Cathodes for Lithium Air Batteries

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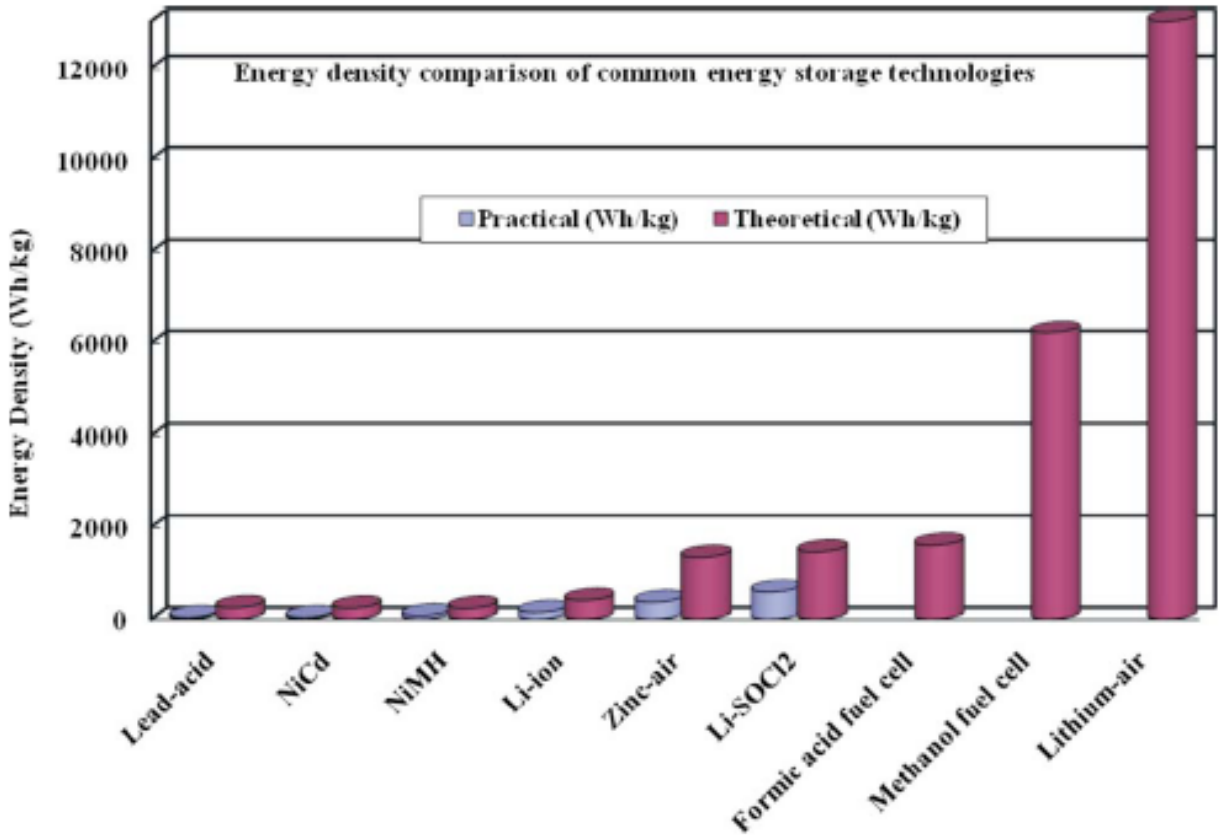
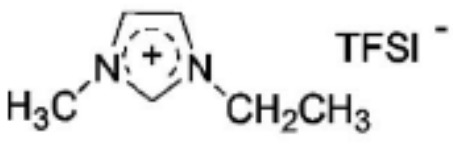
Lithium Air Batteries

- Approaches
  - Li^+ conducting barrier to protect lithium metal from water
  - Non-aqueous solvents
  - Ionic liquids

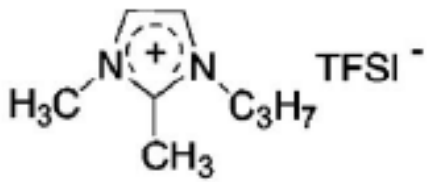


Room Temperature Ionic Liquids

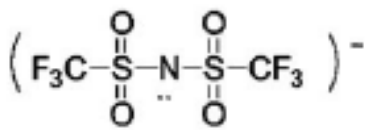
- Non-flammable
- Near zero vapor pressure
- Low conductivity
- Low transference number of lithium
- Oxygen solubility



