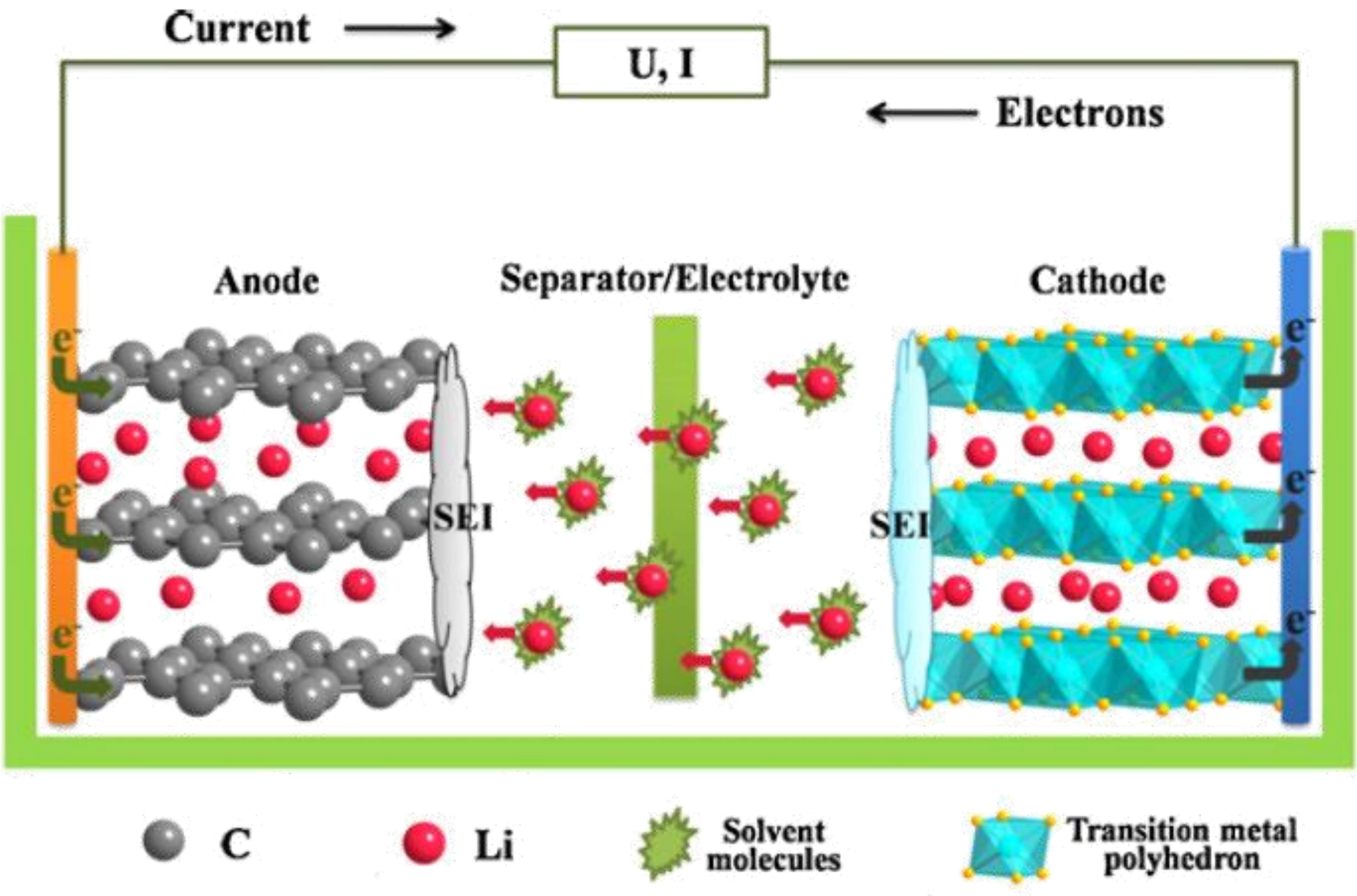
South 8 Technologies

Next Generation Energy Storage Devices

NASA Battery Workshop
Huntsville, AL
November 15th, 2017

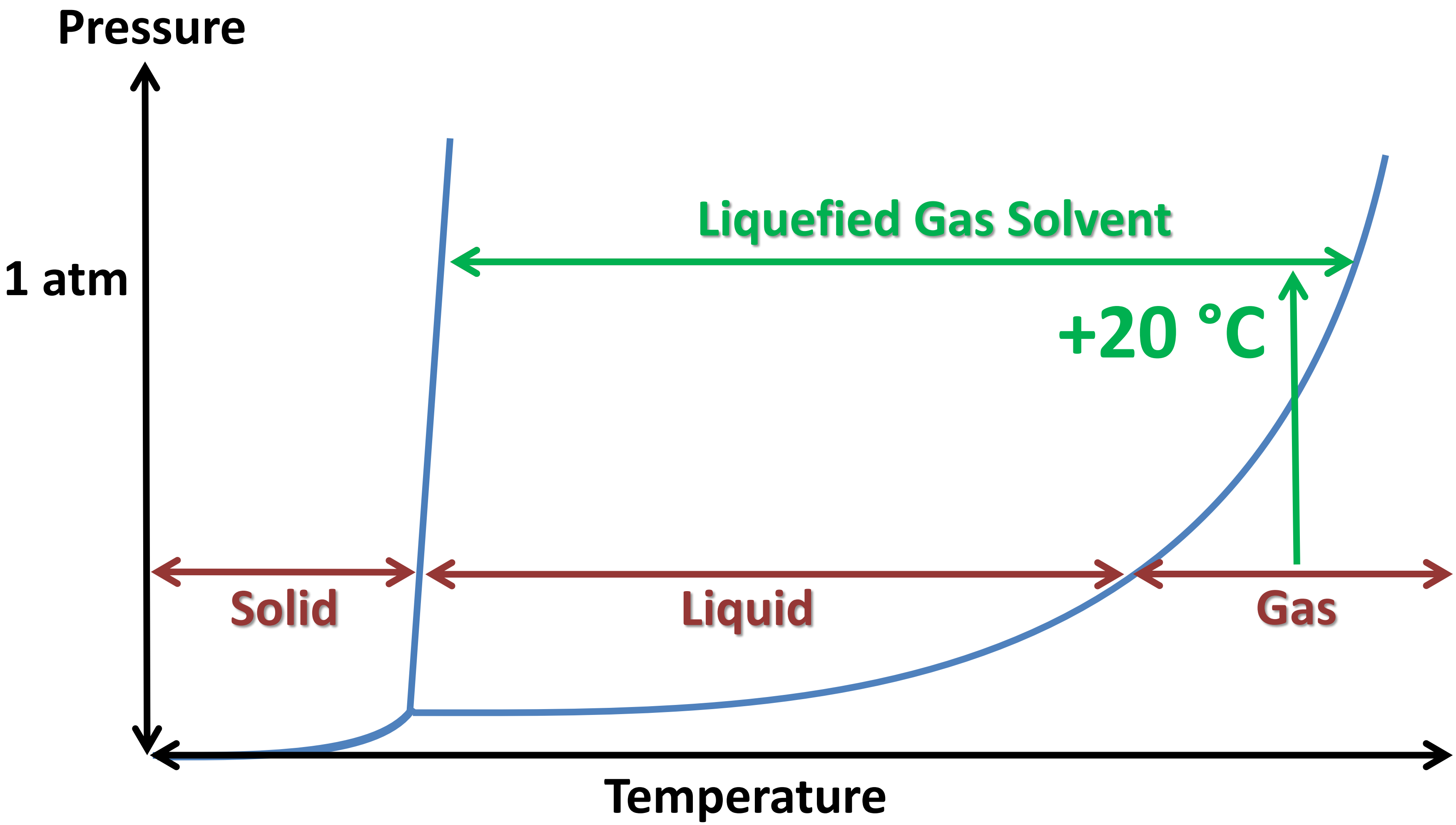
Speaker: Dr. Cyrus S. Rustomji

Li-Ion Battery

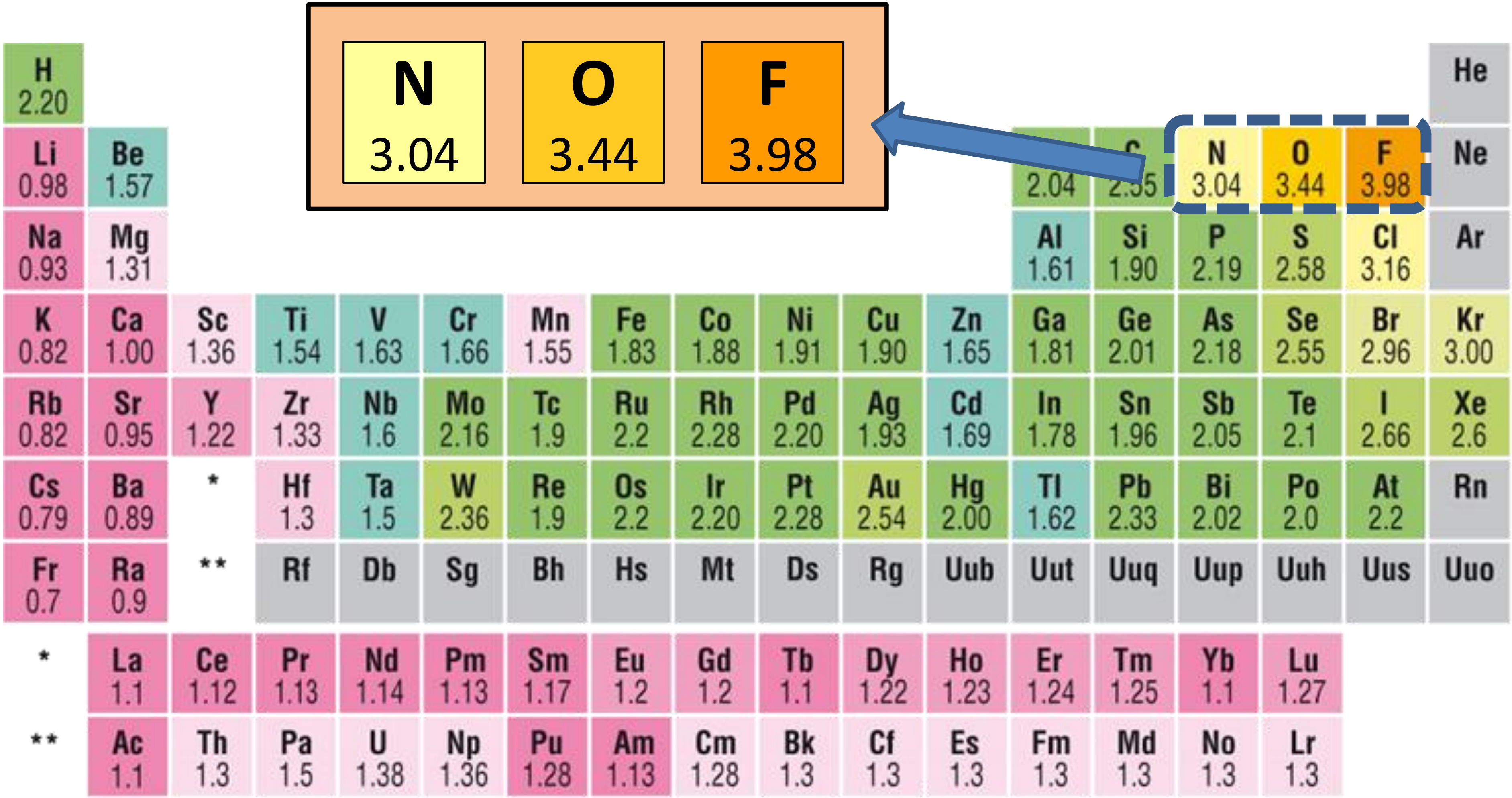


Y. Meng., Mat. Sci. and Eng. R, 73, 2012, 51-65

Exploration of New Solvents



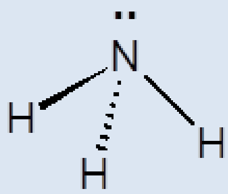
Exploration of New Solvents



Exploration of New Solvents

N 3.04

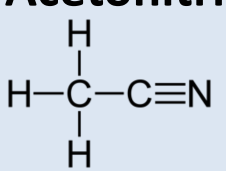
Ammonia, T_b = -28 °C



Hydrogen Cyanide, T_b = +26 °C

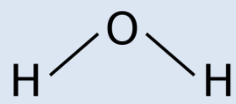
H—C≡N

Acetonitrile, T_b = +82 °C

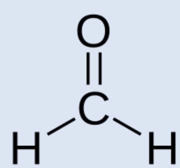


O 3.44

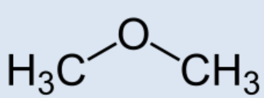
Water, T_b = +100 °C



Formaldehyde, T_b = -19 °C



Dimethyl Ether, T_b = -24 °C

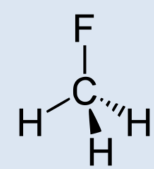


F 3.98

