Non-Aqueous Solvents and Supporting Salts – Improving Redox Flow Battery Electrolytes

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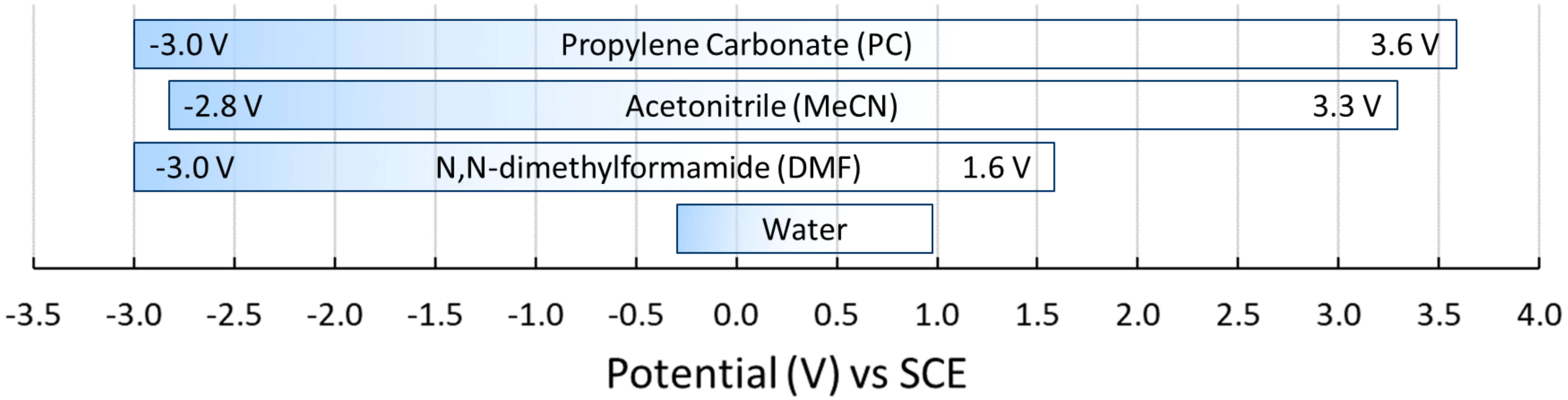
Workshop on Non-Aqueous Flow Batteries

2019 January 30

Non-aqueous Solvents

- High potential redox flow batteries through wide voltage window electrolytes

- Key properties for suitable solvents
  - Voltage window
  - Viscosity (conductivity)
  - Solvency

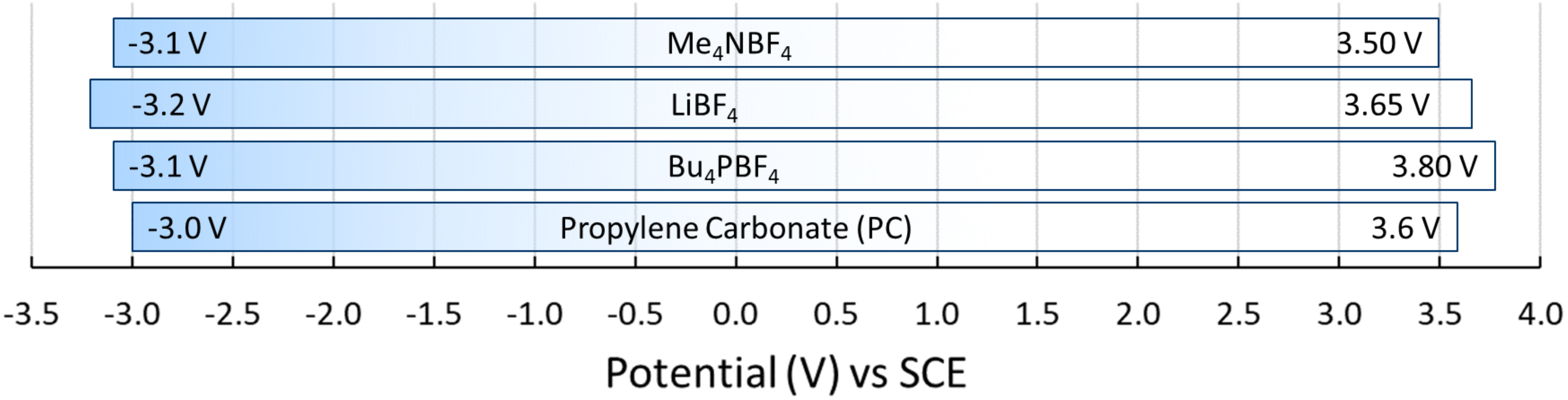


1. Ue, M; et al. *J. Electrochem Soc.* **1994**, *141* (11), 2989-2996
Supporting salt: 0.65 M $TEABF_4$

Supporting Salts

- Supporting salts are required for sufficient conductivity
  - Organic solvents have multiple order of magnitude lower conductivities than water[2]

- Key properties for suitable supporting salts
  - Voltage window
  - Ionic radii (limiting conductivity)
  - Solubility



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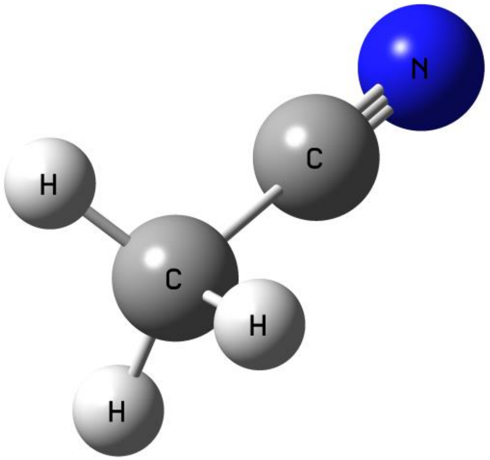
2. Gong, K.; et al. *Energy Environ. Sci.* **2015**, *8*, 3515-3530

Electrolyte: PC

Commonly used Electrolytes

- Key properties for suitable electrolytes
  - Voltage window
  - (Limiting) Conductivity
  - Solubility
  - Viscosity
  - Critical concentration