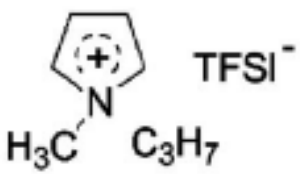
EMITFSI



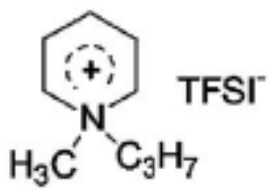
PMMITFSI



TFSI⁻



P_{13}TFSI



PP_{13}TFSI

Alternative to Zinc Air

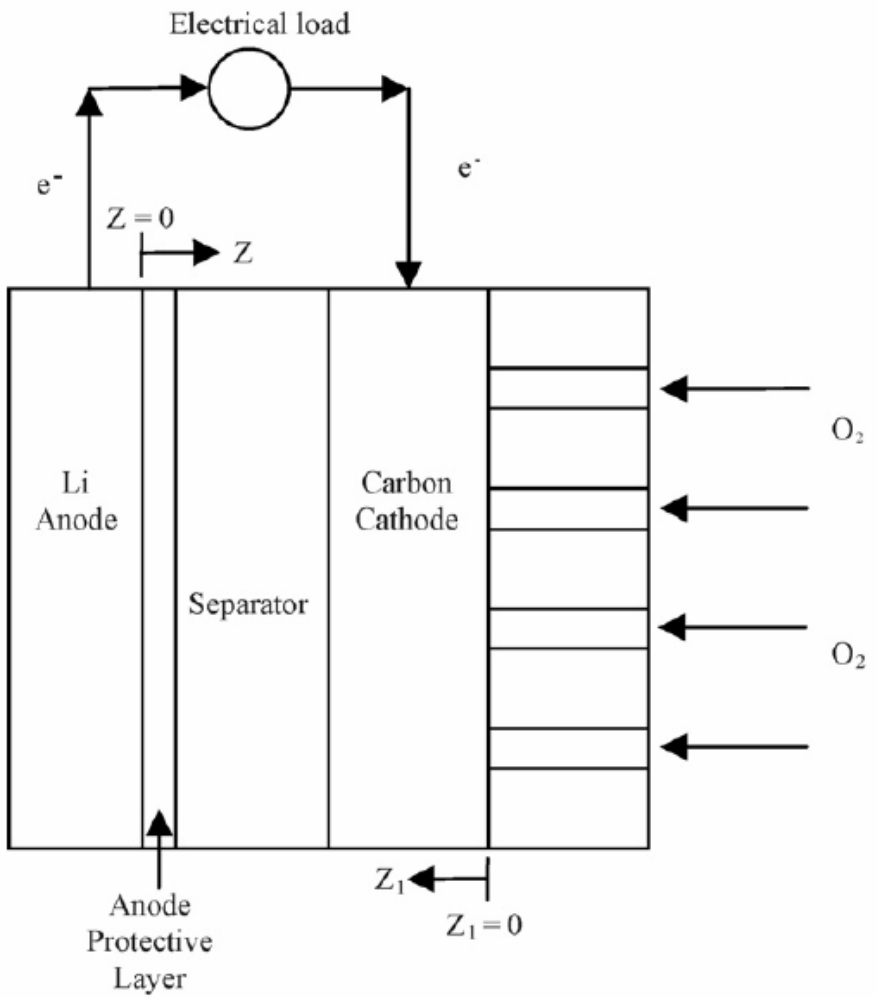
- Military communications BA-8180/U

Li-air requirements

- Higher energy density
- Long shelf life
- Reasonable power

Li-Air Battery Challenges

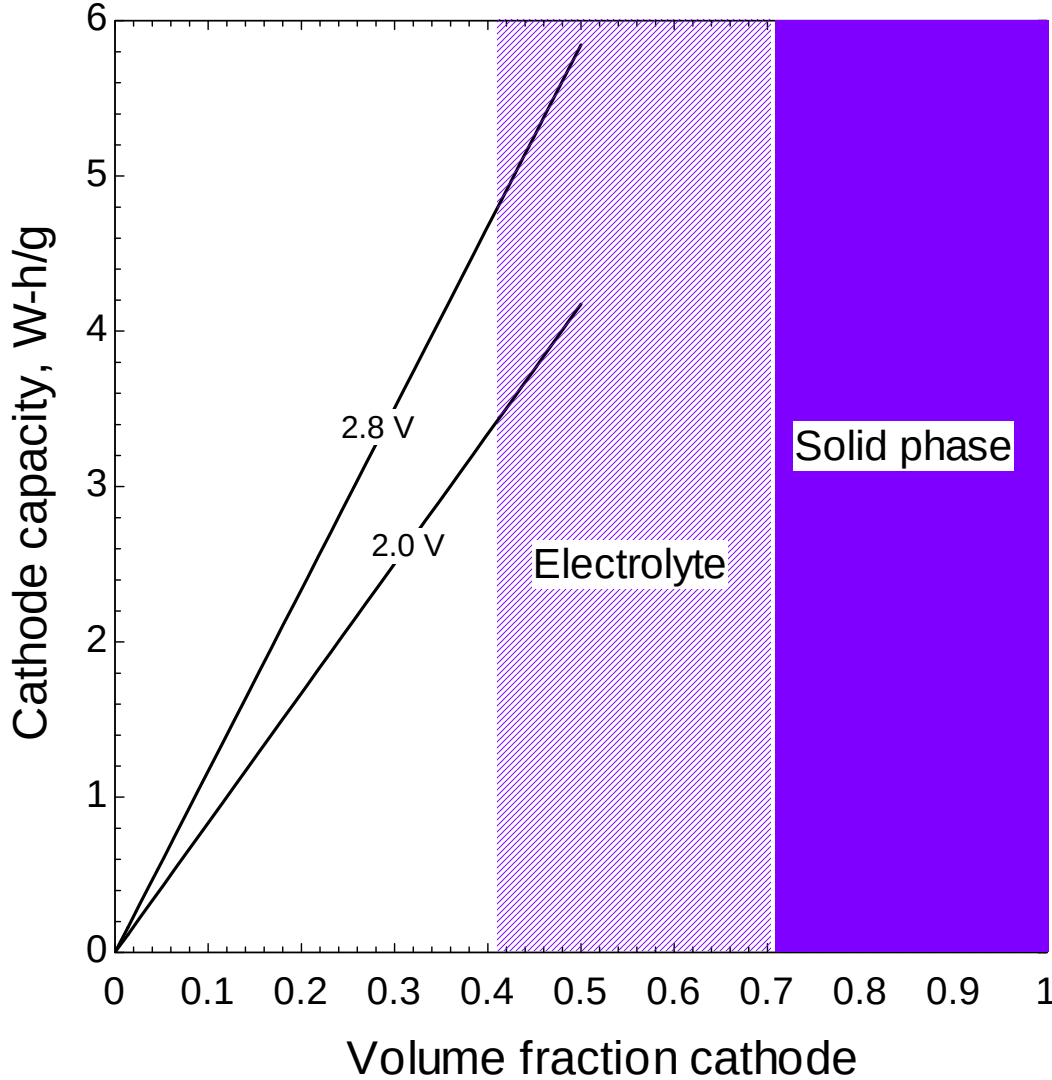
- Rate capability
  - Conductivity
  - Oxygen solubility
- Capacity
  - Solubility of lithium peroxide
- Shelf life
  - Absorption of water
  - Self-discharge