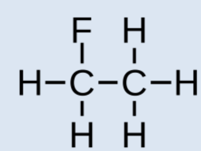
Hydrogen Fluoride, T_b = +20 °C

H−F

Fluoromethane, T_b = -78 °C



Fluoroethane, T_b = -38 °C



= Toxicity = Electrochemical Stability

Liquefied Gas Solvents

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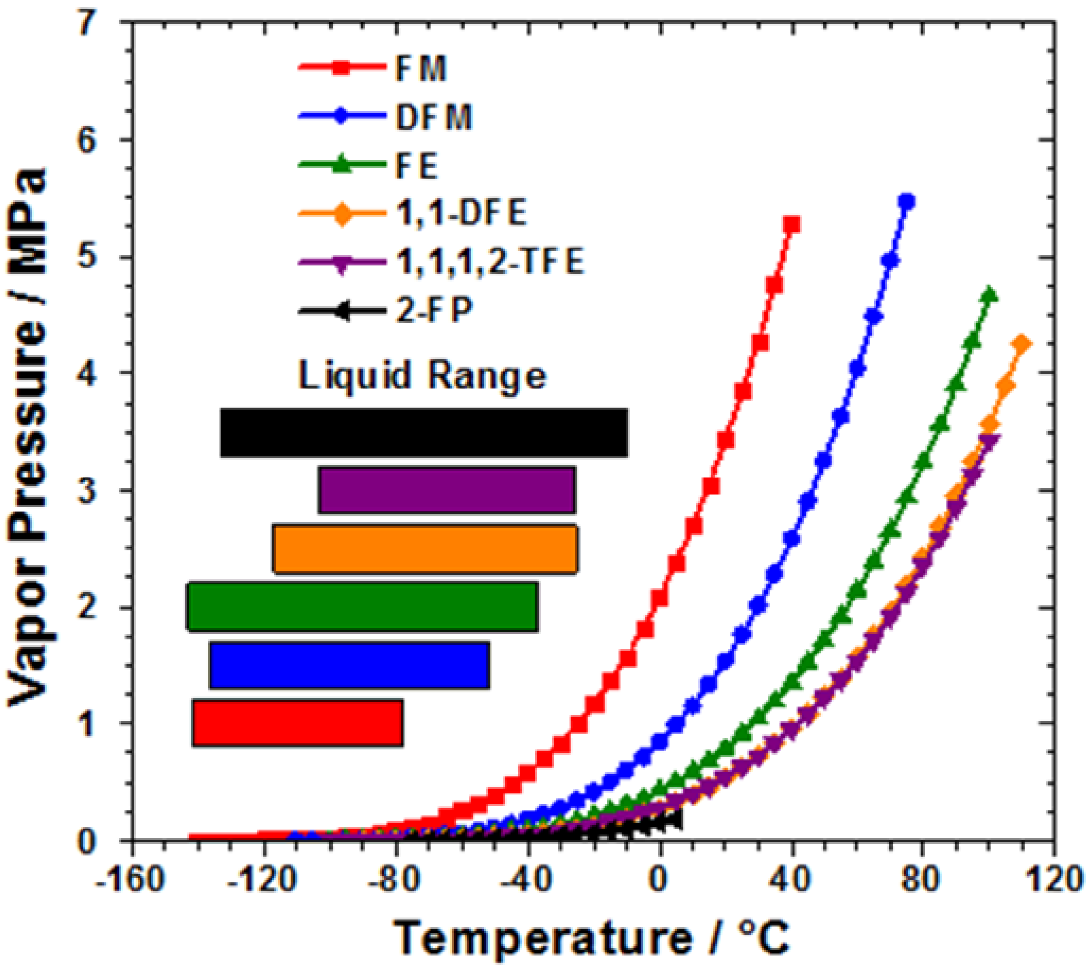
Next Generation Energy Storage Devices



Moderate Pressures

Natural gas vehicles ~25 Mpa

Ni-Hydrogen Battery ~6.5 MPa

Should have excellent low temperature performance.

Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Solvents

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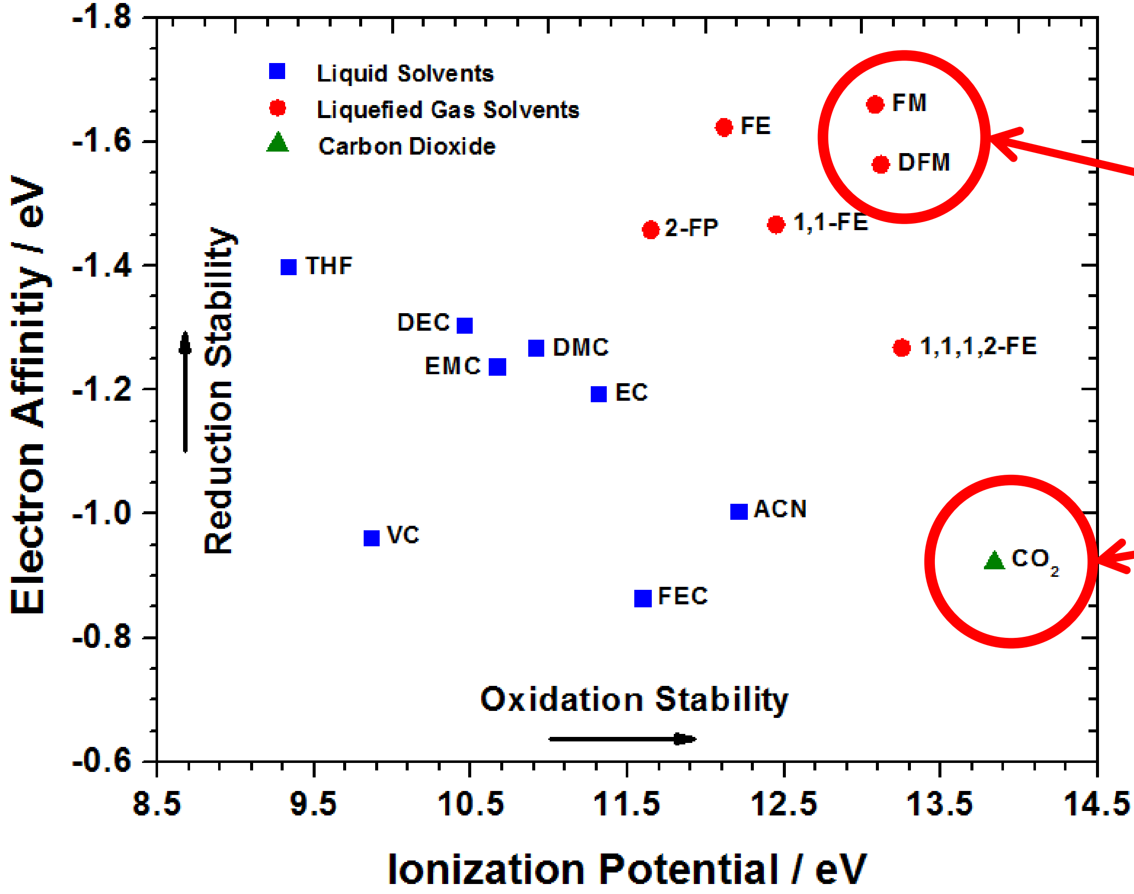
Calculated via DFT at the B3LYP/6-31+g(d,p) level of theory.



Solvents of interest
- **Fluoromethane**
- **Difluoromethane**

More on CO_2 later…

Calculated via DFT at B3LYP/6-31+g(d,p) level of theory.

Should have excellent electrochemical stability window.

Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Solvents

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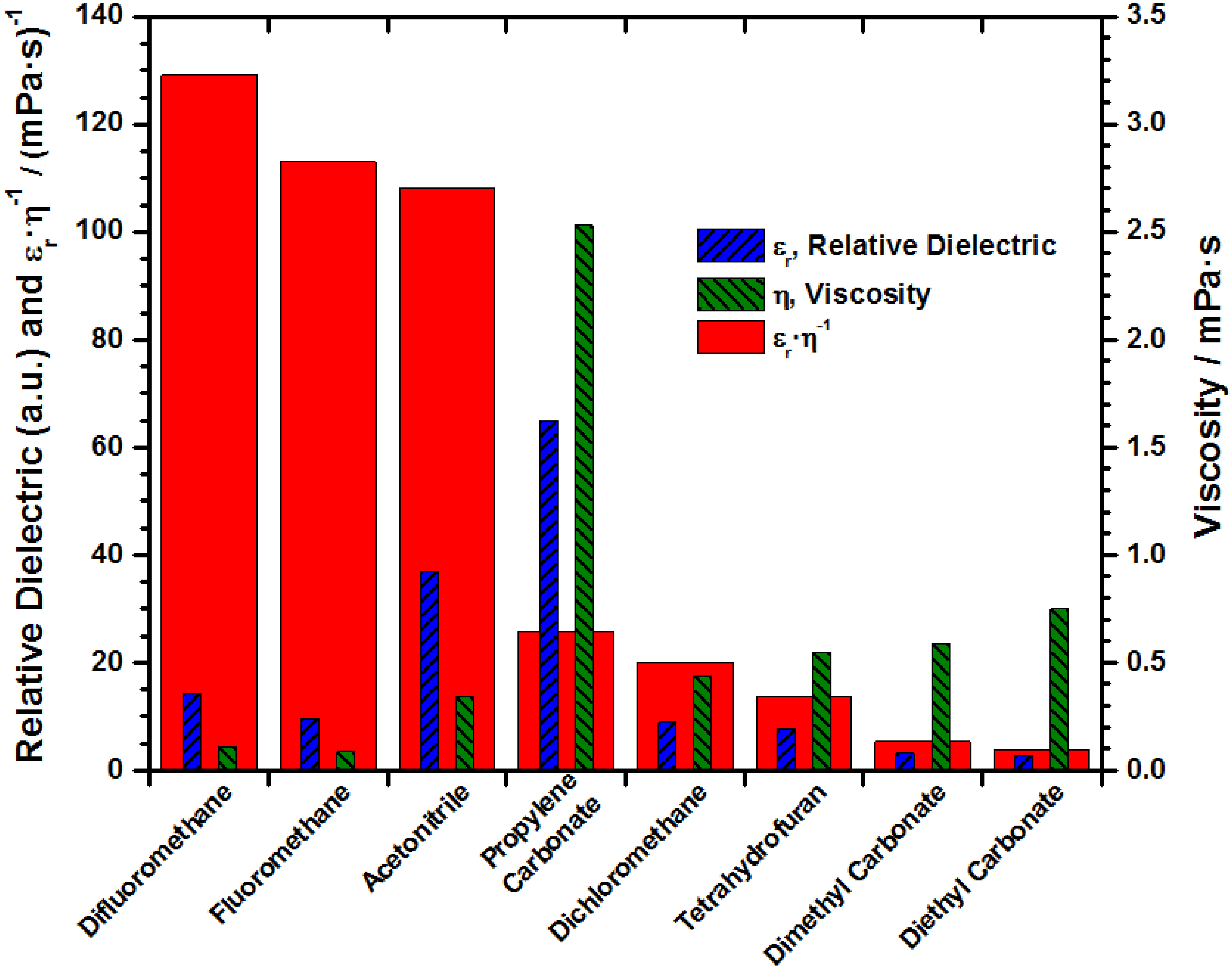
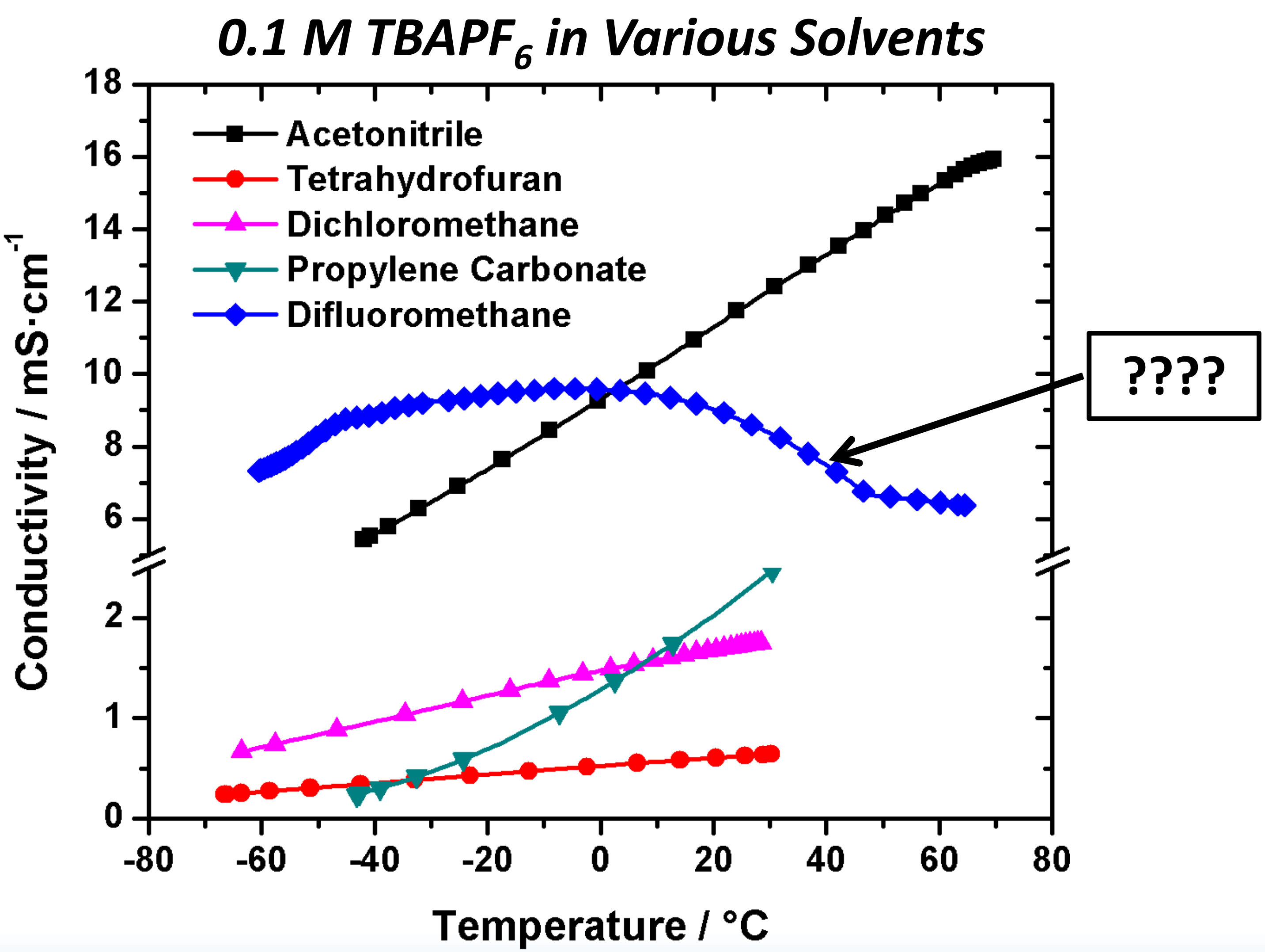


High $\varepsilon_r \cdot \eta^{-1}$ factor → Relatively high electrolytic conductivity.

Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Electrolyte



Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Electrolyte

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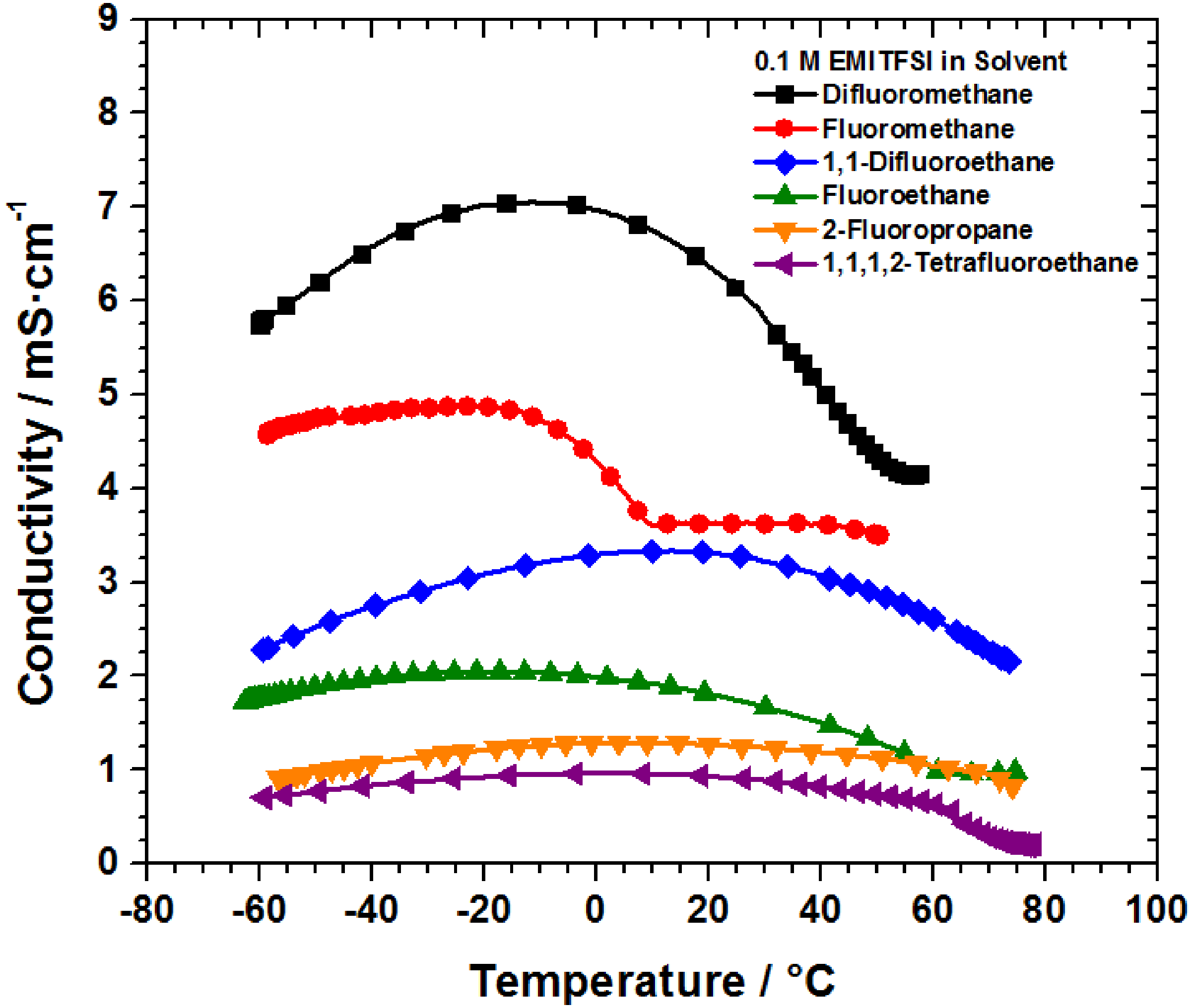

Tried various salts & solvents– same pattern!!

Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Electrolyte

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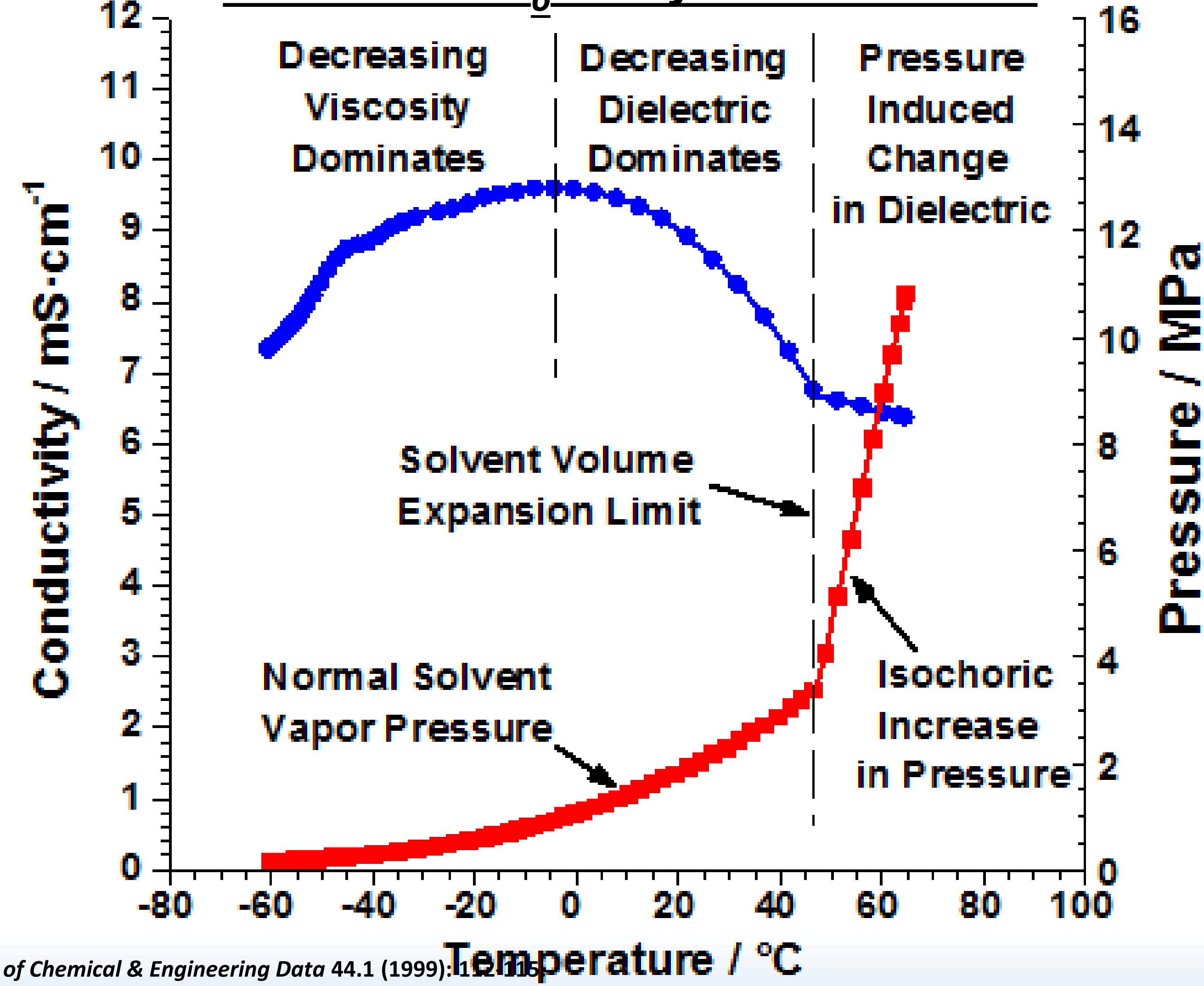
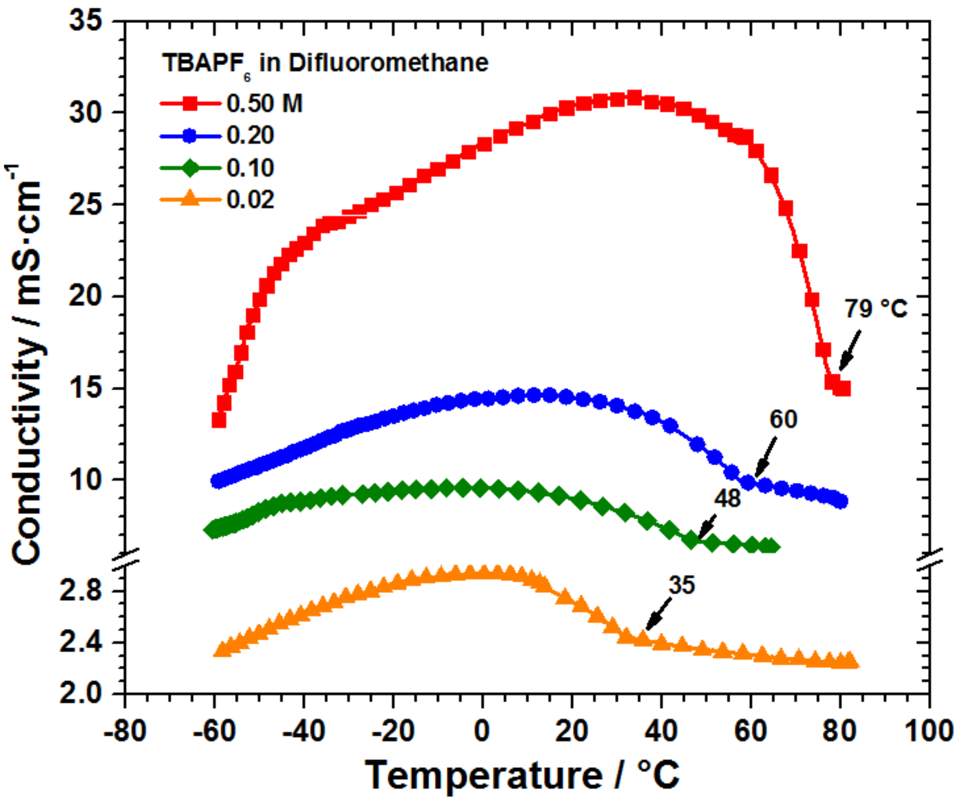
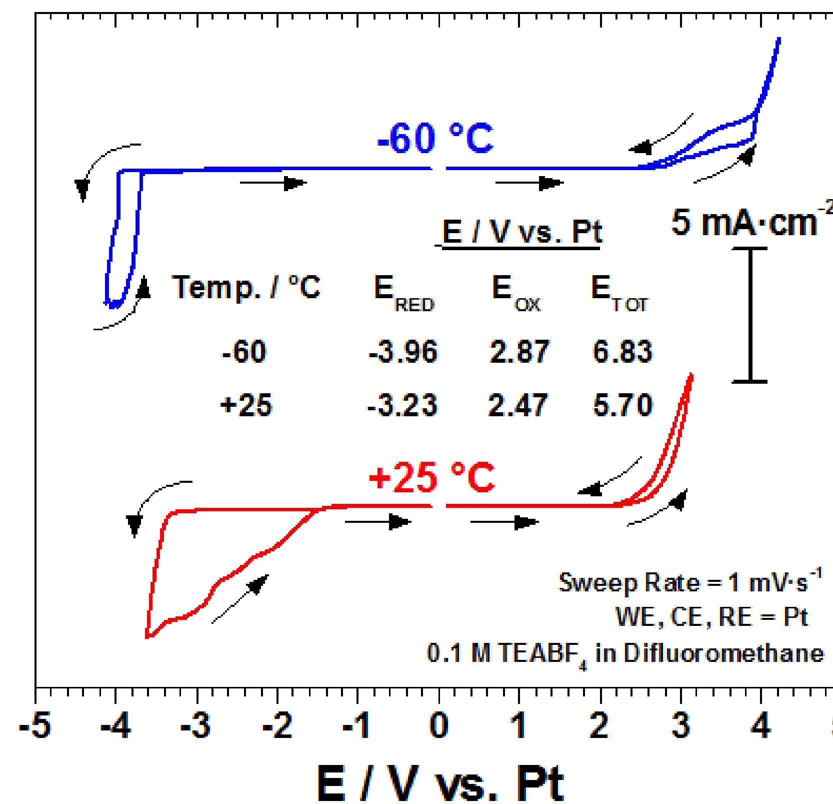
0.1 M $TBAPF_6$ in Difluoromethane