- Polar, aprotic solvents are most commonly used[3,4]
  - Acetonitrile provides the best combination of key factors[2]

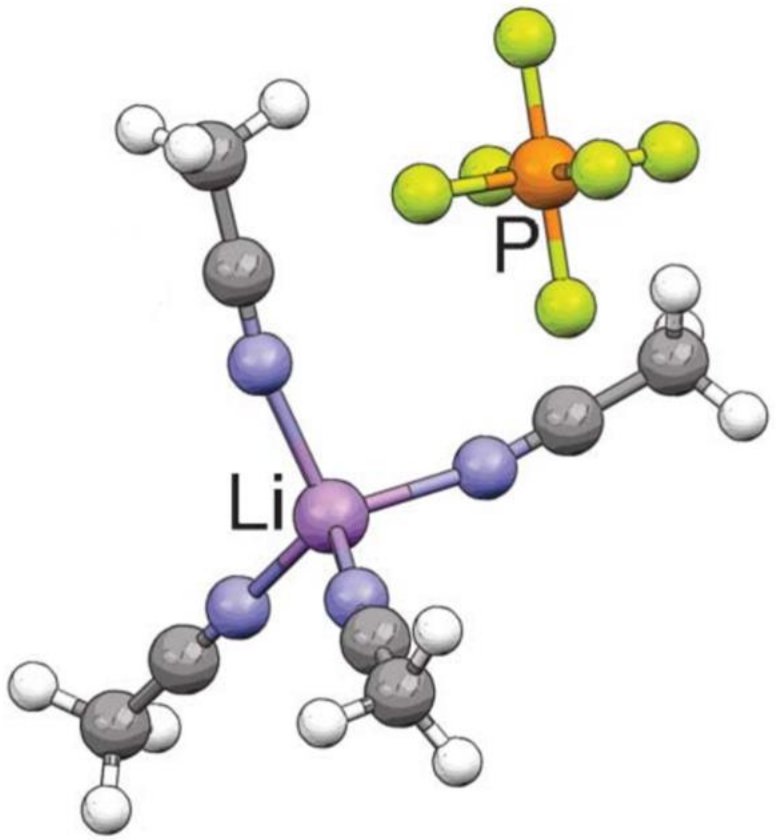
- Less standardization among supporting salts
  - Lithium and alkylammonium salts both see use
  - Anion choice among supporting salts is generally less impactful on electrolyte properties

2. Gong, K.; et al. *Energy Environ. Sci.* **2015**, *8*, 3515-3530
3. Zhang, J.; et al. *J. Phys. Chem. C*, **2018**, *122*, 8159-8172
4. Sevov, C.; et al. *J. Am. Chem. Soc.*, **2015**, *137*, 14465-14472

Supporting Salt choice for Acetonitrile

- Lithium vs Alkylammonium
  - Similar voltage windows[1]
  - Similar range of conductivities and solubilities depending on anion choice
  - Alkylammonium salts generally have higher critical concentrat

- Lithium and other small cations are strong Lewis acids
  - Strong interactions with acetonitrile[5,6]
  - Strong interactions with active material anions[3,7]



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3. Zhang, J.; et al. *J. Phys. Chem. C*, **2018**, *122*, 8159-8172

5. Seo, D. M.; et al. *RSC Adv.*, **2012**, *2*, 8014-8019

6. Yamada, Y.; et al. *J. Am. Chem. Soc.*, **2014**, *136* (13), 5039-5046

7. Izutsu, K.; *Electrochemistry in Nonaqueous Solutions*, 2nd ed.; Wiley-VCH, **2009**

Current Electrolyte Limitations

- Key properties for suitable electrolytes
  - Voltage window (> 6.0 V for MeCN)[1]
  - Conductivity (55.5 mS/cm for 1 M Et_4NBF_4 in MeCN)[7]
  - Solubility (4.2 M LiTFSi in MeCN)[6]
  - Viscosity (0.75 cP for 1 M LiTFSi in MeCN)[6]
  - Critical concentration (> 2.0 M for Et_4NBF_4 in PC)[1]

- In the absence of active materials, non-aqueous electrolytes have the necessary performance for flow battery use

- Competing solubility of supporting salts and active materials leads to poor experimental performance

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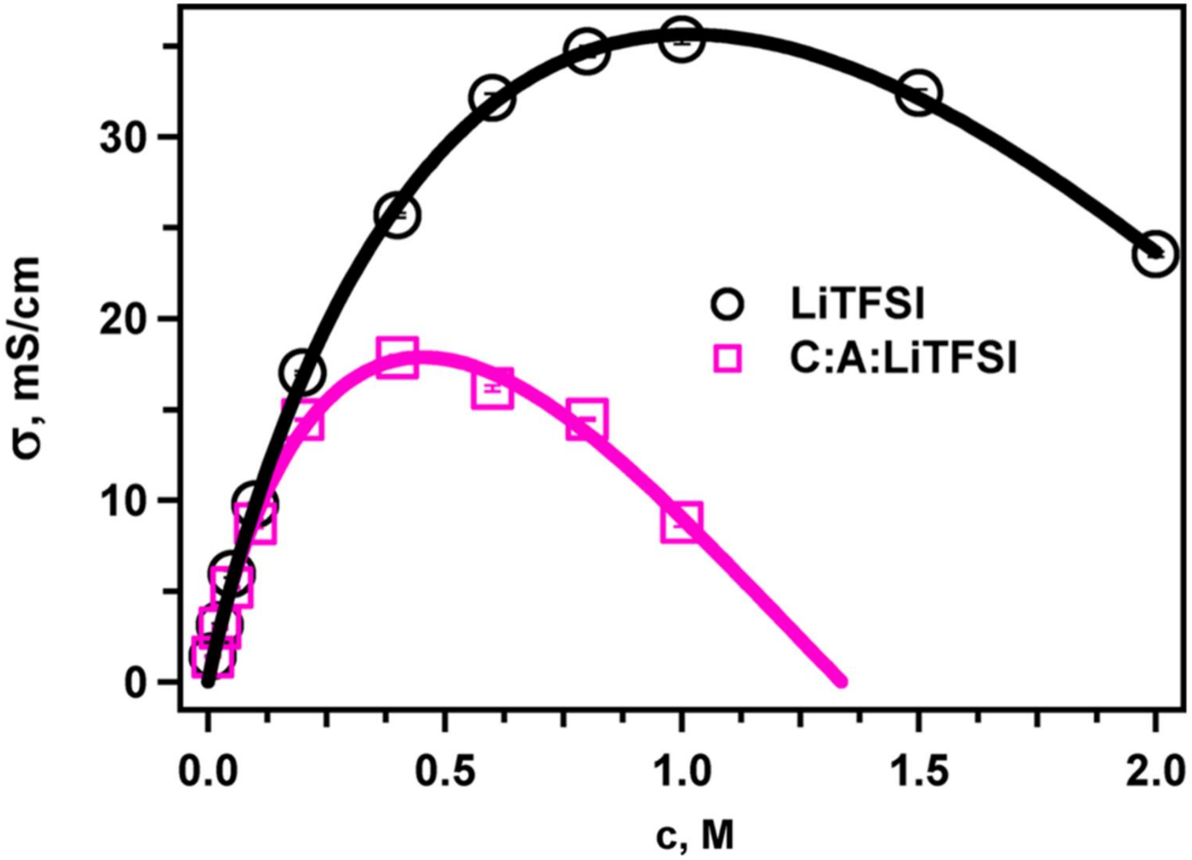