Cathode

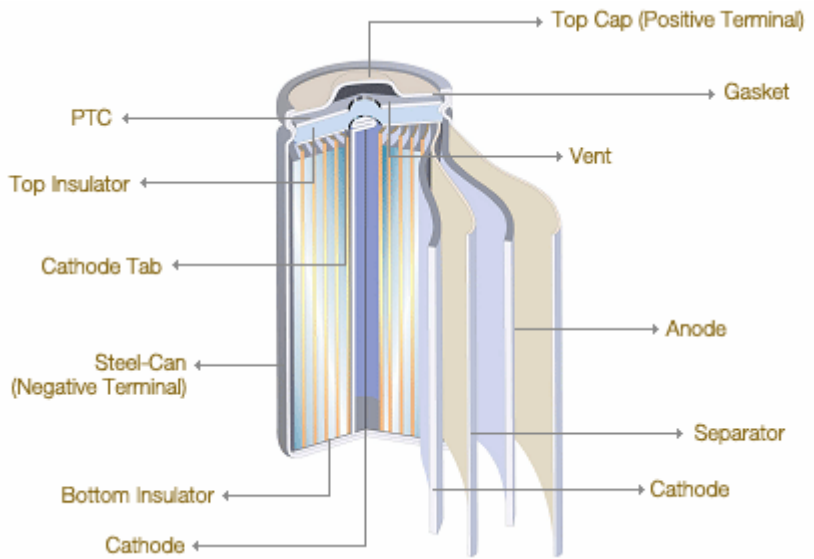
- Reaction products insoluble
- Sufficient volume in cathode for precipitation
- Morphology of deposit is important

$$2\mathrm{Li} + \mathrm{O_2} \rightarrow \mathrm{Li_2O_2}$$



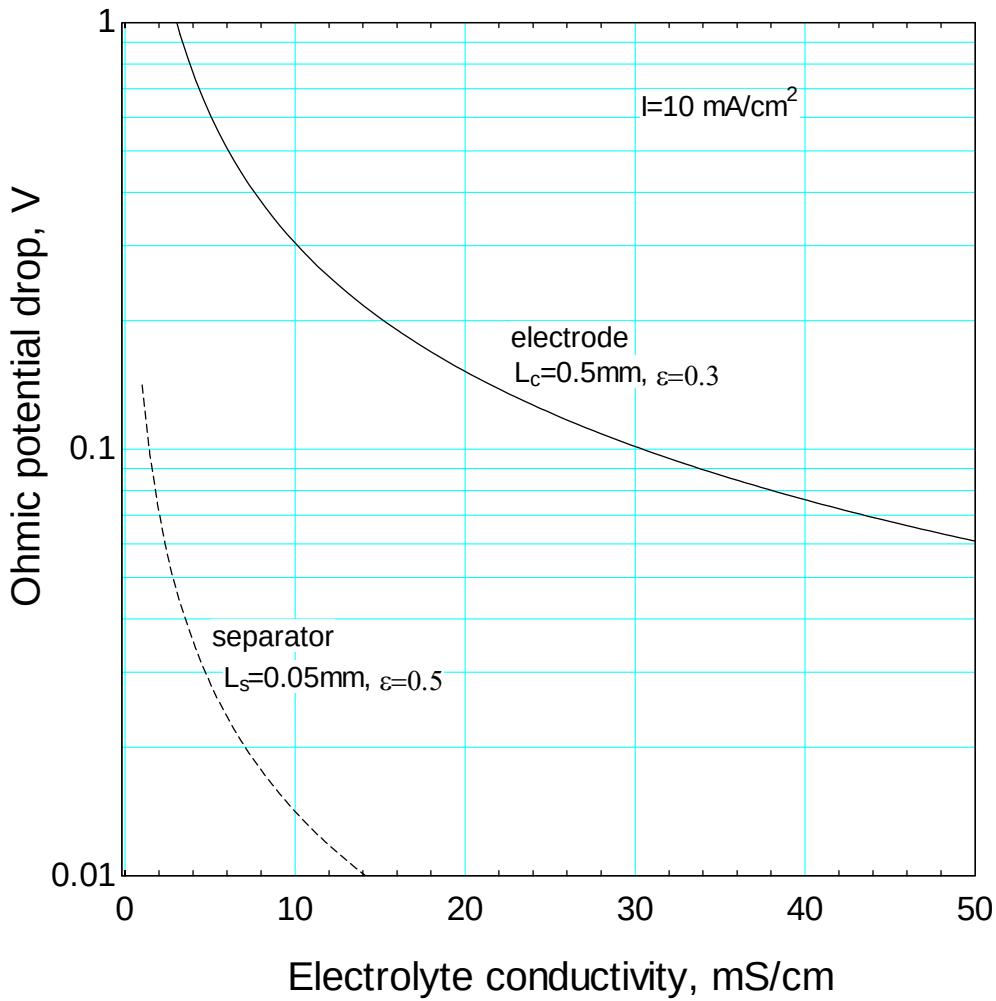
Comparison with Li-ion batteries

- Spirally wound on current collector, no gas access
- Air access is needed on cathode
  - Higher current density needed to achieve good energy and power density



Ohmic losses

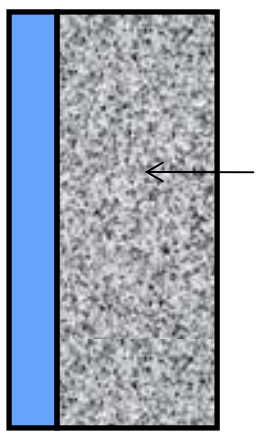
- Ohmic polarization for current of 10 mA/cm^2
- Electrode resistance more important than separator