Abbott, Andrew P., *Journal of Chemical & Engineering Data* 44.1 (1999): 112-115.
Kraus, Charles A., *Physical Review (Series I)* 18.2 (1904): 89.
Rustomji et al., Science 356, 1351 (2017)

Liquefied Gas Electrolyte



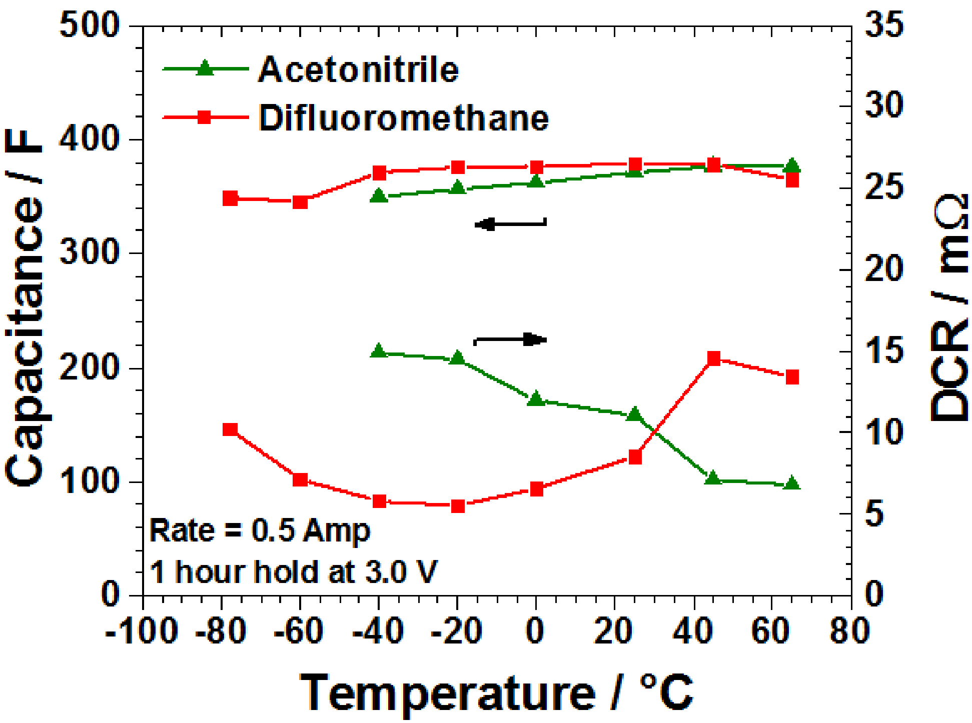


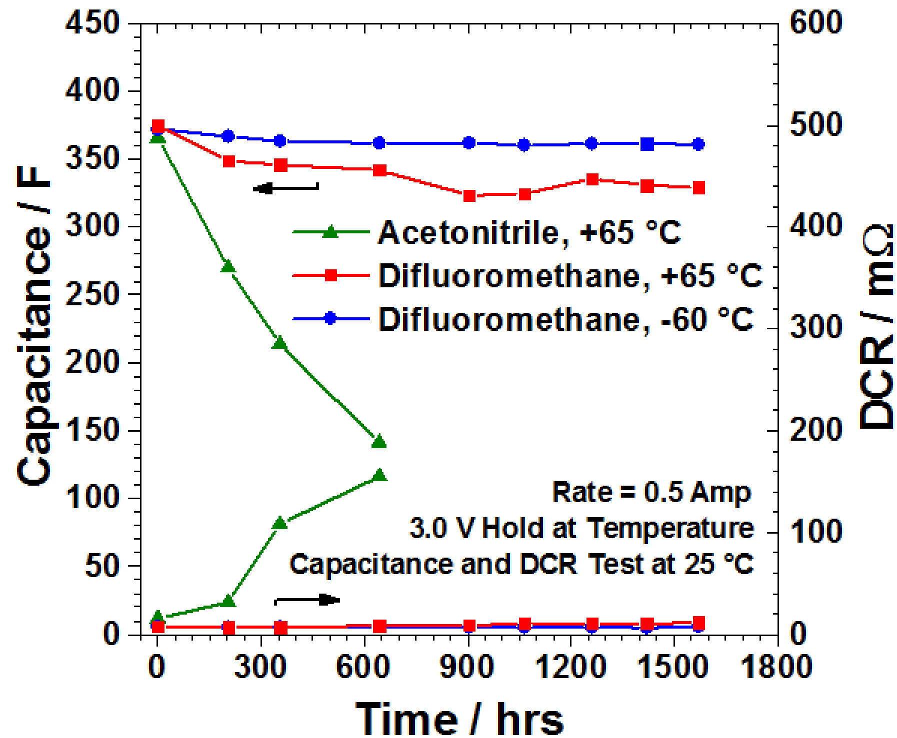
Exceptionally high electrolytic conductivity from -60 to +80 °C

Excellent electrochemical stability

Rustomji et al., Science 356, 1351 (2017)

Electrochemical Capacitor



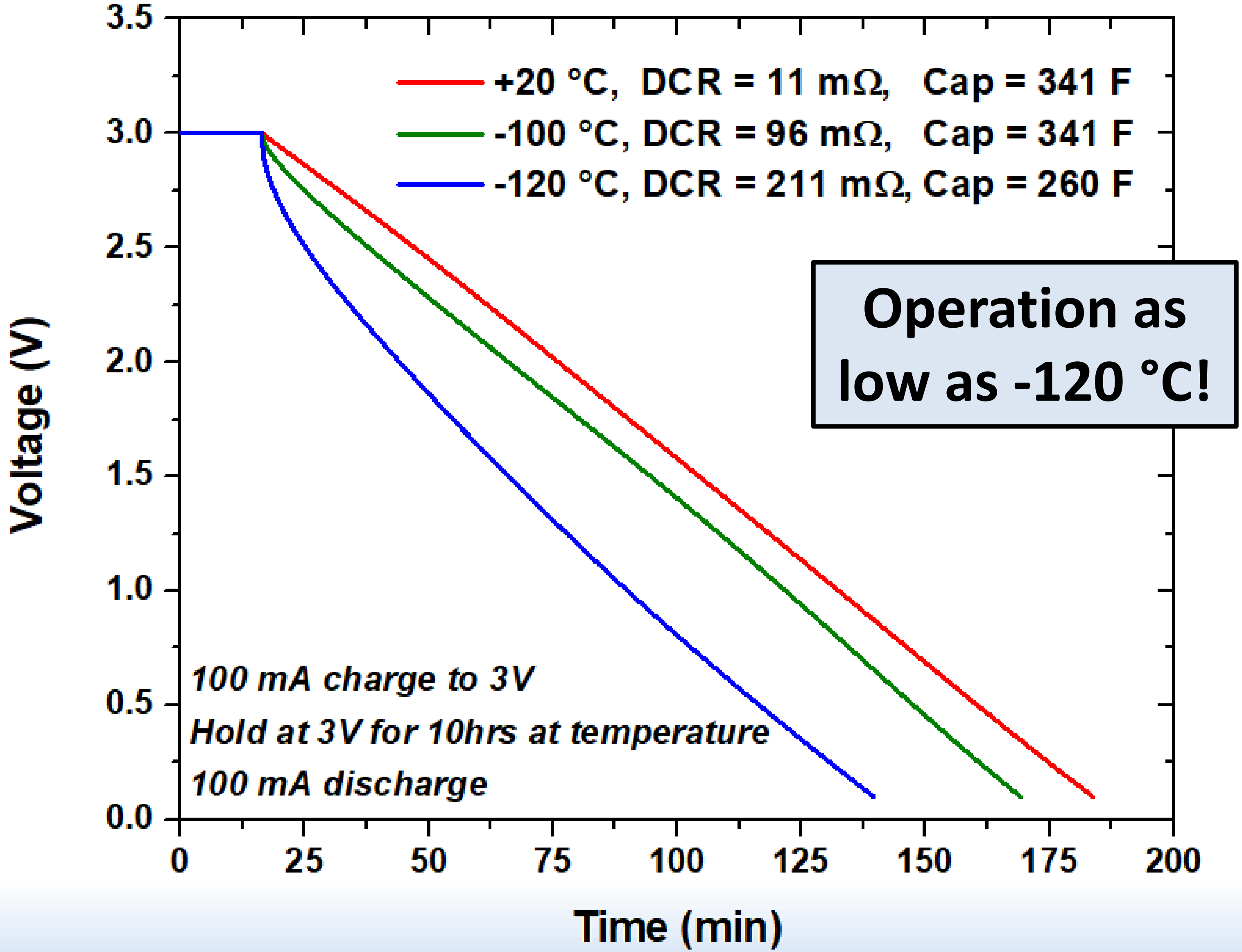


1M $TEABF_4$ in Acetonitrile, 0.5 M $TEABF_4$ in Difluoromethane

- **Stable at increased voltages → 23% Increase in energy density**
- **Demonstrated over wide temperature window -80 to +65 °C**
- **Low-Flammability & Non-Toxic Electrolyte**
- **Temperature performance verified by National Renewable Energy Lab (NREL)**

Rustomji et al., Science 356, 1351 (2017)

Electrochemical Capacitor



Rustomji et al., Unpublished

Lithium Liquefied Gas Electrolyte

Difluoromethane is an *excellent* solvent for electrochemical capacitors.