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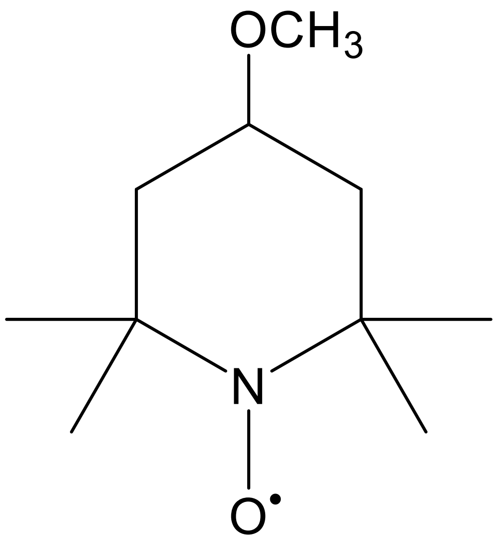
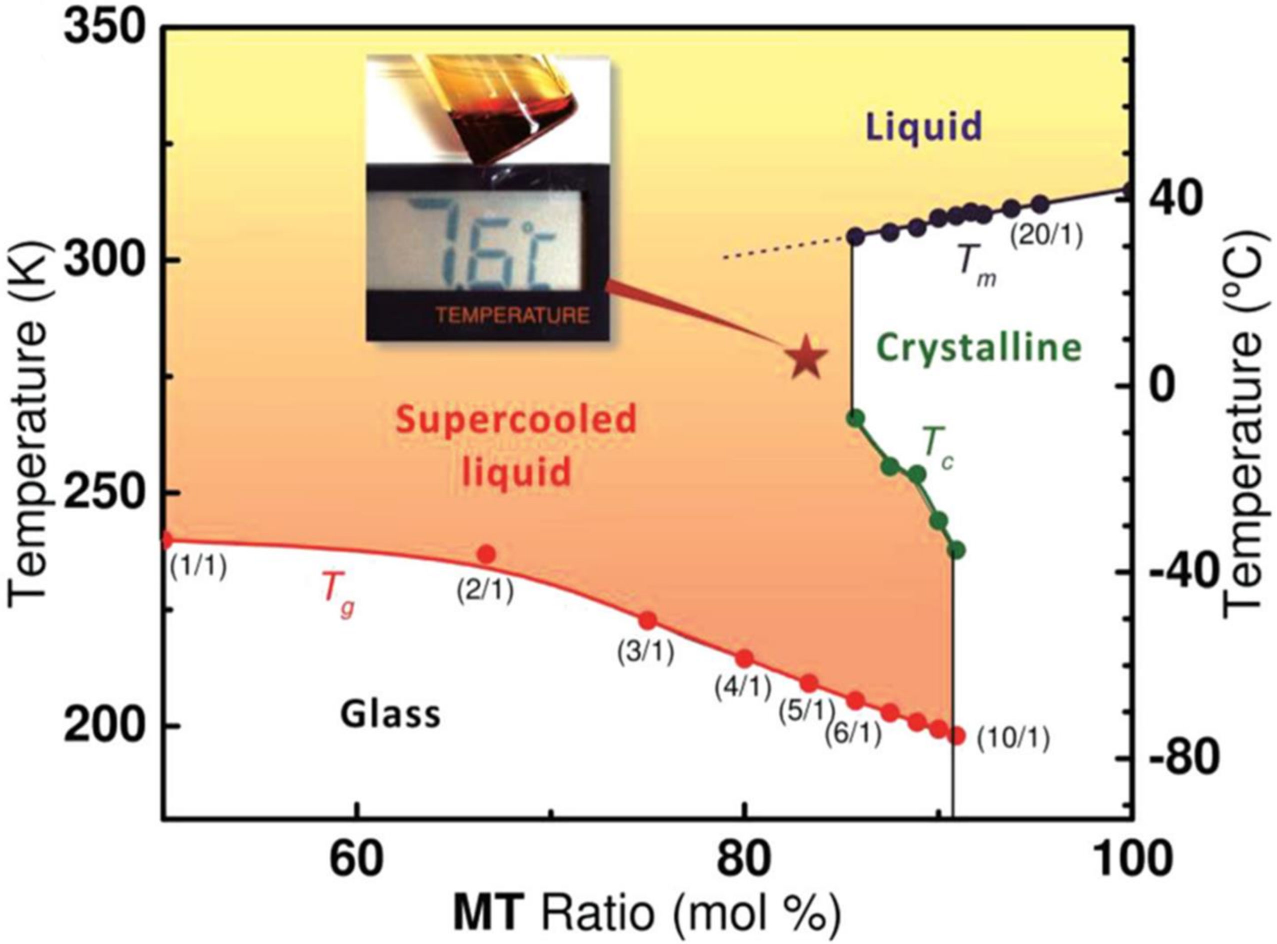
Ionic Liquids as Electrolytes