Flooded Agglomerate Model

- ϕ must be near 1

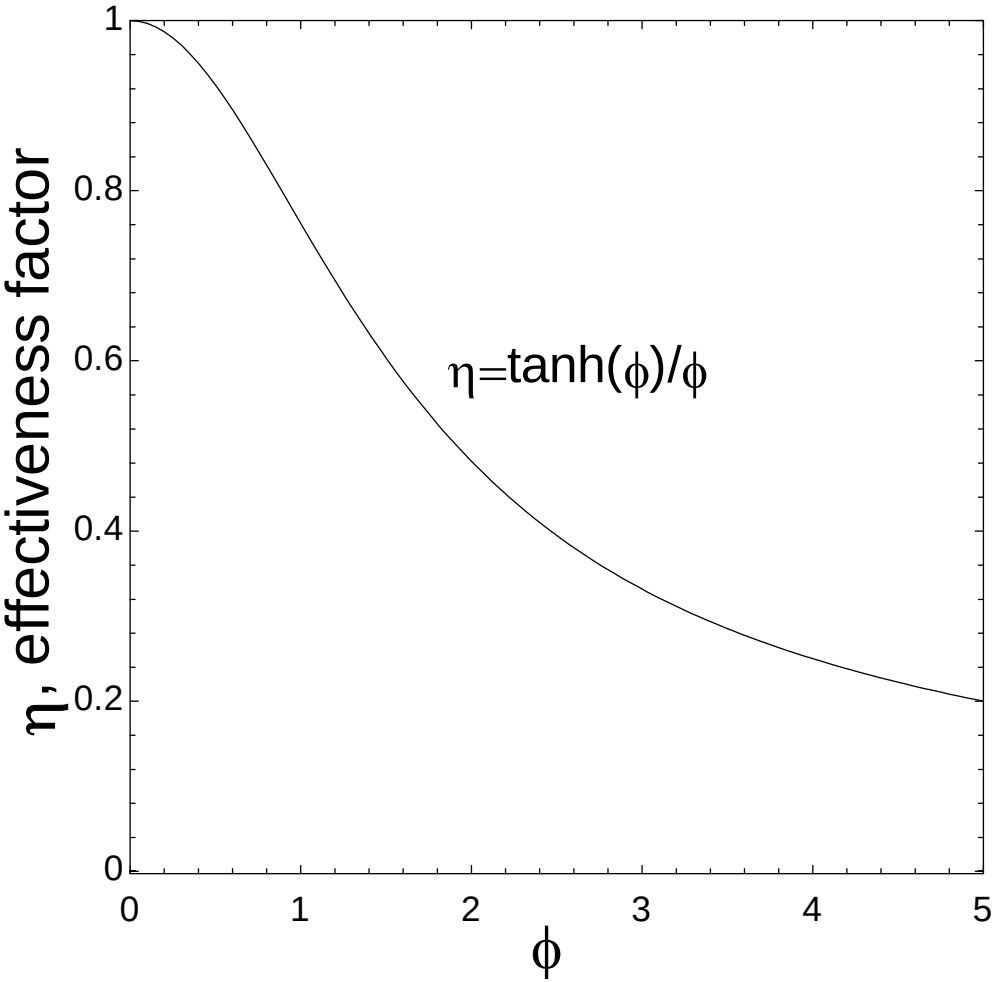
$$\phi^2 = \frac{kaL_e^2}{D_{O_2}}$$



electrolyte

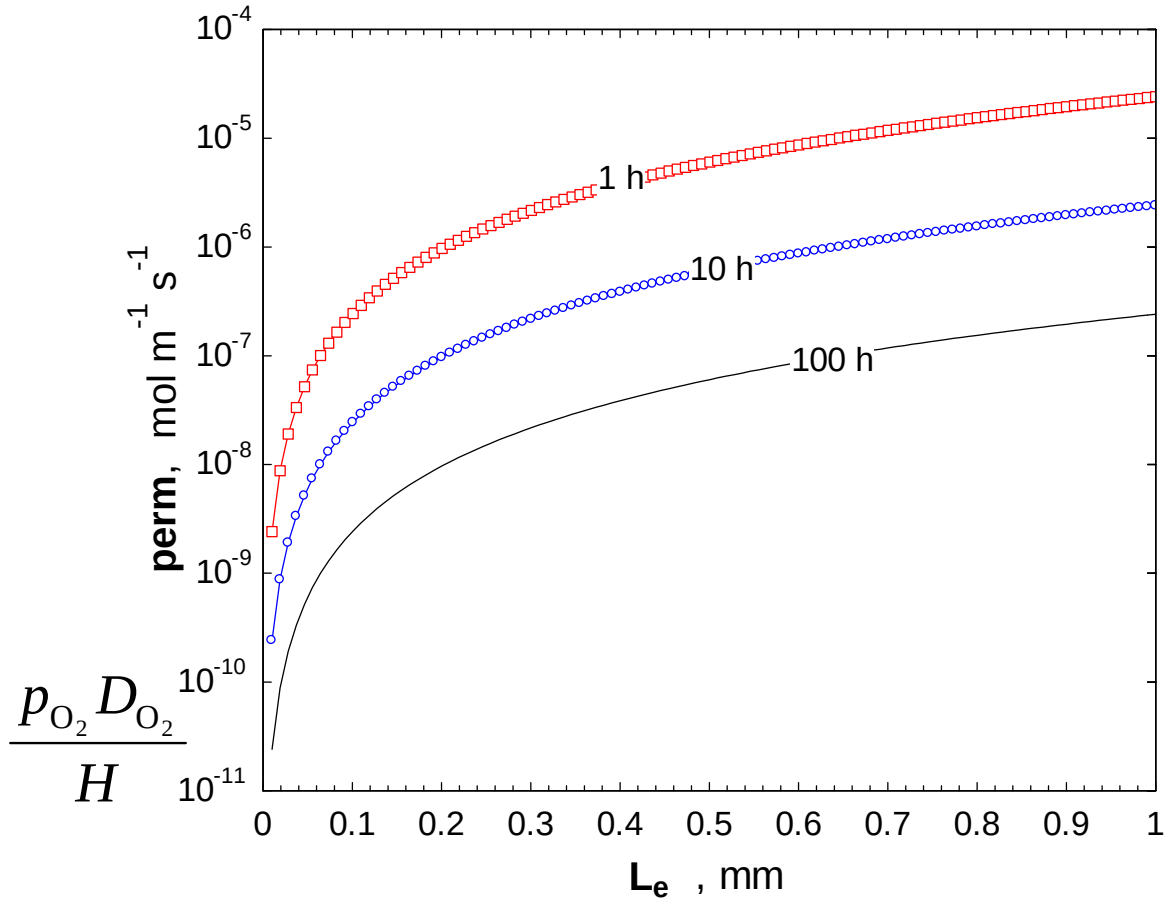
diffusion and reaction of O_2

electrode



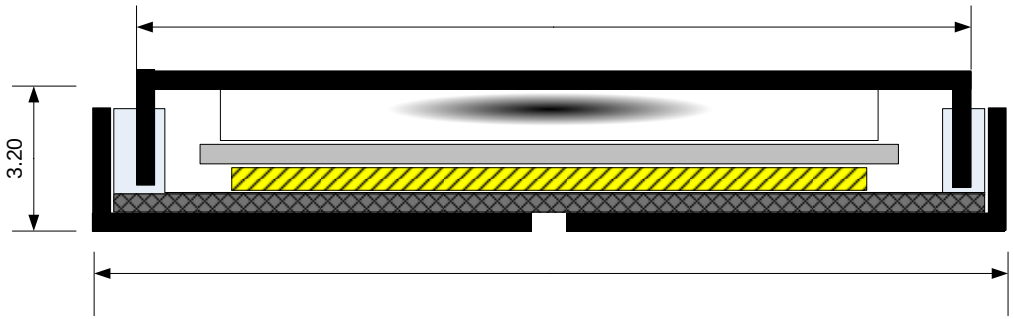
Permeability and runtime

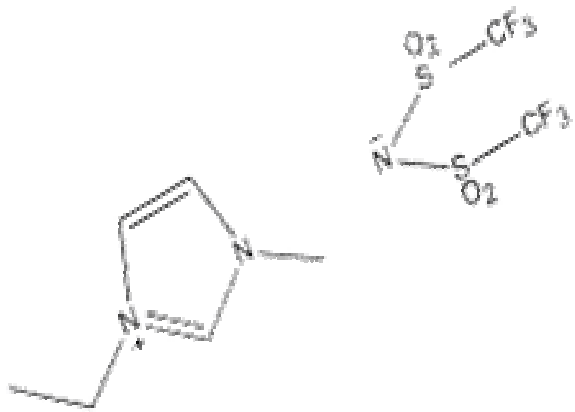
- Permeability is of order 10^{-10}
- Completely flooded electrode not feasible



Cell Testing

- CR2032 coin cell
- Li foil negative
- Nonwoven separator
- EMITFSI
- Air electrode
  - Ni current collector
  - Hydrophobic phase
  - Hydrophillic catalyst phase

