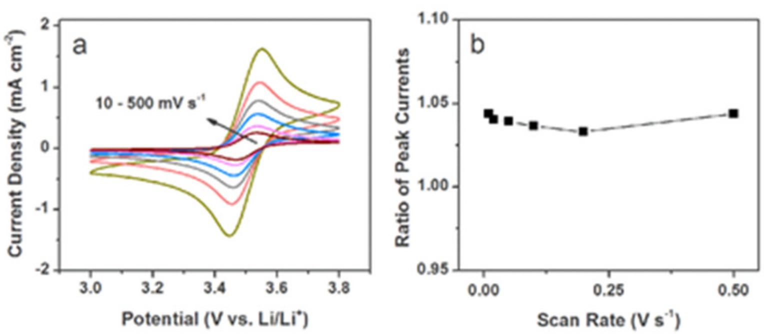
Viswanathan et al J. Power Sources 2014, 247, 1040-1051

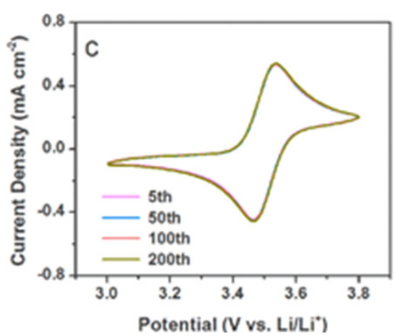
TEMPO: High Cell Voltage & High Solubility

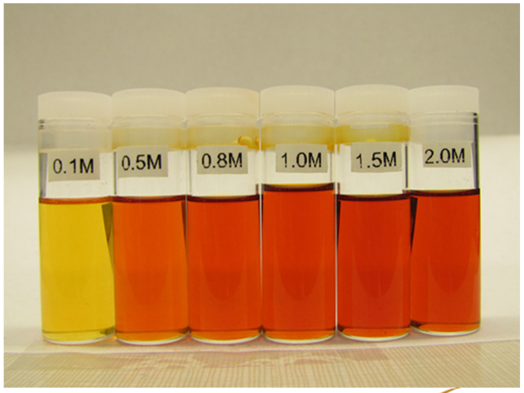


TEMPO   oxoammonium

- ❑ 5mM TEMPO / 1.0M LiPF6 / EC-PC-EMC (4-1-5 wt)
- ❑ Li|TEMPO: 3.5 V
- ❑ Excellent reversibility and stability of redox reaction





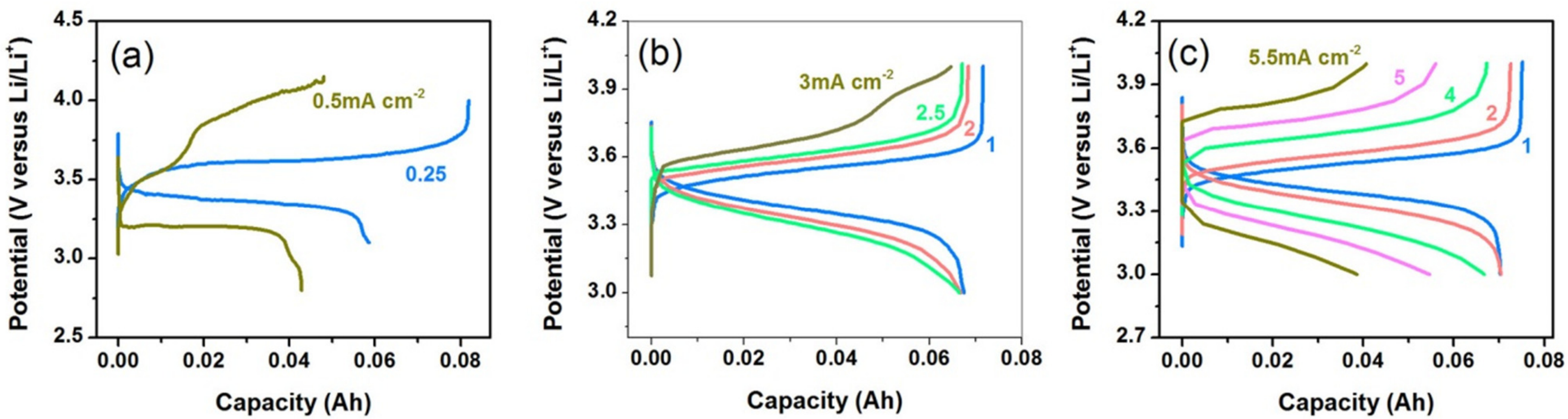


- ❑ 5.2M / EC-PC-EMC (4-1-5)
- ❑ 2.0M / 2.3M LiPF6 / EC-PC-EMC
- ❑ Theo. energy density: 188 Wh/L