- Avoids competing solubility between active materials and supporting salt
  - Poor conductivities (< 5 mS/cm)[8,9]
  - High viscosities (> 100 cP)[8,9]





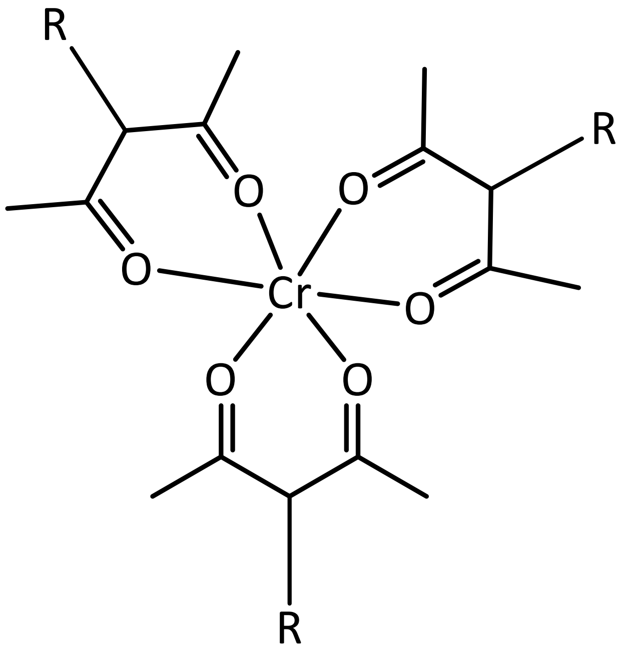
8. Takechi, K.; et al. *Adv. Mater.*, **2015**, *27*, 2501-2506

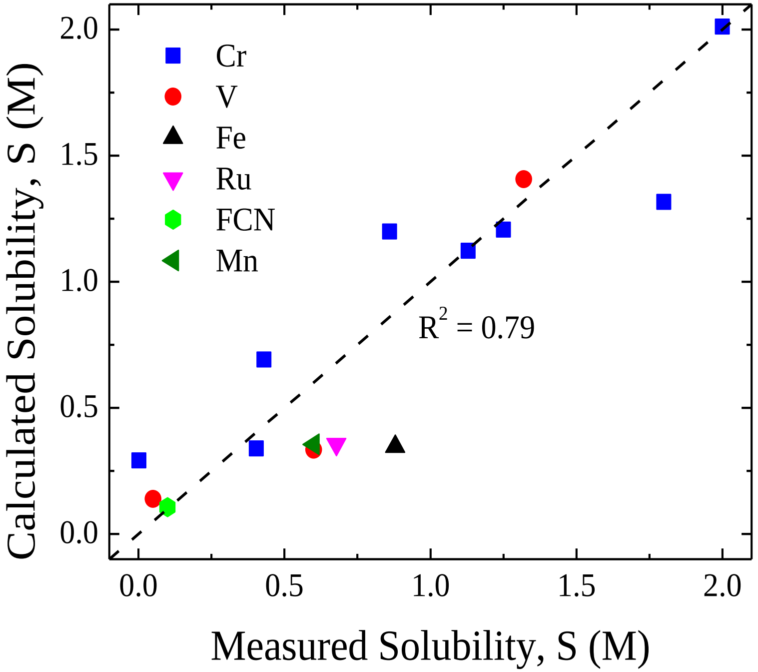
9. Anderson, T. M.; et al. *Dalton Trans.*, **2010**, *39*, 8609-8612

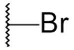
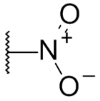
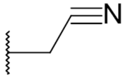
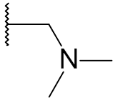
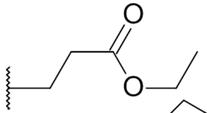
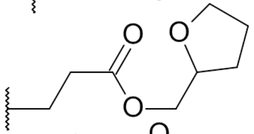
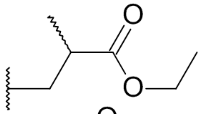
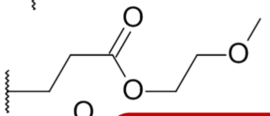
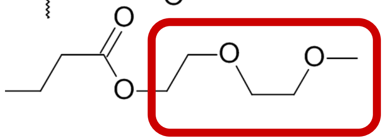
Design of Metal Coordination Complexes for Solubility

- Metal and ligand substitutions
  - Active material solubility can be greatly improved or hindered
  - Polyethylene glycol addition greatly improves solubility

$$Solubility = \alpha(\Delta G_{sol})^{1.8} + \beta\mu^{2.5}$$





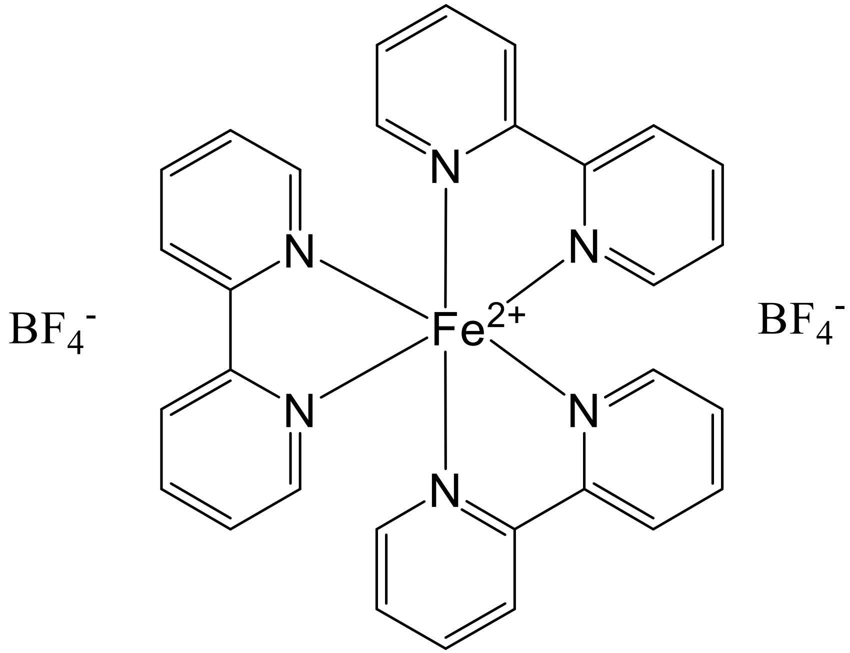
Functional Group (A)	Solubility (M)
-	0.404±0.002
	0.00212±0.00002
	0.0547±0.0003
	0.43±0.02
	1.92±0.04
	0.86±0.05
	1.13±0.01
	1.25±0.01
	1.8±0.04
	>1.8