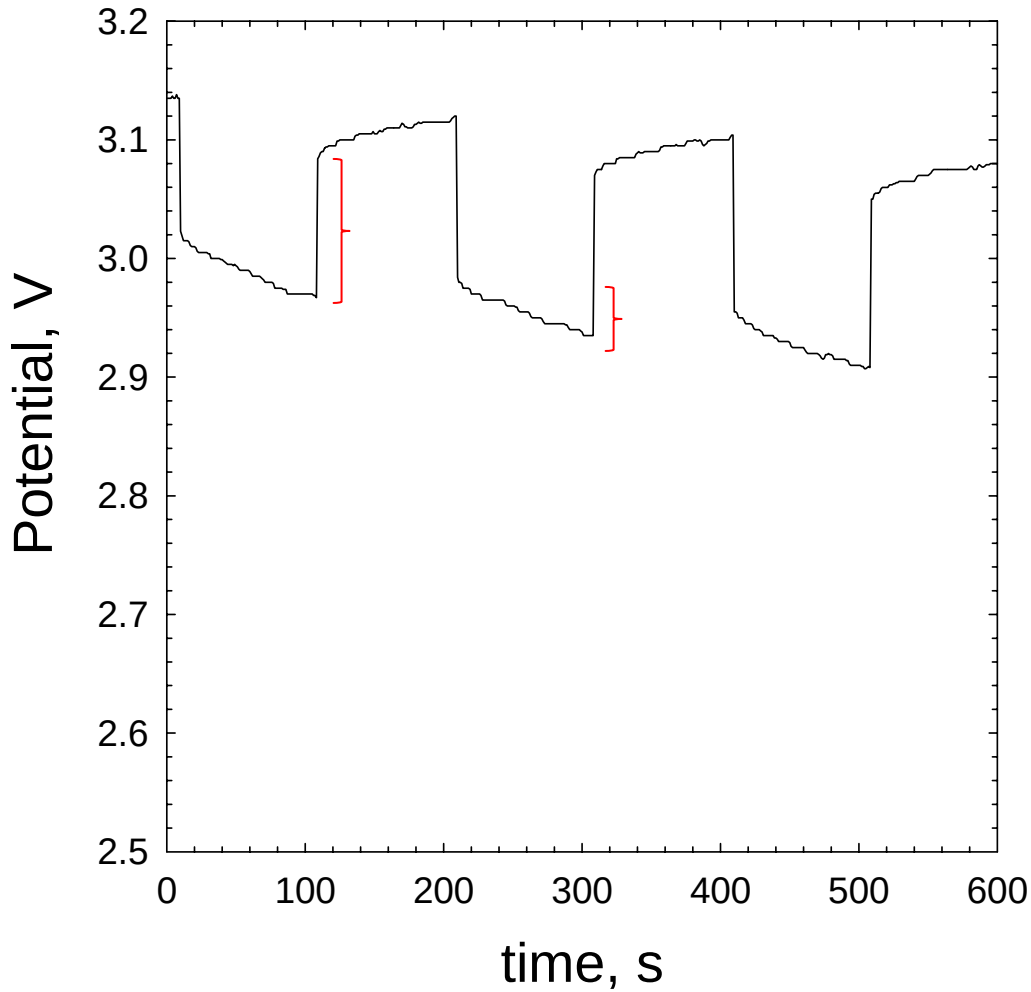




▪EMI^{+} TFSI^{-} Image

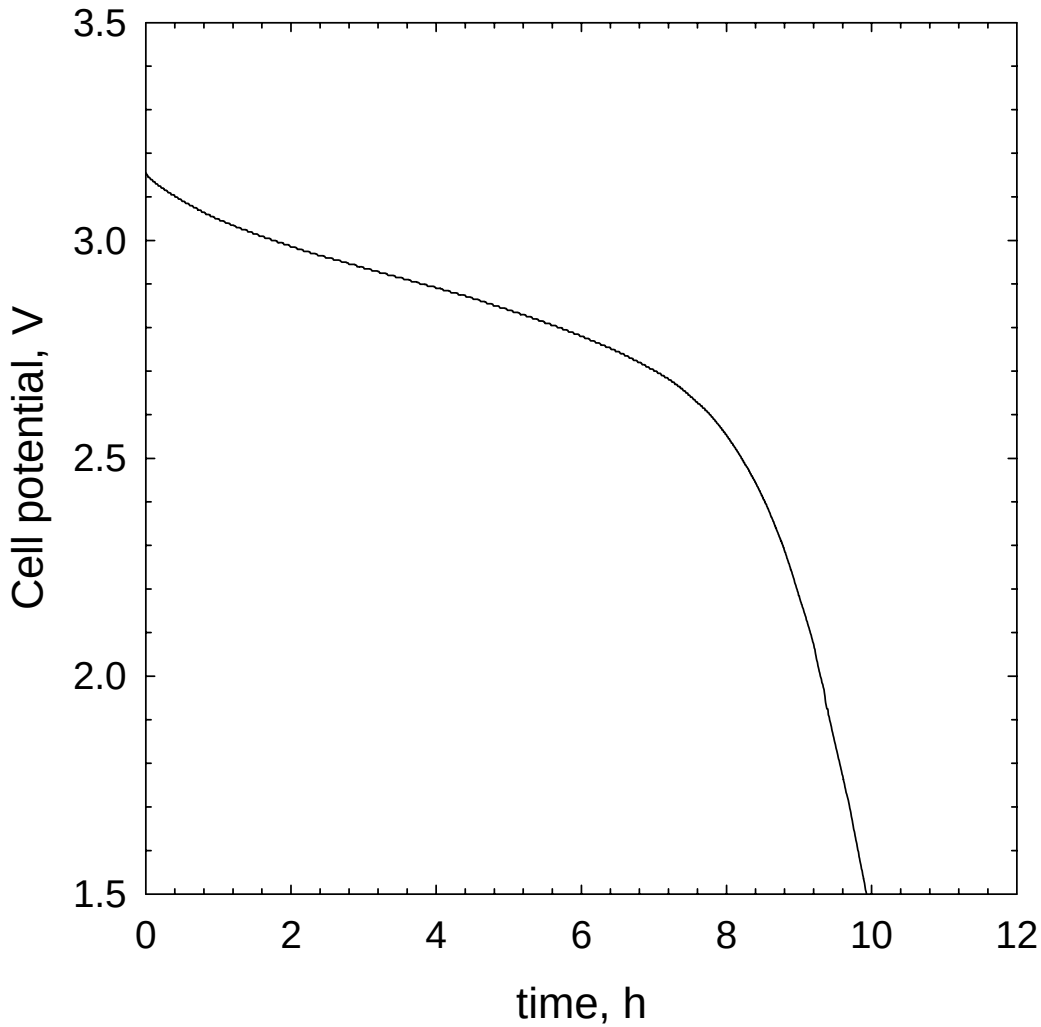
Testing

- Square wave cycling
  - 0-0.5 mA
- Ohmic polarization estimated from current interruption