Li Anode Protection I: SEI – Stabilizing Additive

- 0.1M organic
- SEI – stabilizing additive is essential to achieve cycling at decent current density

No additive | 2wt% VC | 2wt% FEC



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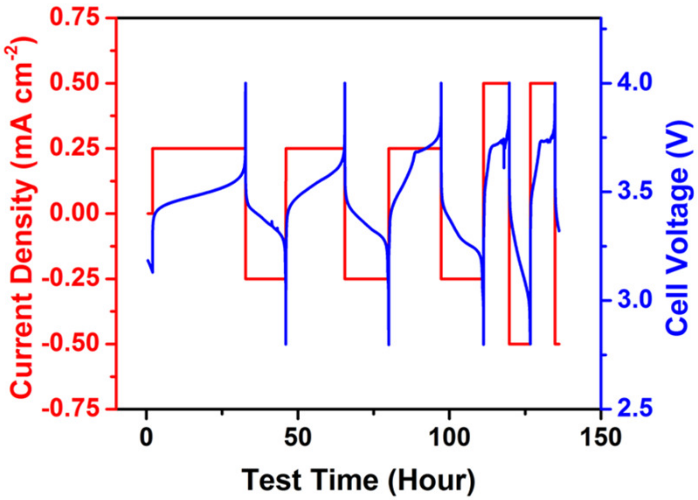
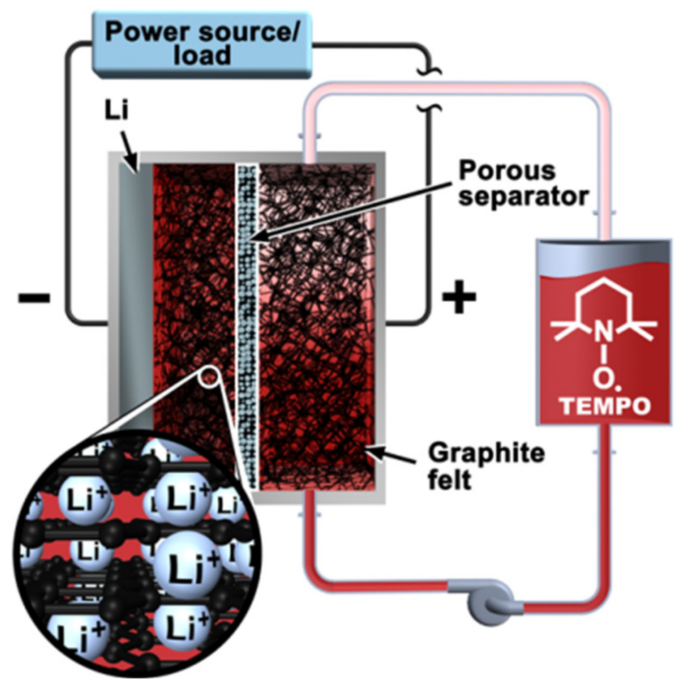
Li Anode Protection II: Li-Graphite Hybrid Anode

- Flow cell was not successful even at 0.2M organic with 15wt% FEC due to excessive Li dendrite growth.
- Li-graphite hybrid anode
- Change Li deposition/stripping chemistry to Li^+ ion intercalation