Can we solubilize Li salts for batteries as well???

Lithium Liquefied Gas Electrolyte

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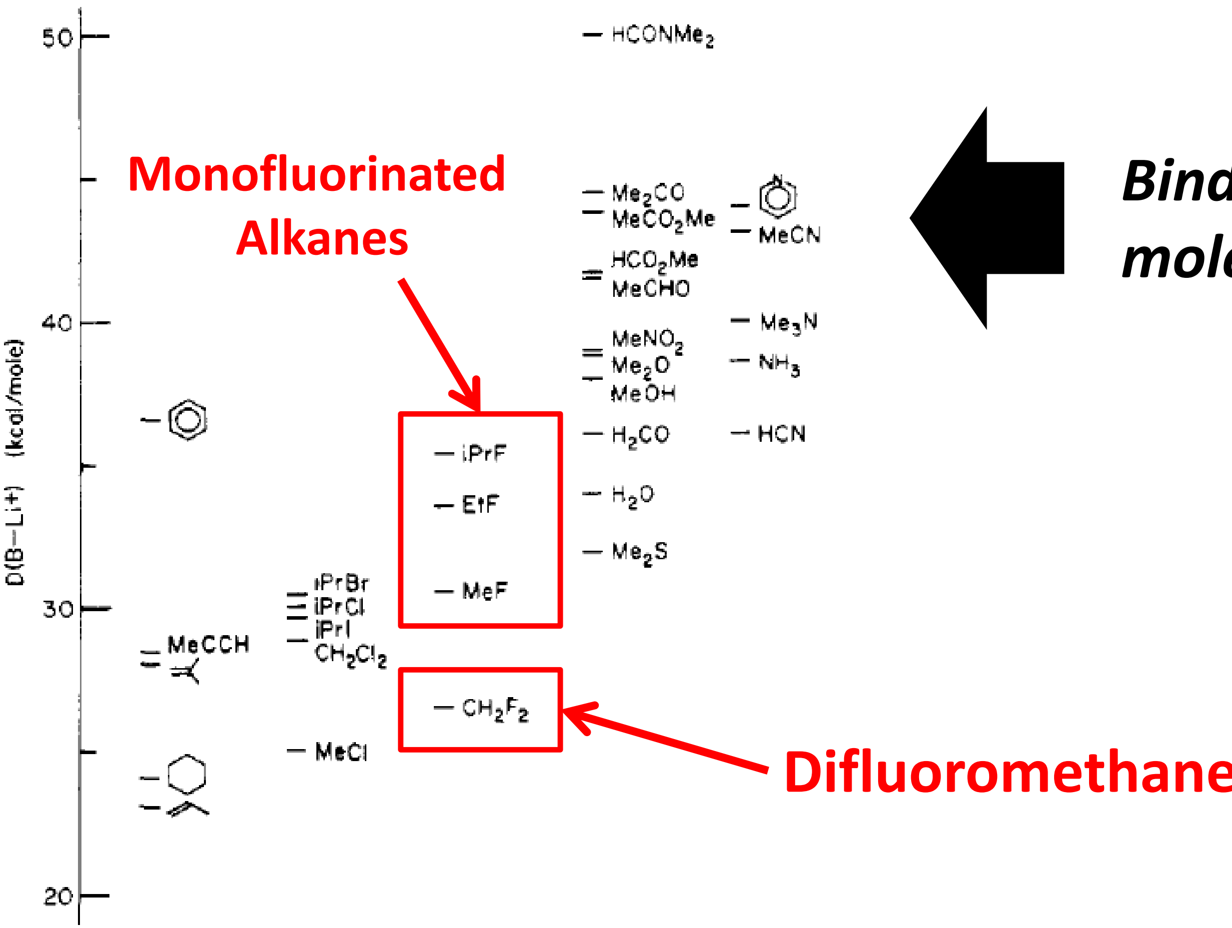
Intrinsic Acid–Base Properties of Molecules. Binding Energies of Li^+ to π- and n-Donor Bases



Binding energies of molecules to Li^+

Staley, Ralph H., and J. L. Beauchamp.,
Journal of the American Chemical Society 97.20 (1975): 5920-5921.

Lithium Liquefied Gas Electrolyte

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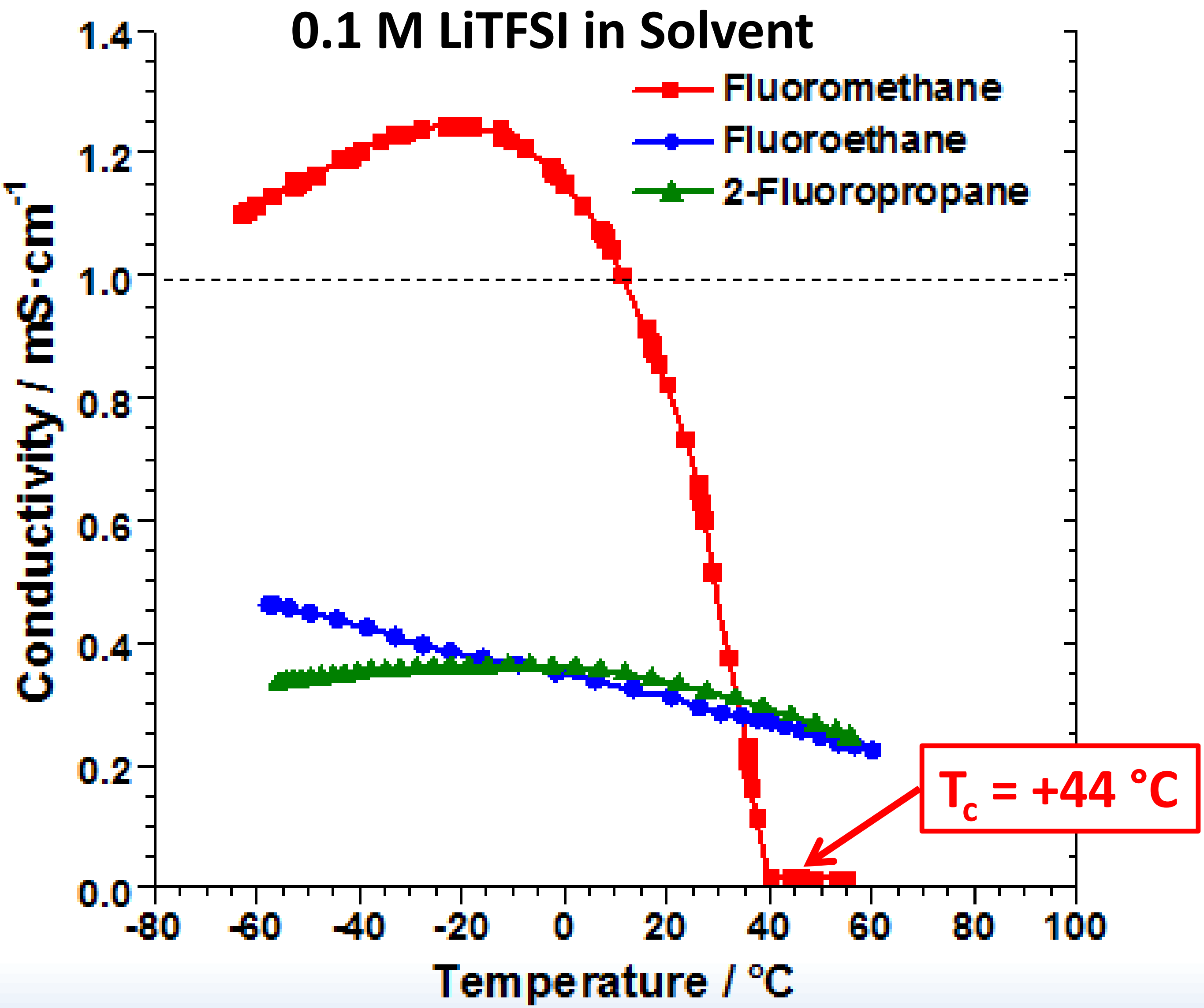

Rustomji et al., Science 356, 1351 (2017)

Lithium Liquefied Gas Electrolyte

Lithium Metal Soak Test

Fluoromethane
Decomposed after ~20 days

Fluoroethane
Decomposed after ~2 hrs

Fluoropropane
Decomposed after ~3 hrs

All solvents decomposed Li metal into LiF and Alkyl Lithium components…

Can we stabilize Li Metal to run electrochemical tests??

Rustomji et al., Science 356, 1351 (2017)

Lithium Liquefied Gas Electrolyte

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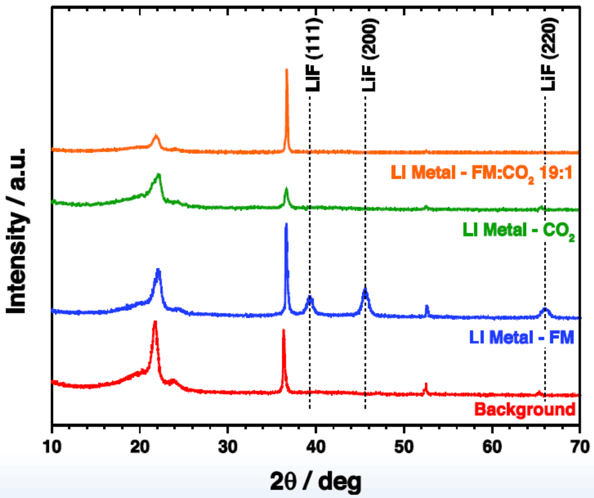
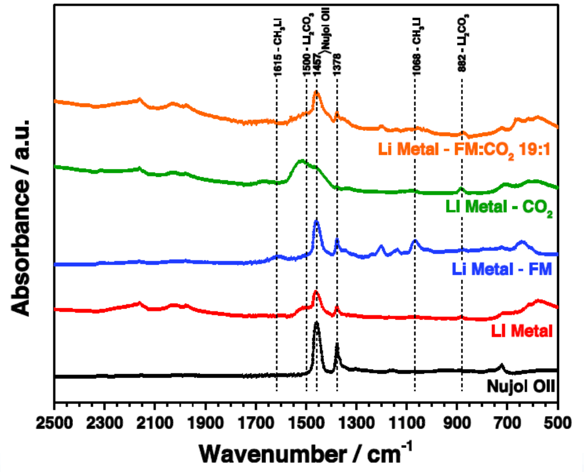
Li Metal Soaked in Fluoromethane