- Concentration polarization evident



Testing

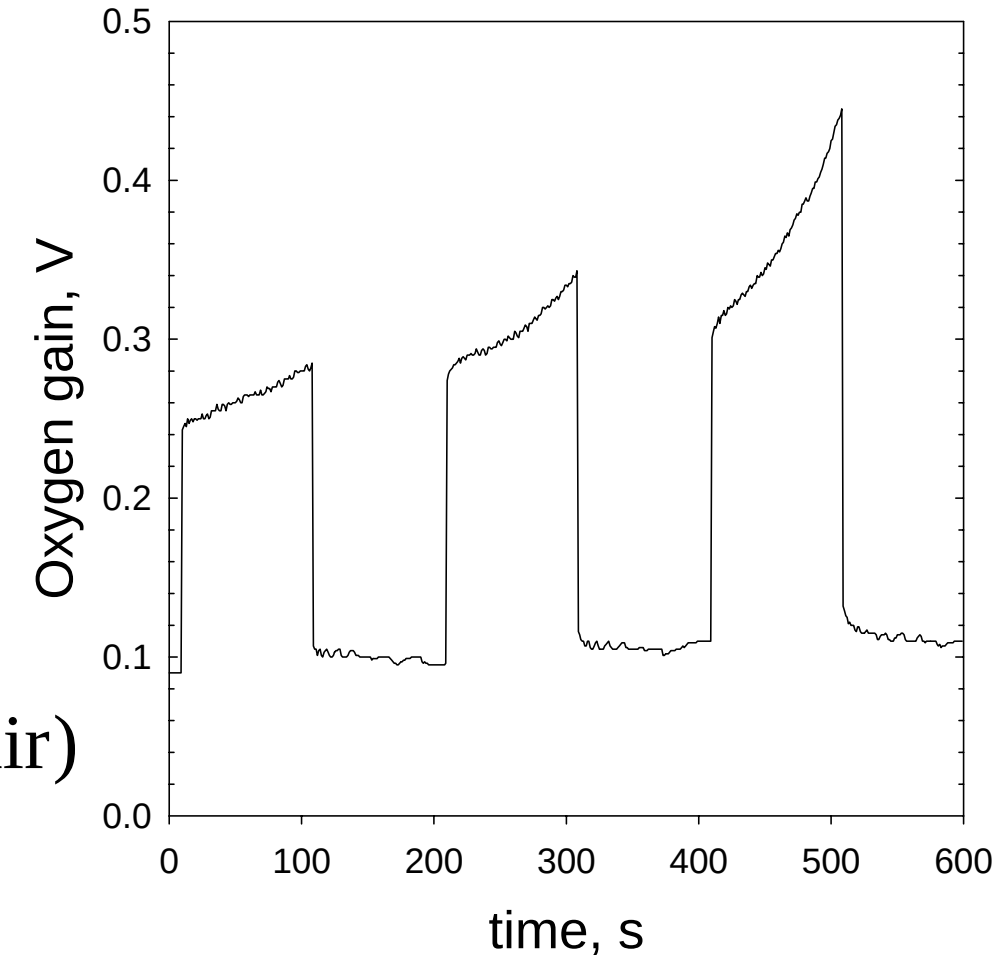
- Galvanostatic hold
- Relatively rapid decrease in performance