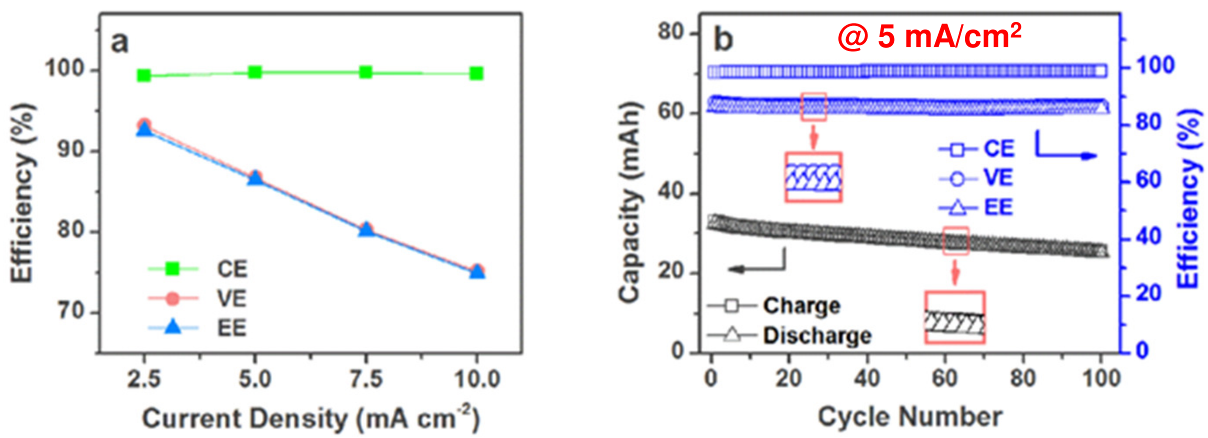
  → decreased involving of Li metal
- Hybrid anode is a shortened cell → not sacrificing cell potential





Li|TEMPO Flow Cell Tests

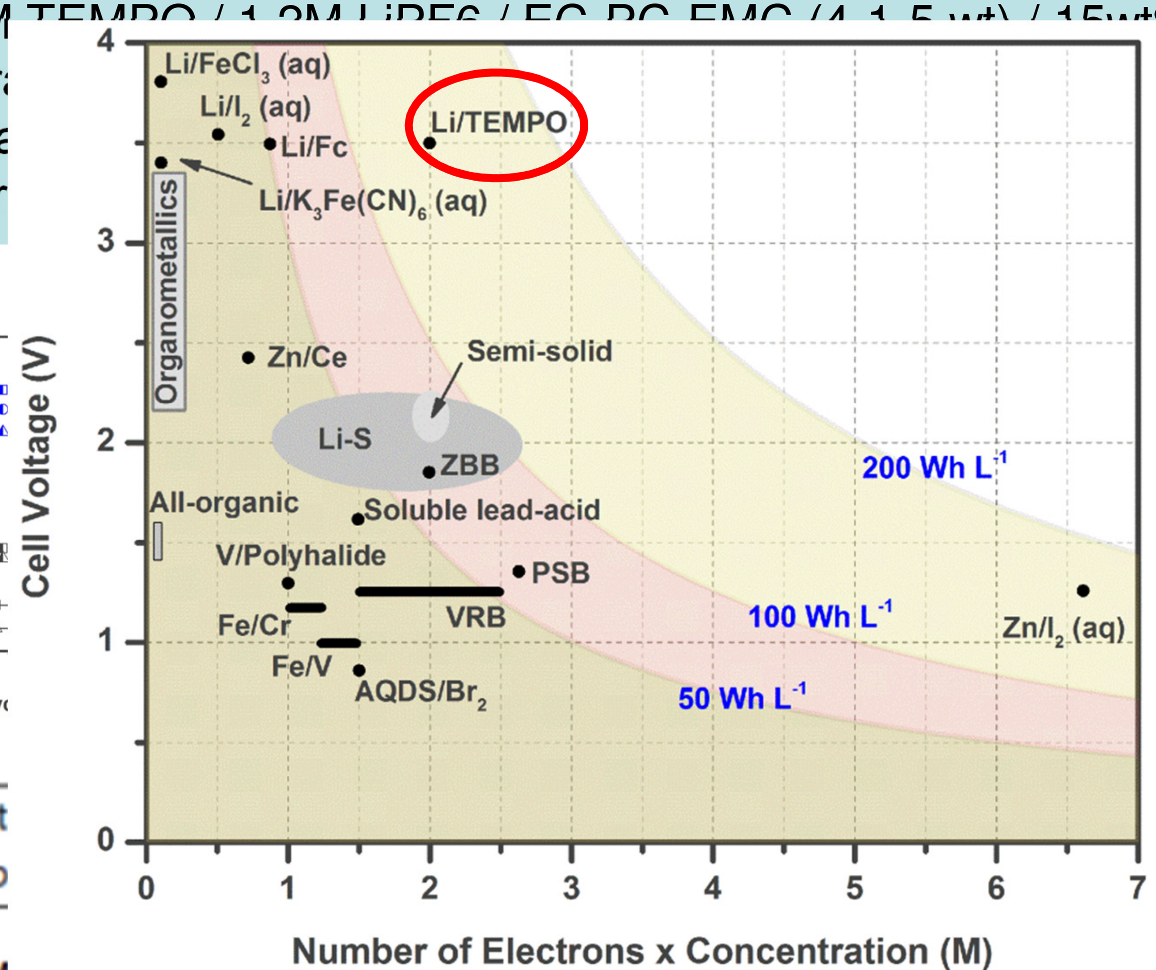
- 0.1M TEMPO / 1.0M $LiPF_6$ / EC-PC-EMC (4-1-5 wt) / 15wt% FEC
- Li-graphite hybrid anode
- Voltage range: 3.0 – 4.0 V