10. Suttil, J. A.; et al. *J. Mater. Chem. A,* **2015**, *3*, 7929-7938
11. Kucharyson, J. F.; et al. *J. Mater. Chem A*, **2017**, *5*, 13700-13709
12. Milshtein, J. D.; et al. *ChemSusChem*, **2017**, *10*, 2080-2088
13. Wei, X.; et al. *Adv. Energy Mater.*, **2015**, *5*, 1400678

Design of Metal Coordination Complexes for Solubility

- Metal and ligand substitutions
  - Active material solubility can be greatly improved or hindered
  - Polyethylene glycol addition greatly improves solubility

- Using ionic active species
  - Removes the need for a supporting salt



- Maximum solubilities ~ 2 M in acetonitrile

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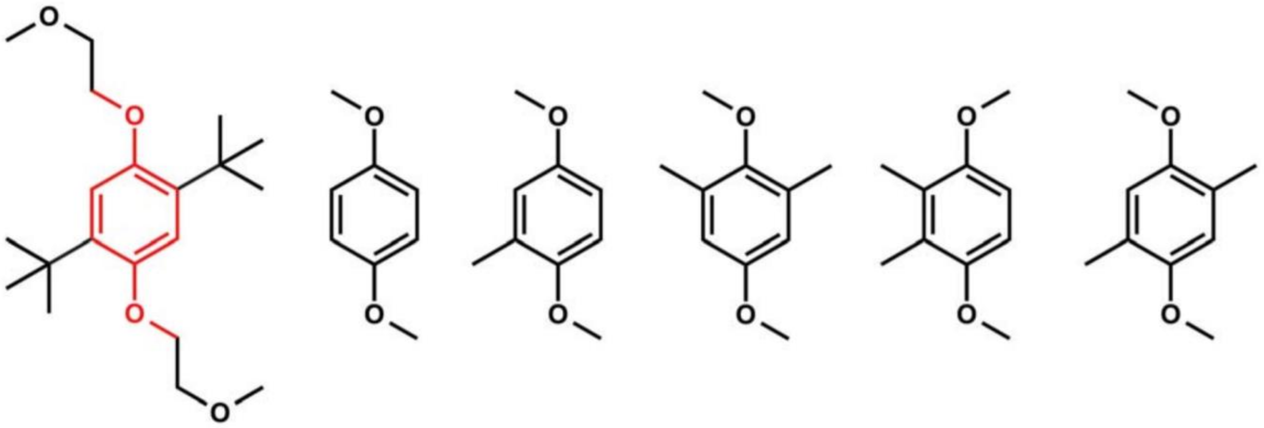
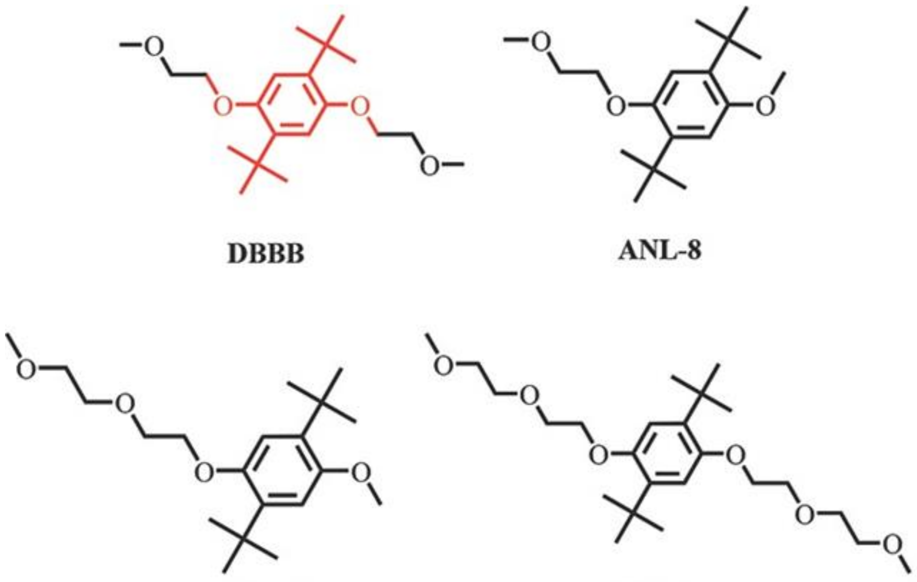
Design of Redox Active Organics for Solubility

- Functional group modification
  - Polyethylene glycol addition
  - Subtractive modification





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14. Milshtein, J. D.; et al. *Energy Environ. Sci.*, **2016**, *9*, 3531-3543
15. Huang, J.; et al. *Adv. Energy Mater.*, **2014**, *5* (6), 1401782
16. Huang, J.; et al. *J. Mater. Chem. A*, **2015**, *3*, 14971-14976
17. Wei, X.; et a. *Adv. Mater.*, **2014**, *26*, 7649-7653