Testing

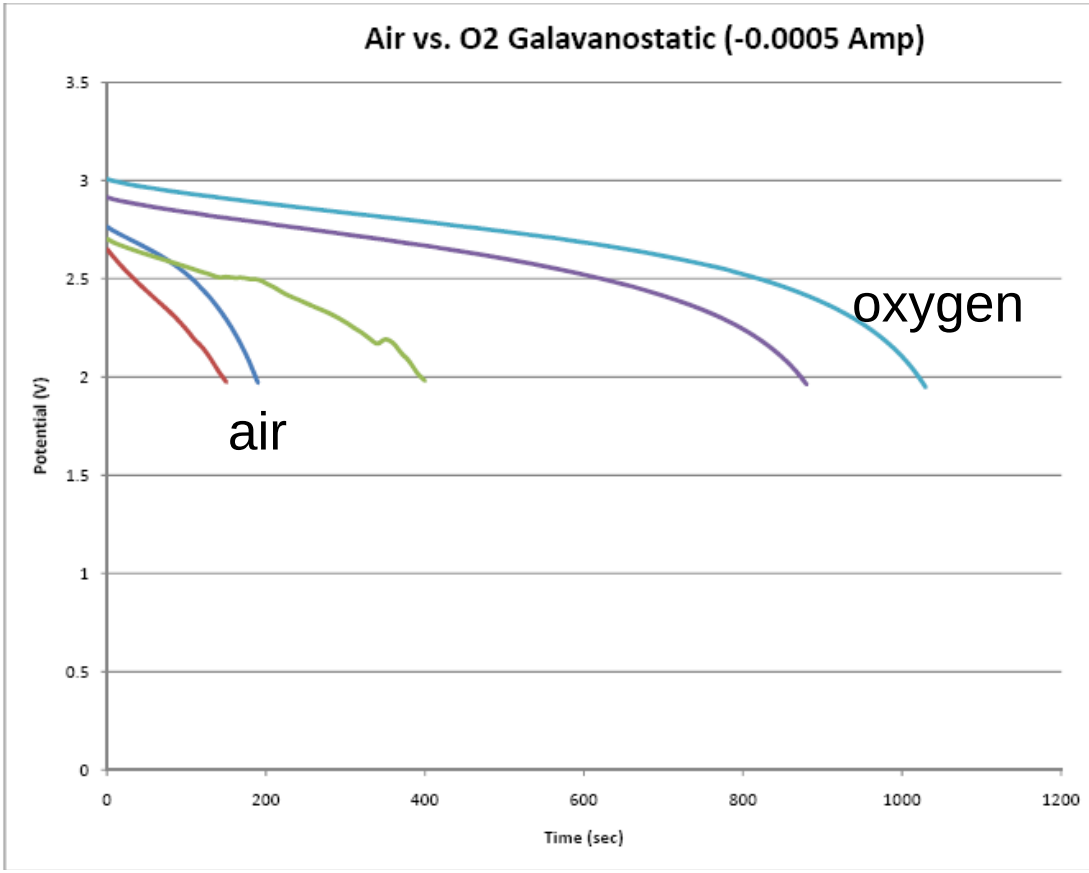
- Oxygen gain during square wave cycling
- Significant transport limitations

$$\text{oxygen gain} = V(\text{O}_2) - V(\text{air})$$



Testing Summary

- Conductivity of electrolyte too low
- Proper electrode structure not achieved
- Concentration polarizations appear to be significant

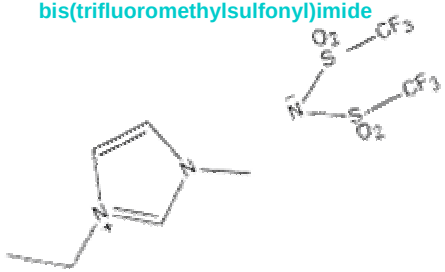


Ionic liquids

- Transport properties
  - Conductivity
  - Li-TFSI solubility
  - Water uptake
  - Oxygen permeability
- Development of new materials

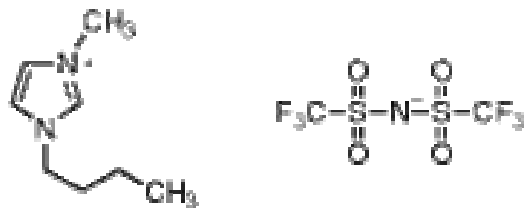
Ionic liquids

▪1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide



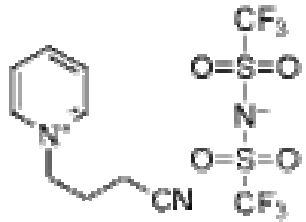
▪EMI^+ $TFSI^-$ Image

▪$bmim^+$ TFSI-

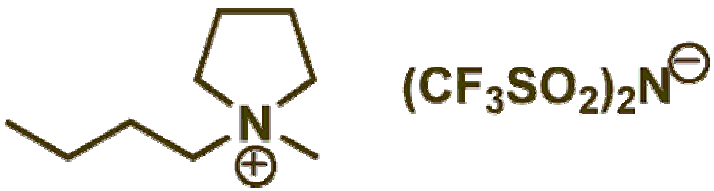


▪1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

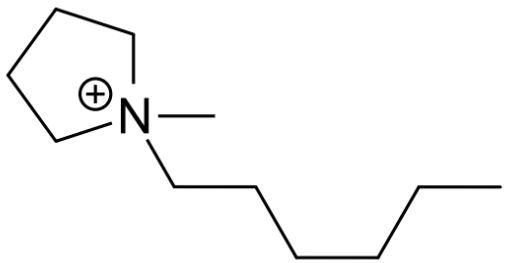
▪1-Butylpyridinium bis(trifluoromethylsulfonyl)imide