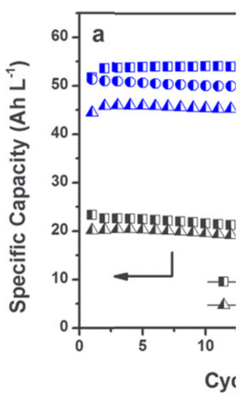


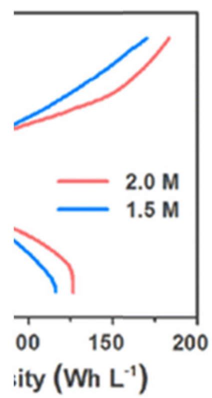
	Li|TEMPO	Other nonaqueous systems
Current density (mA/cm^2)	10	0.5
CE / EE	99% / >75%	<60%
Capacity retention	98% for 100 cycles	Serious capacity fading

Li|TEMPO Flow Cell Tests

- 0.8M TEMPO / 1.2M LiPF6 / EC-PC-EMC (4-1-5 wt) / 15wt% FEC
- Li-gr
- Capa
- Ener



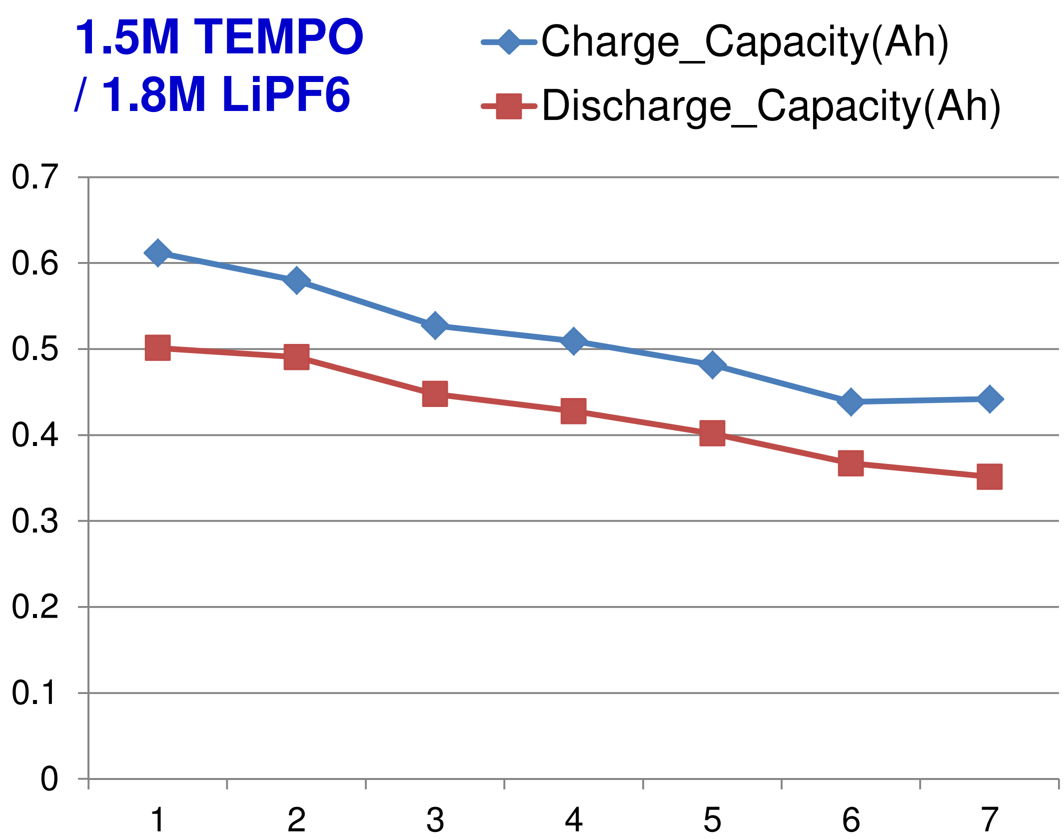




Elect Comp					EE
0.8 M/1.2 M	5.0	80 / 64	91%	85%	76%
1.5 M/1.8 M	2.5	170 / 119	85%	81%	68%
2.0 M/2.3 M	1.0	183 / 126	84%	82%	69%

Key Challenges of Li|Organic Systems

- ❑ Poor long-term Li anode protection at high current density
- ❑ Trade-off between crossover self-discharge and cycle overpotential
  → to operate at optimal current density (i.e. CE and VE)



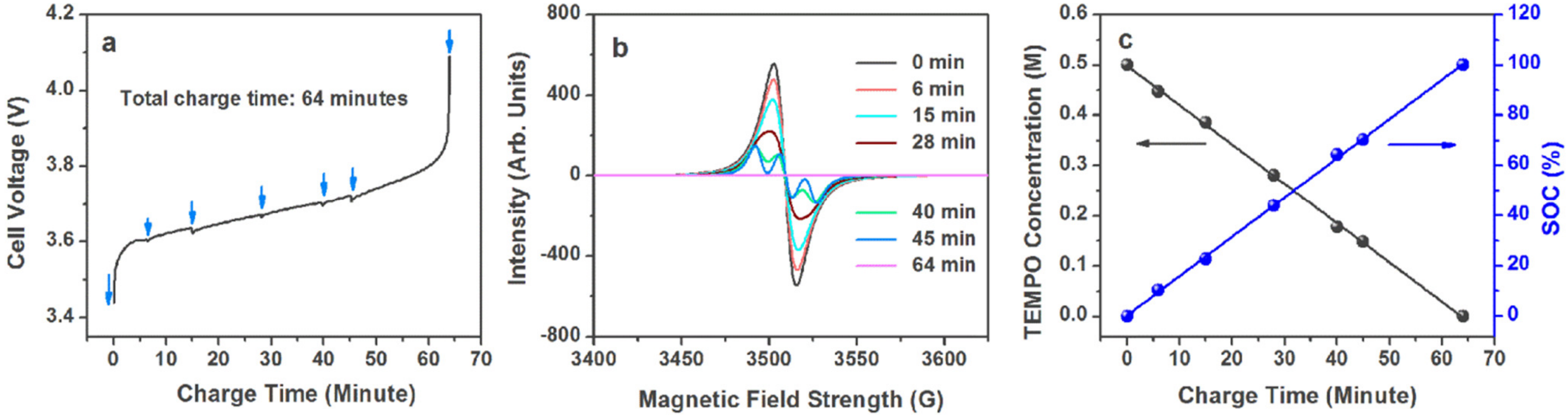
Li|TEMPO: State-of-Charge Monitoring

- State-of-Charge (SOC) definition (in terms of cathode side):

SOC = [oxidized species]/[overall species]

= [oxoammonium] / [initial] = ([initial] – [TEMPO]) / [initial]

- Electron spin resonance (ESR) to measure [TEMPO] due to an unpaired electron



Conclusions

- We have successfully demonstrated hybrid Li-organic redox flow batteries based on several organic candidates.
- Hybrid anode and electrolyte additive provide synergistic protection to the Li metal anode, making flow cell tests at high catholyte concentrations feasible.
- Li|TEMPO delivers an energy density of 126Wh/L, an order of magnitude higher than other nonaqueous flow chemistries.
- Key challenge is long-term anode protection. Alternative anode candidates are being studied.

Acknowledgements

- Financial Support from financial support from the U.S. DOE's Office of Electricity Delivery & Energy Reliability (OE): Dr. Imre Gyuk.
- PNNL's William R. Wiley Environmental Molecular Sciences Laboratory (EMSL) for ESR measurement.
- Team members: Vincent Sprenkle, Wei Wang, Wu Xu, Jun Liu, Tianbiao Liu, Bin Li, M. Vijayakumar, Yuyan Shao, Jie Xiao, etc.

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