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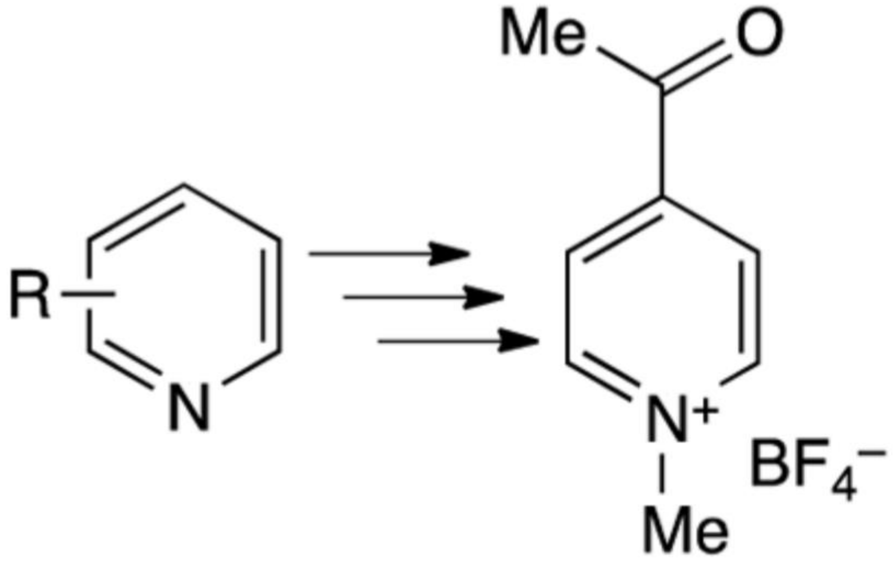
- Ionic active species



- Maximum solubilities ~ 2.5 M in acetonitrile
  - TEMPO has > 2 M solubility in Li^+ electrolytes[18]

4. Sevov, C. S.; et al. *J. Am. Chem. Soc.*, **2015**, *137*, 14465-14472
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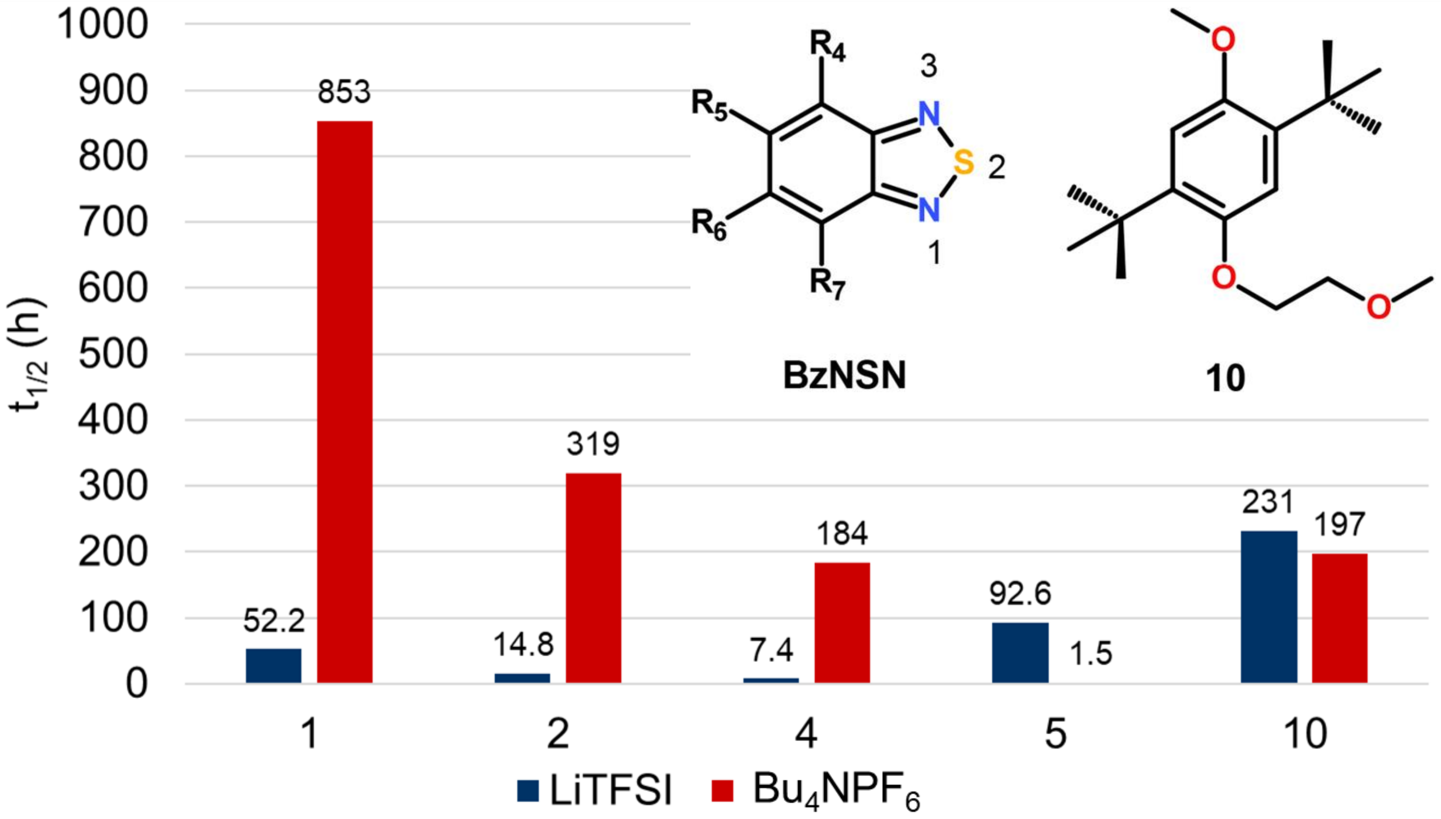
Electrolyte effects on Stability

- Lithium/MeCN electrolytes exhibit negative impacts on anion stability[18]
  - Acetonitrile protonates anolyte radicals[18,19]
  - Lithium has strong interactions with anolyte radicals[3,7]