Li Metal Soaked in Fluoromethane : Carbon Dioxide 19:1

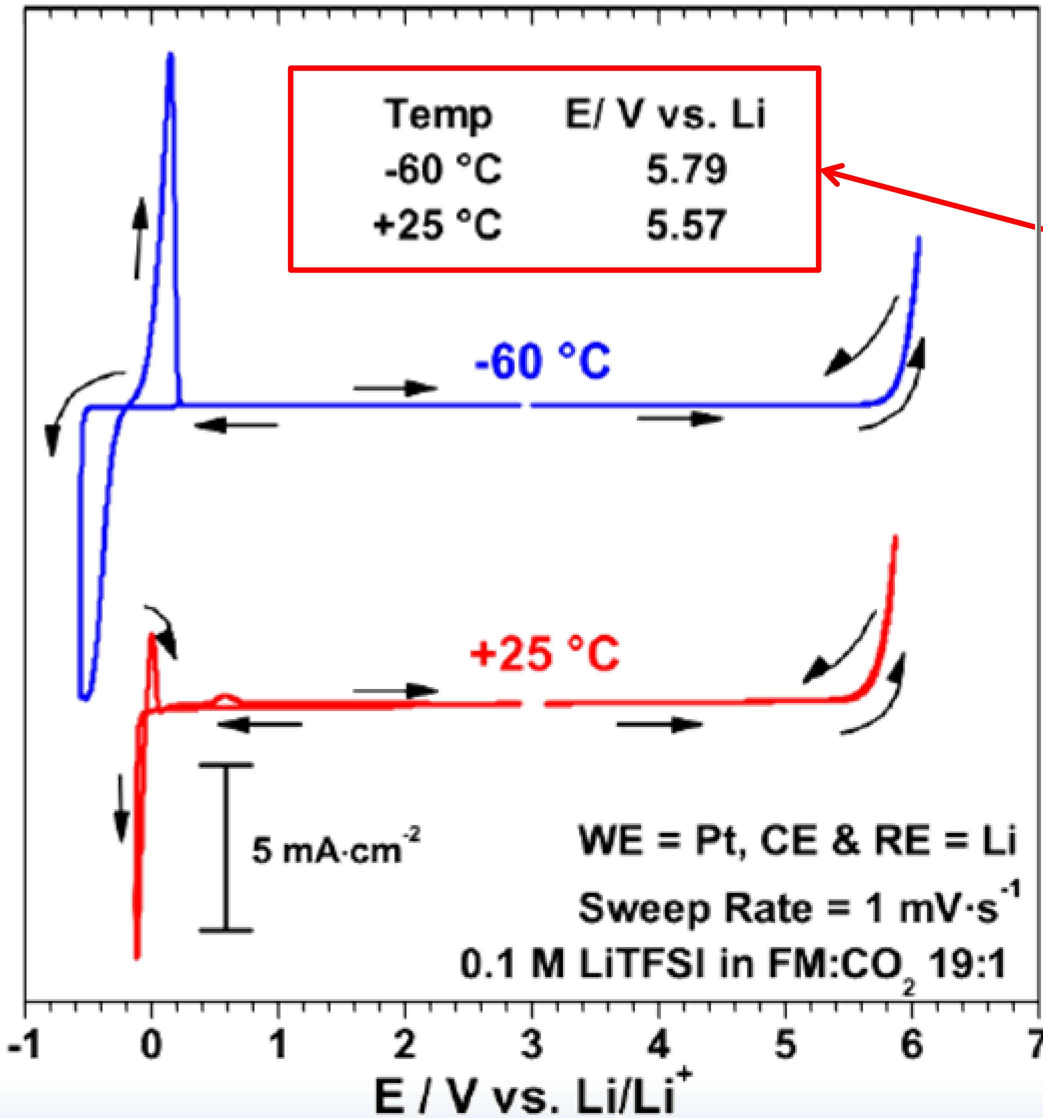




CO_2 is miscible in CH_3F and stabilizes Li metal surface via Li_2CO_3 formation

Rustomji et al., Science 356, 1351 (2017)

Lithium Liquefied Gas Electrolyte



Very high oxidation potential

Rustomji et al., Science 356, 1351 (2017)

$LiCoO_2$ Cathode

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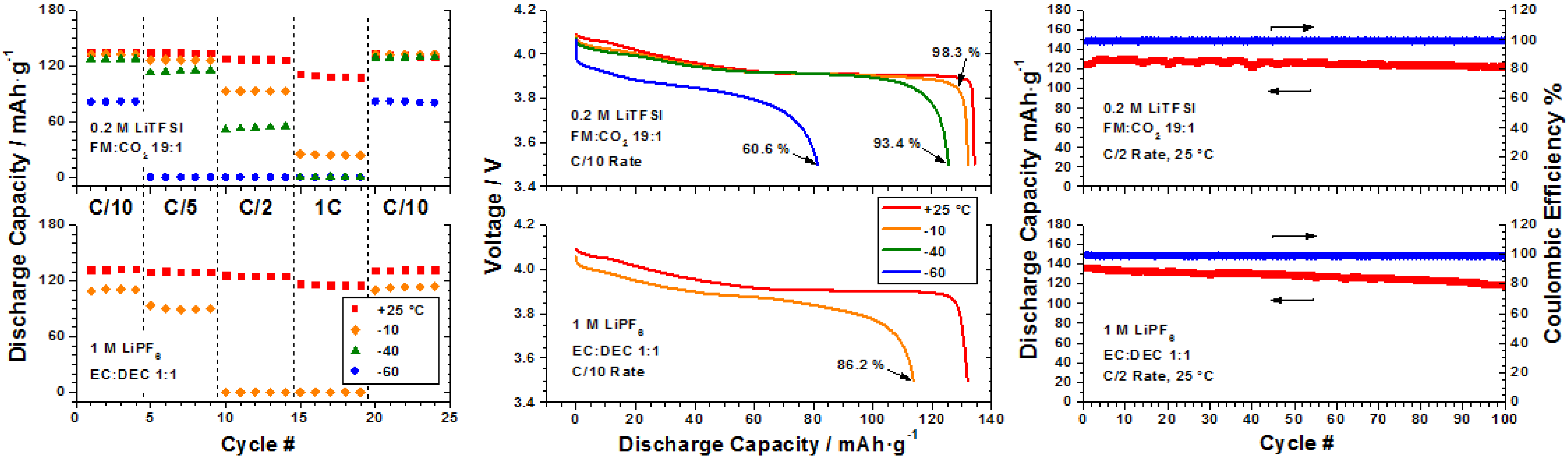
Top Panels: Liquefied Gas Electrolyte (0.2 M LiTFSI in $FM:CO_2$ 19:1)



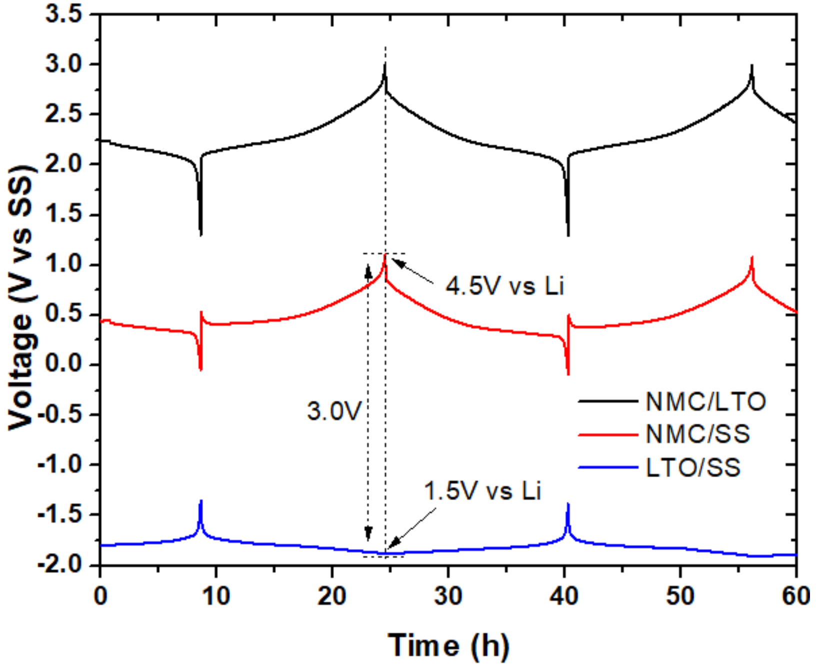
Loading ~0.9 mAh·cm^{-2}

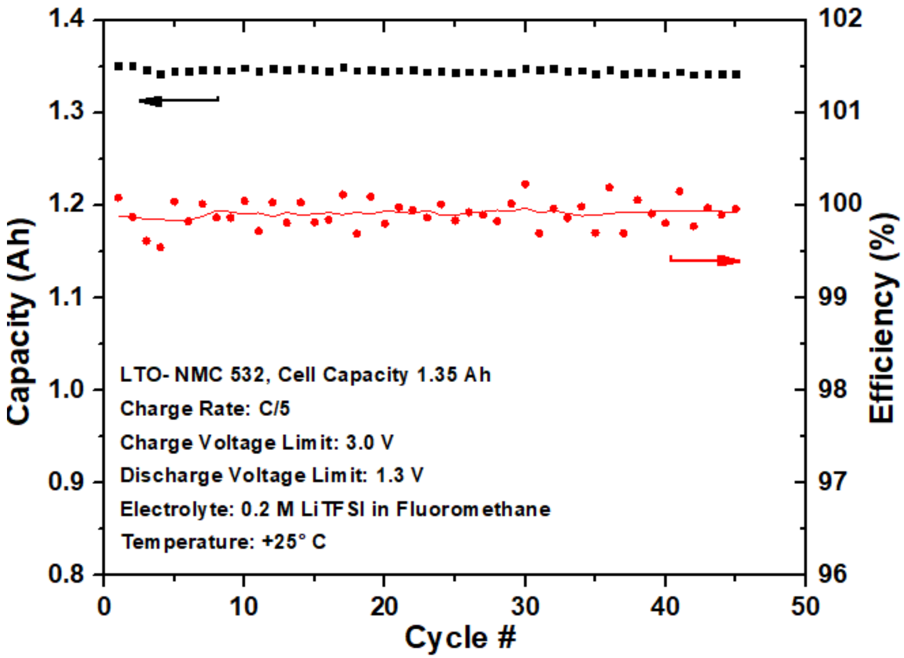
Bottom Panels: Conventional Liquid Electrolyte (1 M $LiPF_6$ in EC:DEC 1:1)

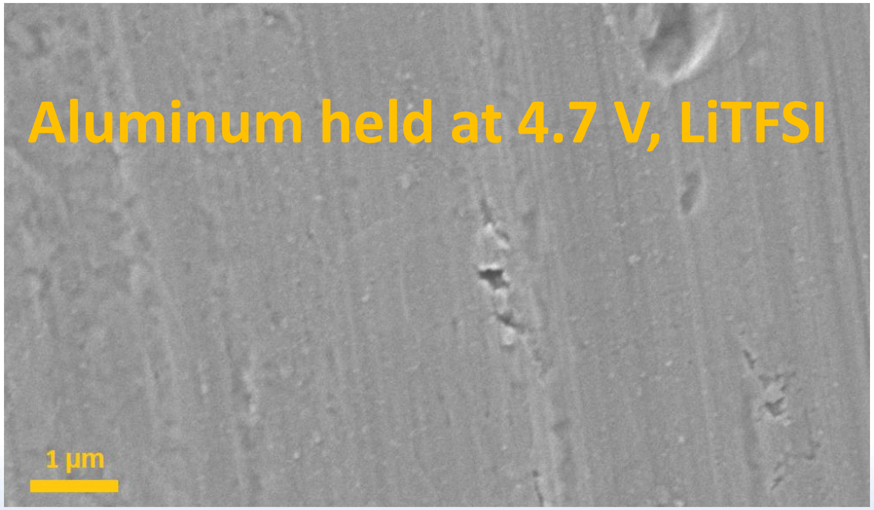
- **Stable with 4-V $LiCoO_2$ cathode**
- **Excellent low temperature performance down to -60 °C**
- **Temperature performance verified by National Renewable Energy Lab (NREL)**

Rustomji et al., Science 356, 1351 (2017)

NMC Cathode







~99.9% efficiency on 4.5 V NMC
No aluminum etching, even with LiTFSI (protective AlF_3 layer?)