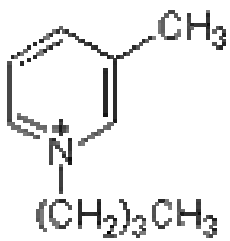
▪$bpdm^+$ $TFSI^-$



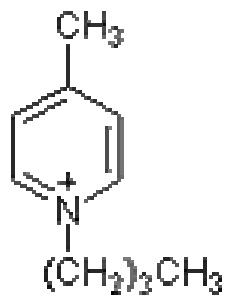
▪1-butyl-1-methylpyrrolidinium



▪1-hexyl-1-methylpyrrolidinium



▪1-butyl-3-methylpyridinium



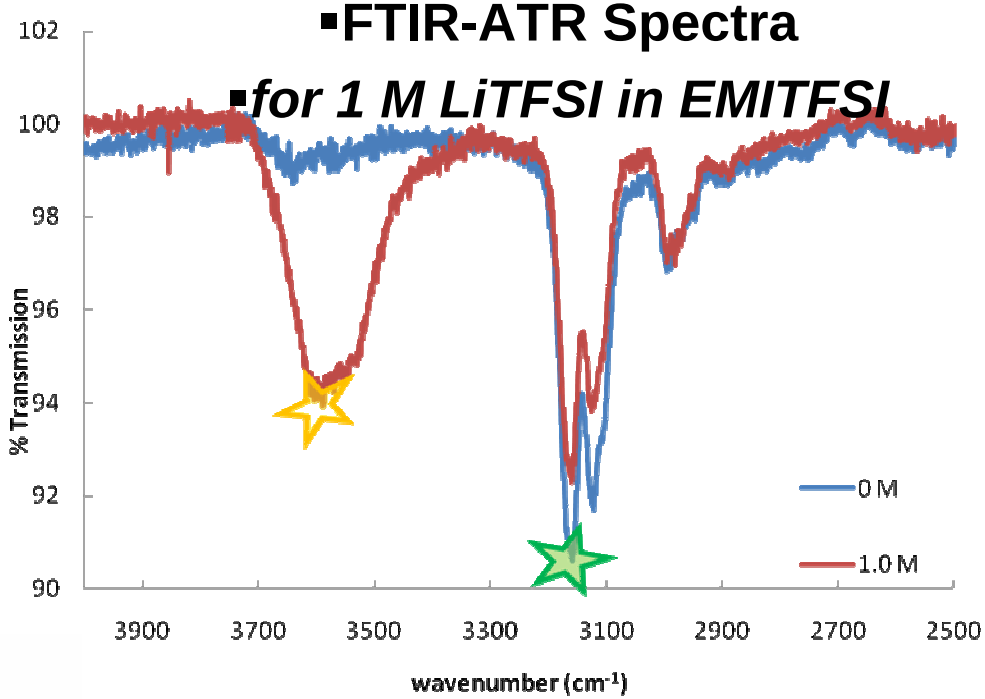
▪1-butyl-4-methylpyridinium

Li TFSI solubility in EMI TFSI

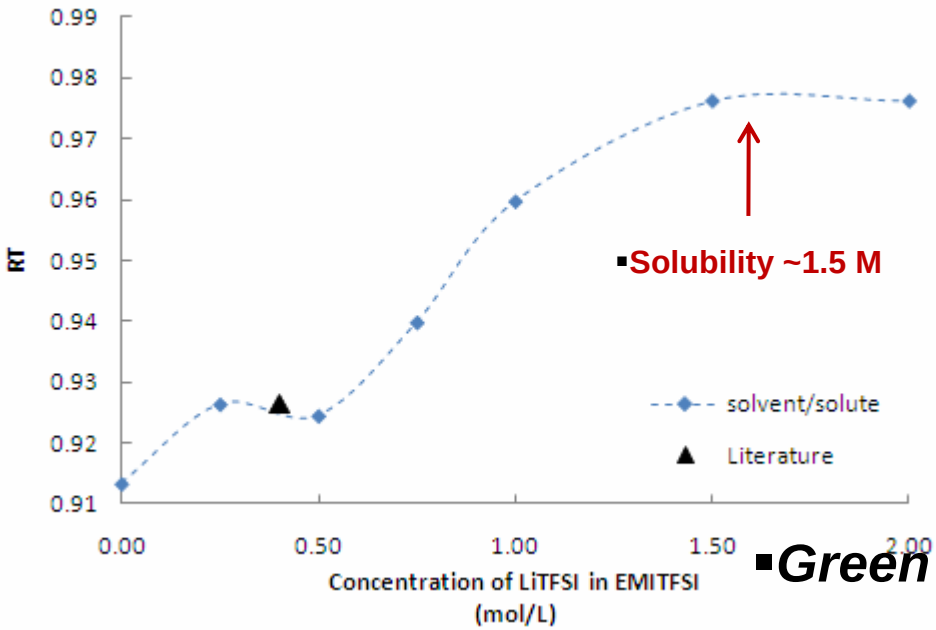
	% Transmission		Transmission Ratio
Concentration *M*	3150 *cm^{-1}*	3550 *cm^{-1}*	*(IL @ 3150):(Salt @ 3550)*
0.00	90.6	99.2	0.91
0.25	90.6	97.8	0.93
0.50	91.8	98	0.92
0.75	92.2	96.4	0.94
1.00	92.4	94.4	0.96
1.50	93.2	92.8	0.98
2.00	94.2	92.8	0.98

▪**FTIR-ATR Spectra**

▪***for 1 M LiTFSI in EMITFSI***



▪**Transmission Ratio (RT)**



▪**Solubility ~1.5 M**

$$RT = \left[\frac{\%T\left(solvent@3150cm^{-1}\right)}{\%T\left(solute@3550cm^{-1}\right)}\right]$$

▪***Green Chem.*, 11, 1453-1457 (2009).**

Ionic liquids

- Transport properties
  - Conductivity: EMITFSI highest, but still lower than desired
  - Li-TFSI solubility: does not appear to be an issue
  - Water uptake: all absorb water but impact on primary cell unclear
  - Oxygen permeability (in progress)

Future work

- Identify new room temperature ionic liquids with higher conductivities
- Develop electrode structure with better gas access
- Mathematical model of full cell
- Investigation of transport numbers for electrolytes

Acknowledgements

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