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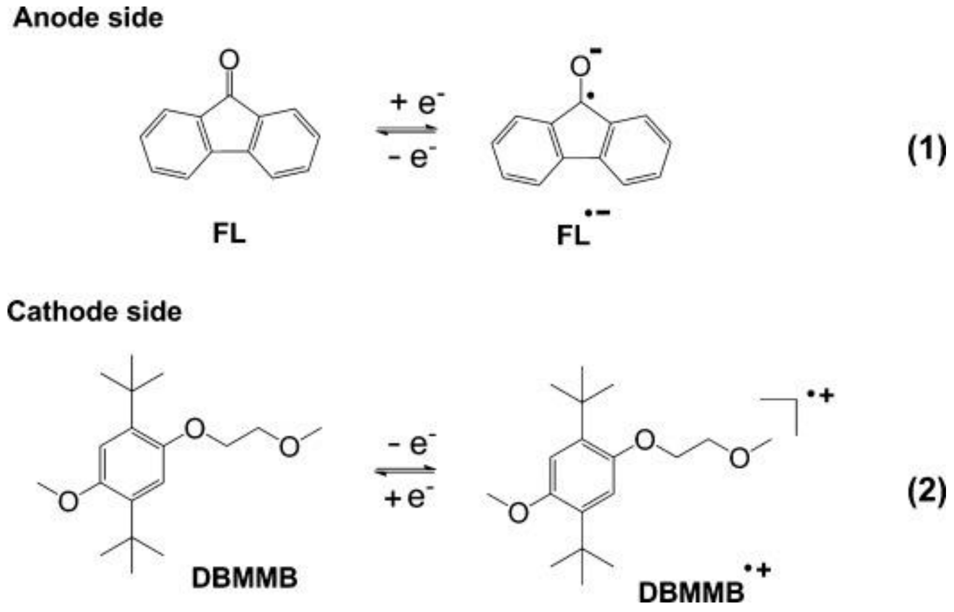
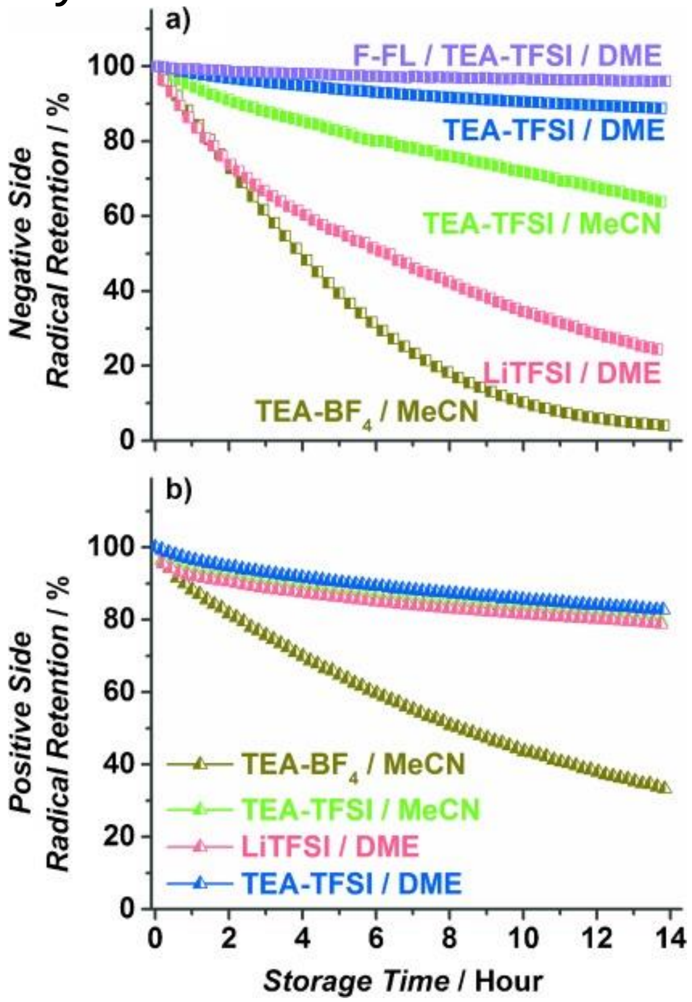
- Anolytes are more strongly affected by electrolyte choice[19,20]
  - Effects are chemistry dependent