Rustomji et al., Unpublished

Lithium Metal Anode

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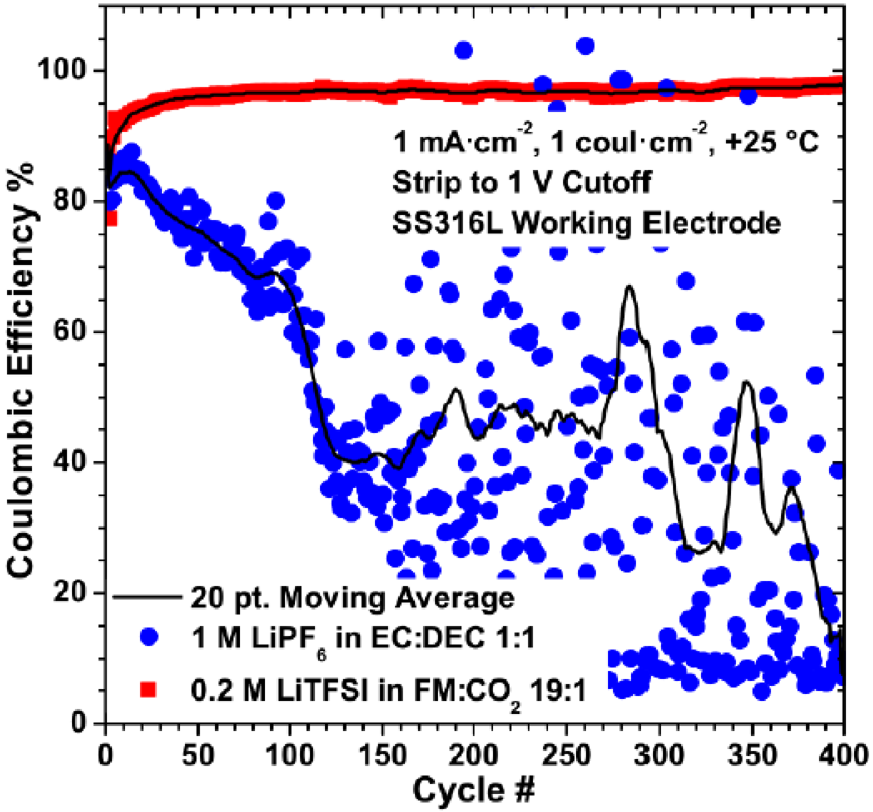
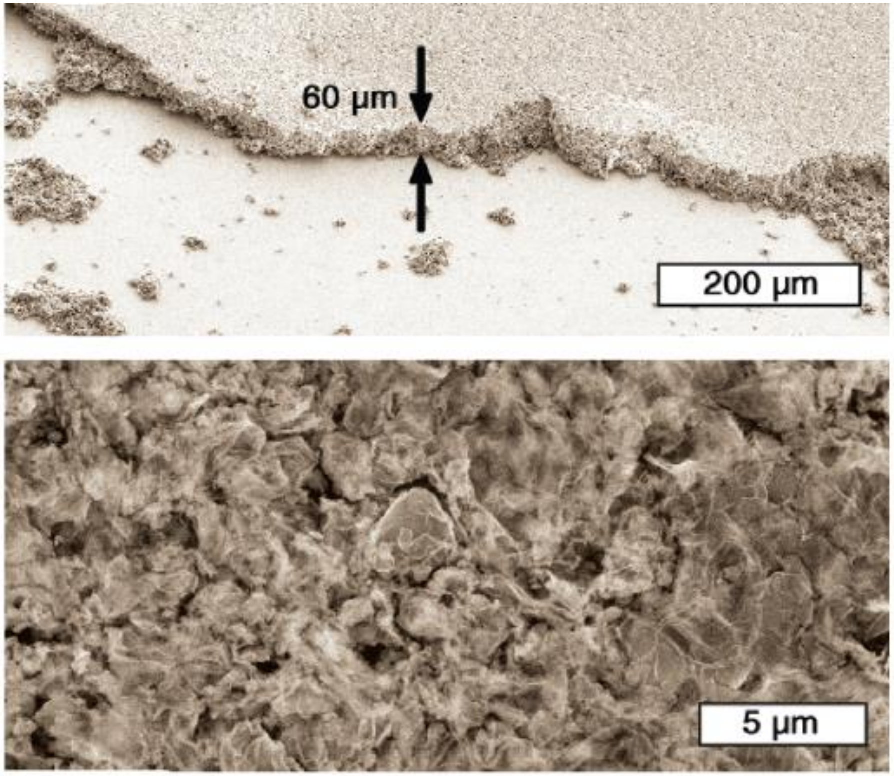
Li Platting/Stripping Efficiency



Stainless W.E. After 400 Cycles



- ~97.5% stable efficiency, among highest reported
- Dendrite free surface

Rustomji et al., Science 356, 1351 (2017)

Lithium Metal Anode

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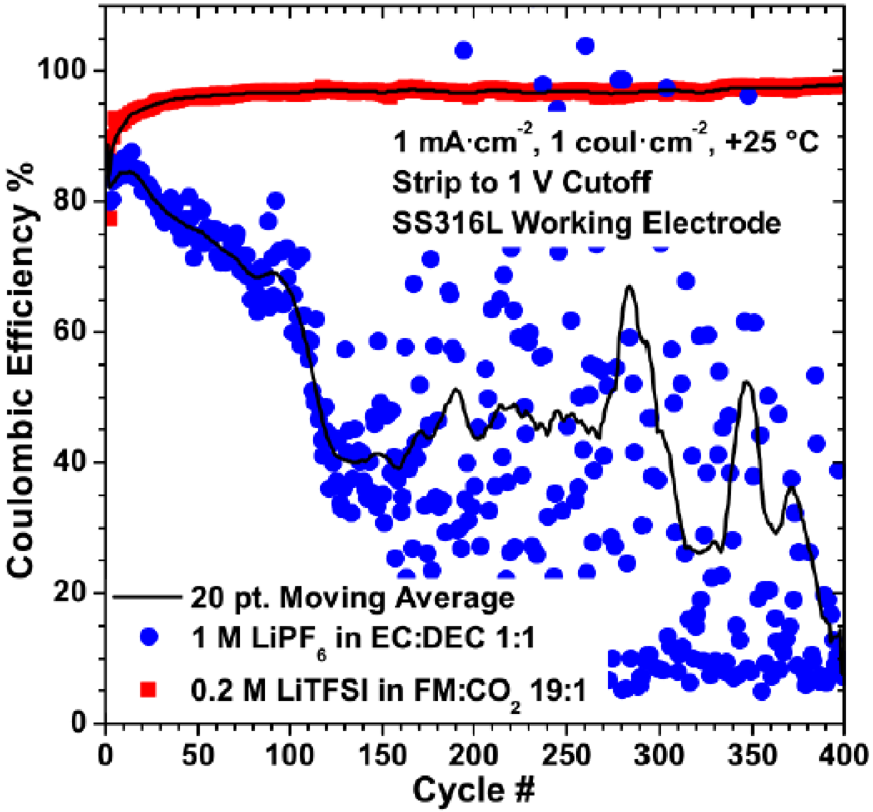
Li Platting/Stripping Efficiency



Factors common to improved Li efficiency

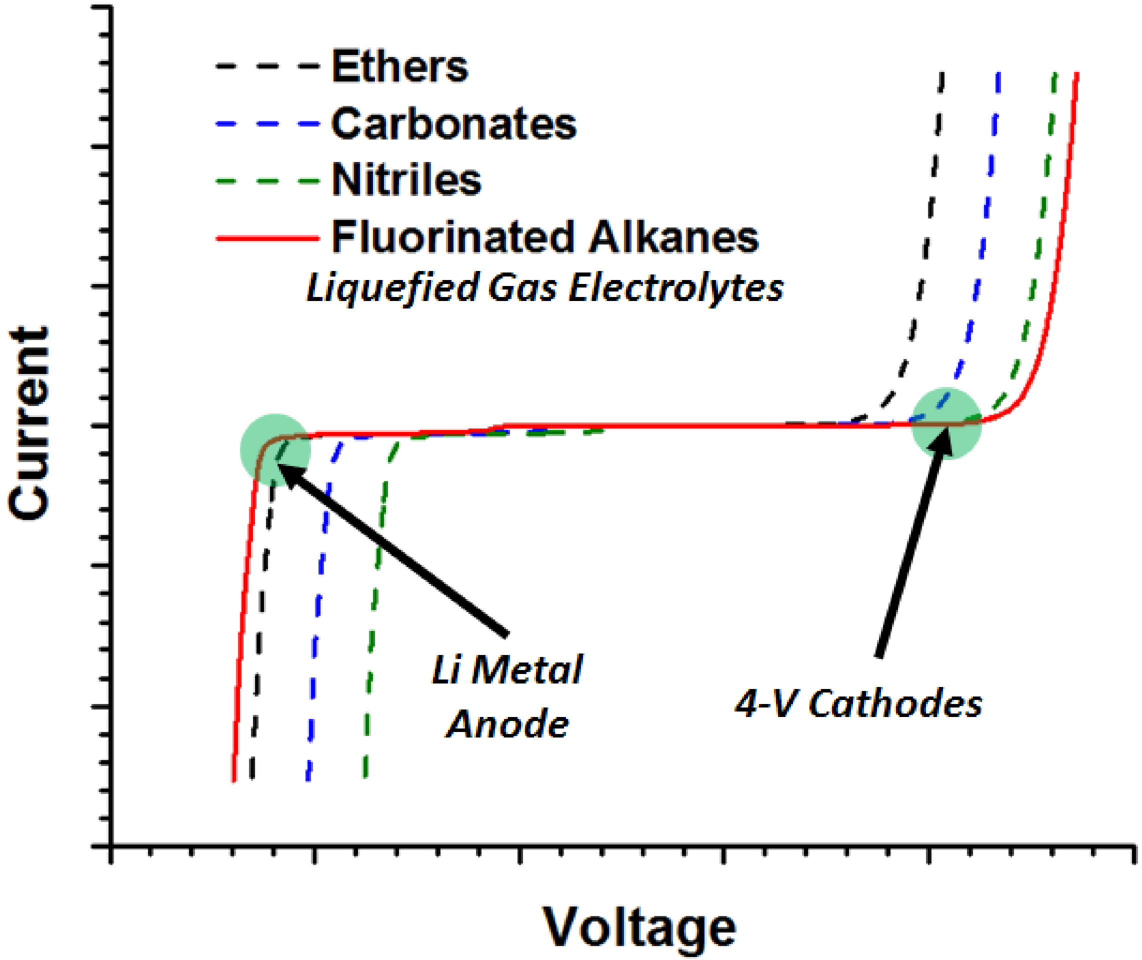
- Low solvent viscosity[1]
- High stack pressure[2]
- LiF in SEI[3]

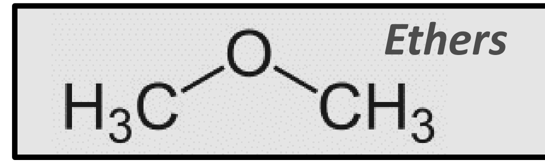
Fluoromethane has all of these!!

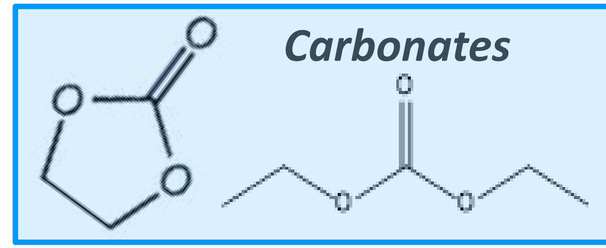
1. Park, Min Sik, et al., Scientific reports 4 (2014): 3815.
2. J. Yamaki, et. al., Journal of The Electrochemical Society 141.3 (1994): 611-614.
3. L. A. Archer, et. al., Nature materials 13.10 (2014): 961-969.

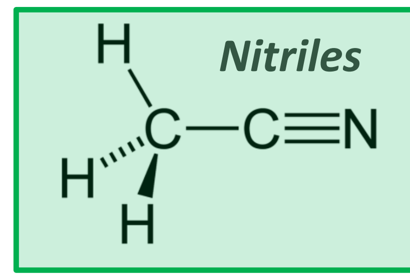
Rustomji et al., Science 356, 1351 (2017)

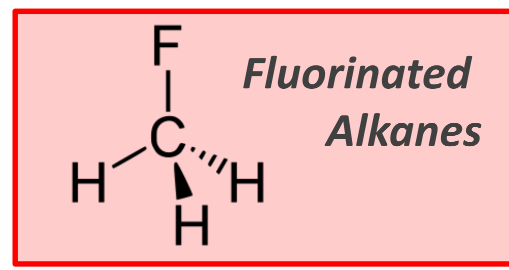
NextGen Lithium Electrolyte











First electrolyte demonstrated to be compatible with lithium metal and 4-V cathodes.

Liquefied Gas - Safety

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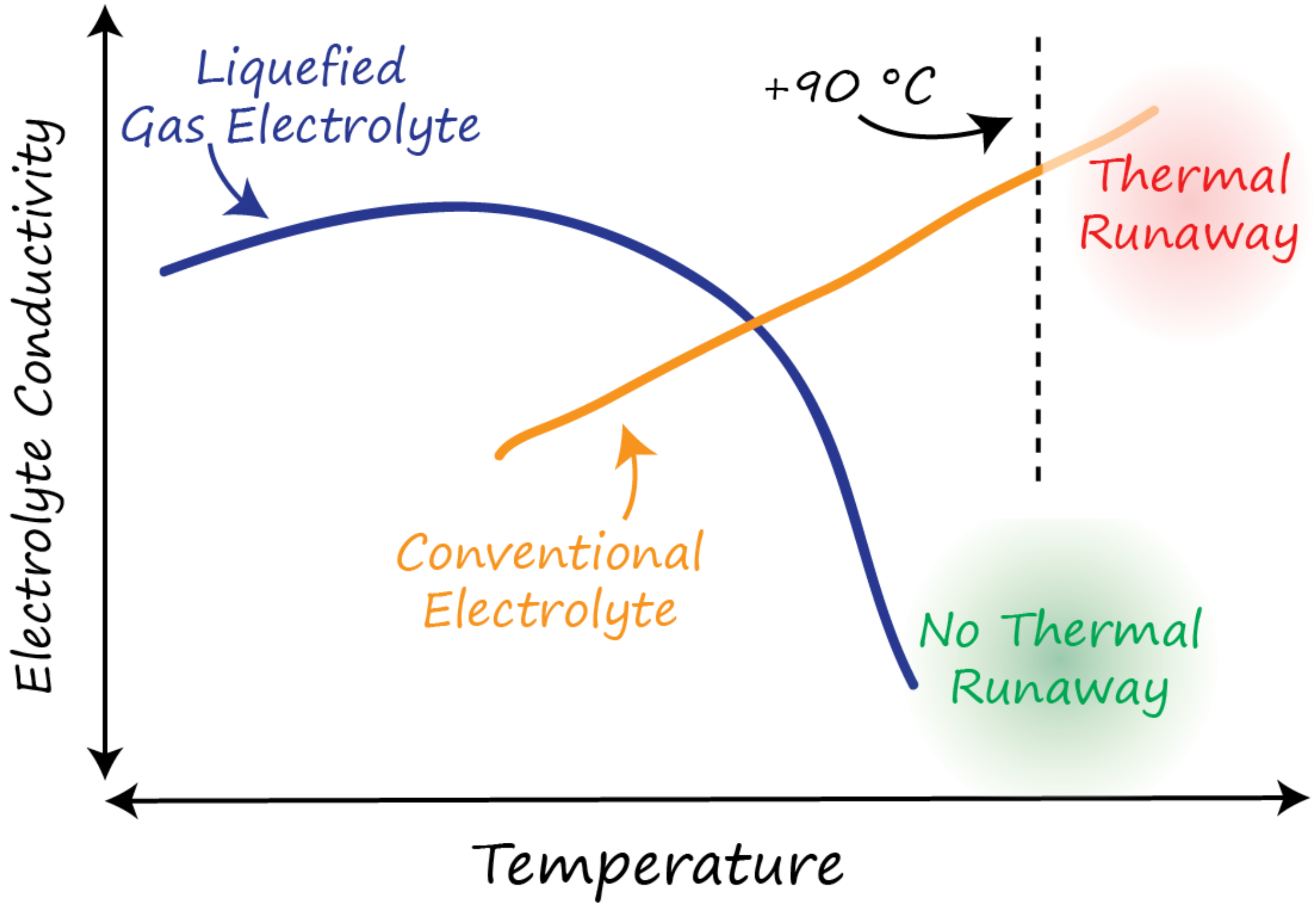
Next Generation Energy Storage Devices



Can we engineer a custom shut-down temperature by modifying super-critical point??

Liquefied Gas - Safety

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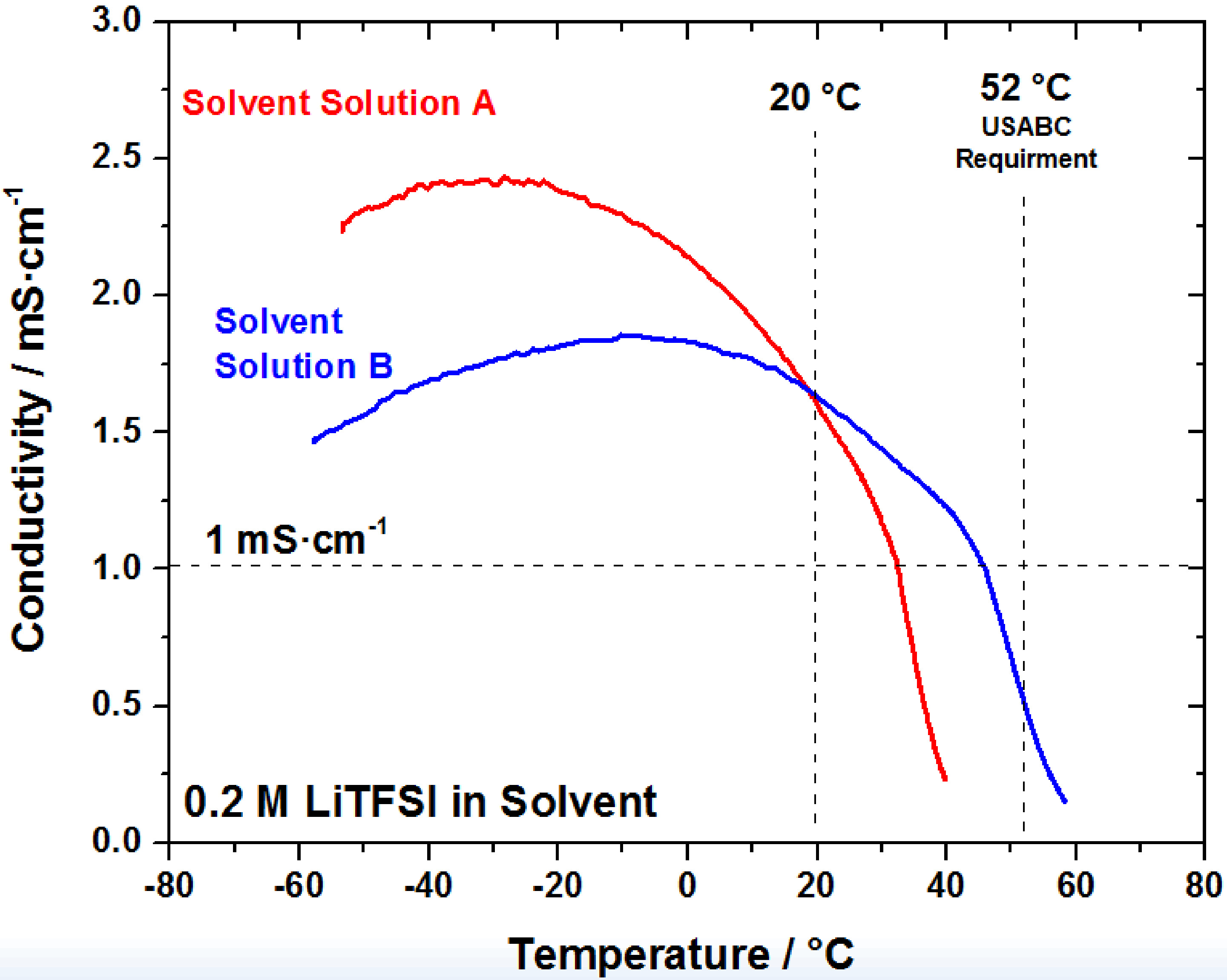
Next Generation Energy Storage Devices



C Rustomji, et. al., Unpublished

Liquefied Gas - Safety

Cell is punctured and electrodes are shorted.

Conventional Liquid Electrolyte	***Liquefied Gas Electrolyte***
Electrolyte remains in the cell	*Electrolyte gas solvent may rapidly escape through cell's punctured hole*
High ion transfer between shorted electrodes heats cell	*No ion transfer between electrodes*
Thermal Runaway	***No Thermal Runaway***

With no organics in SEI, would there even be thermal runaway even if exposed to high temperatures?

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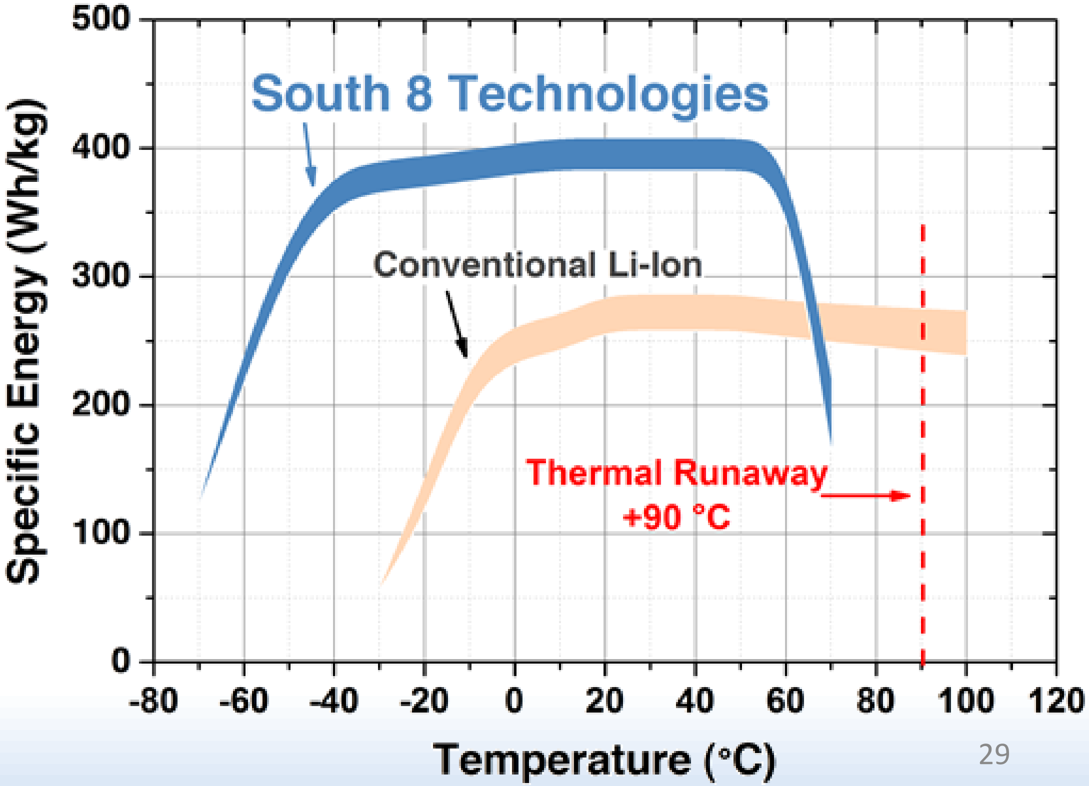
A breakthrough in electrolyte chemistry that offers…

Lithium Battery

- Ultra-low temperature operation down to -60 °C
- Non-toxic solvent
- Increased safety through mitigation of thermal runaway
- Increase in energy density
    - Li Metal anode
    - 4.5 V NMC Cathode



Electrochemical Capacitor

- 3.0 V Operation
- Temperature down to -120 °C
- Low flammable electrolyte
- Non-toxic solvent