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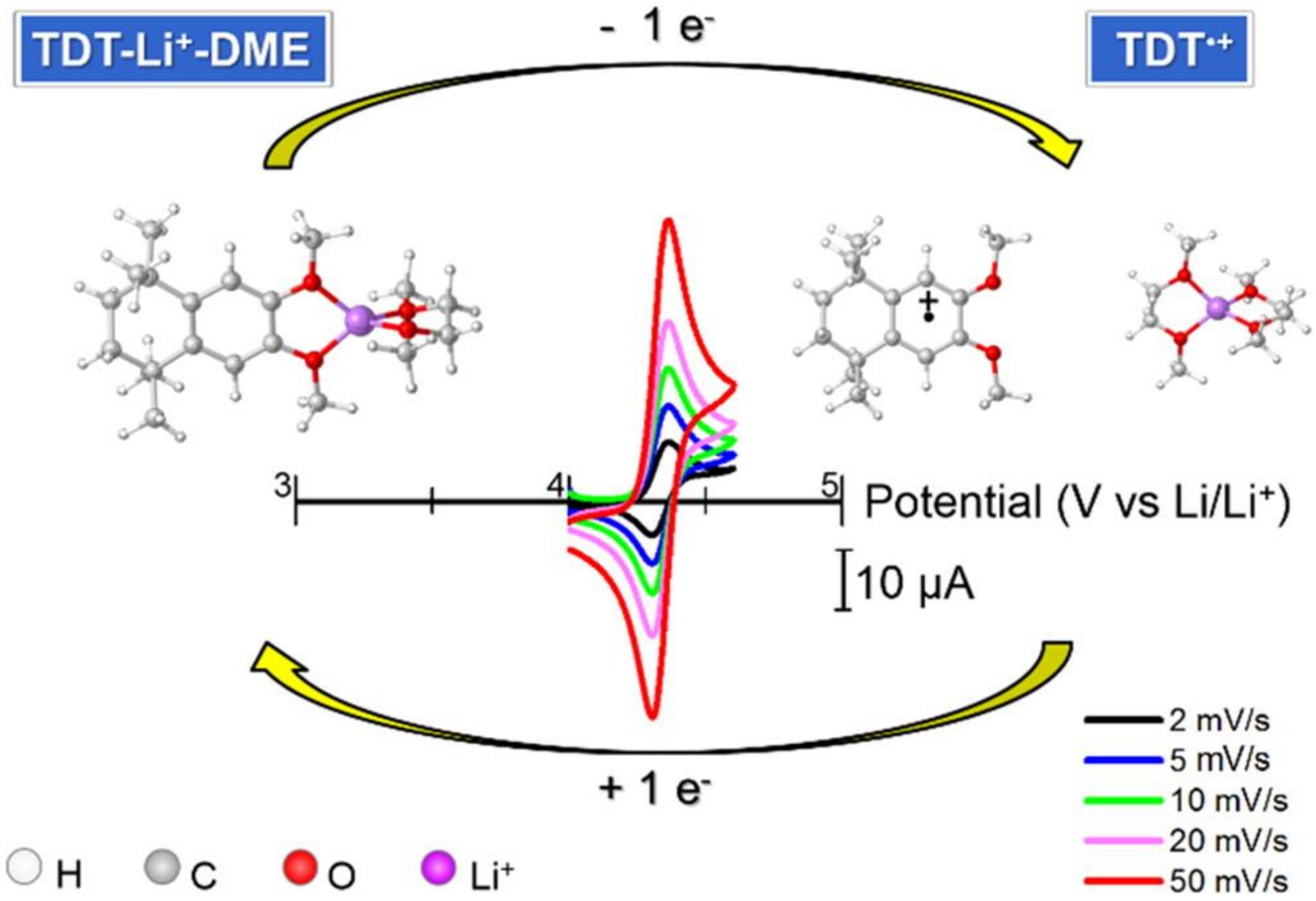
Electrolyte effects on Cyclability

- Lithium ions also coordinate to catholytes, but provide improved cyclability[20]
  - Greatly improved efficiencies



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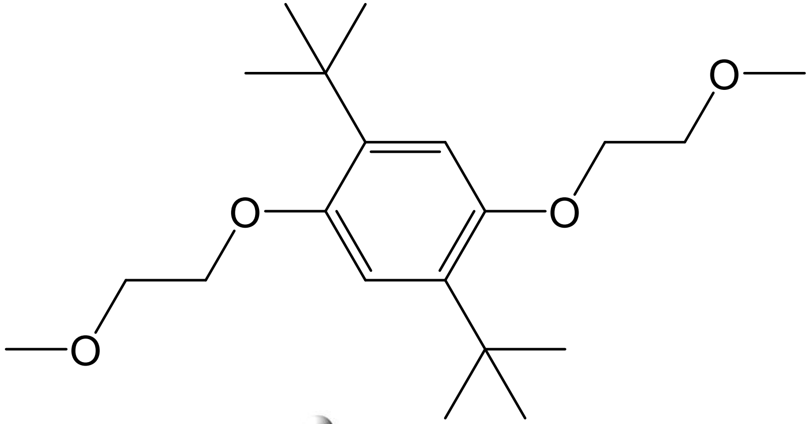
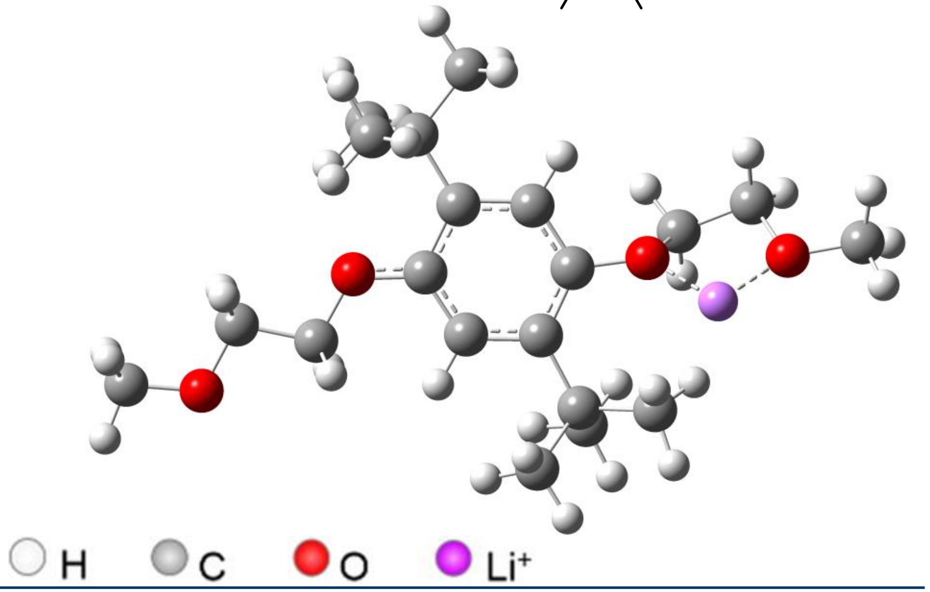
  - Greatly improved efficiencies

- Electrolyte choice significantly impacts cycling performance





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Conclusions

- Modern non-aqueous flow battery electrolytes have the necessary properties for high concentration use
  - Acetonitrile provides the best balance of key properties
  - No de-facto standardization of supporting salts
- Solubility in these electrolytes is the largest challenge for high concentration non-aqueous flow batteries
- Strategies for improving solubility in active material design are well established and have been set aside in favor of improving stability and cyclability
- Interactions between supporting salts and active materials play a strong role in flow battery performance

Further Electrolyte Development Areas

- Organic solvents with increased solvency
  - Limited number of solvents with suitable solvencies and dissociation constants for electrolyte use

- Mixed solvents and electrolytes
  - Successfully applied in lithium ion and aqueous flow battery applications
  - Finer tuning of desired properties