# Battery Power for All-Electric Road Vehicles

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- Modern Society runs on the energy stored in fossil fuels.
- This dependence is not sustainable
- Batteries store clean electric power

# Outline

- Introduction to rechargeable batteries
- Advantages & disadvantages of liquid versus solid electrolytes
- A transforming dielectric amorphous-oxide electrolyte
- Status of battery-cell development

# Batteries

- Large-scale batteries contain multiple identical cells
- Battery cells deliver $P_{dis} = I_{dis}V_{dis}$ for $\Delta t$
- Cell capacity at a constant $I_{dis} = dq/dt$ is

$$\int_0^{\Delta t} I_{dis}\, dt = \int_0^{Q(I_{dis})} dq \quad \text{per unit weight, volume}$$

- Stored energy density:

$$\int_0^{\Delta t} P_{dis}\, dt = \langle V_{dis} \rangle \cdot Q(I_{dis})$$

# Components of a Battery Cell

Anode(−)|$M^+$-Electrolyte| Cathode (+)

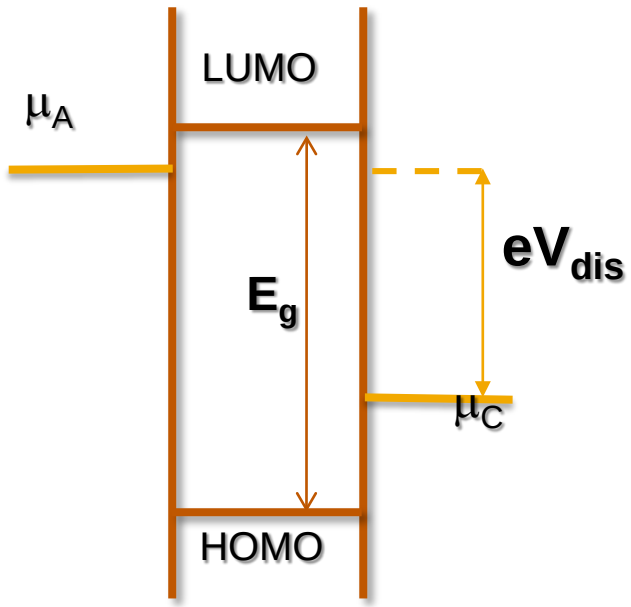
$\mu_A$ |⟵ $\Delta l$ ⟶| $\mu_C$

- Electrolyte is $M^+$ conductor, $e^-$ insulator
- Cell delivers $P_{dis} = I_{dis}\, V_{dis}$

$$V_{oc} = (\mu_A - \mu_C)/e$$

$$I_{dis} \sim \sigma_M A/\Delta l \text{ (neglecting interface resistance)}$$

# Electrolyte $E_g$ Restricts $V_{dis}$




- $\mu_A$ > LUMO or
- $\mu_C$ < HOMO
  require SEI

# Rechargeable Batteries Store $P_{ch}$

- $P_{ch}$ reverses reaction inside cell
- $V_{dis} > V_{oc} - \eta_{dis} I_{dis}$ , $V_{ch} = V_{oc} + \eta_{ch} I_{ch}$
- Storage efficiency: $P_{dis}/P_{ch} < 100\%$
- Coulomb efficiency: $Q(I_{dis})/Q(I_{ch})$ per cycle
- **Can there be a $Q(I_{dis})/Q(I_{ch}) > 100\%$?**

# Critical Engineering Targets

## (for powering a competitive all-electric road vehicle)

Safety: (i) nonflammable components

(ii) environmentally friendly materials

Cost: (i) materials, fabrication, management

(ii) charge/discharge cycle life for 150,000 miles

Rates: (i) (3/4 charge < 10 min.)

(ii) $T_{op}$ down to −30°C

Range: 300 miles between charges: volumetric

$\langle V_{dis}(q) \rangle \cdot Q(I_{dis})$

# Electrolyte Requirements
## (Liquids versus Solids)

- Retain electrode/electrolyte contact during electrode volume change
- Dendrite-free plating/stripping of alkali-metal anode
- $\sigma_M > 10^{-2}$ S cm$^{-1}$ at 25°C
- $E_g > 5$ eV matched to $\mu_A$ and $\mu_C$
- Separators: mechanically robust, chemically inert, thin (< 30 μm), large-area membranes

# Aqueous Electrolytes

- Acidic or Alkaline: $H^+$
- Electrolyte $E_g$ = 1.23 eV: $V_{oc} \lesssim 1.5$ V
- Need large $Q(I)$ of air cathode for large $\langle V_{dis} \rangle$ $Q(I_{dis})$

# Organic-Liquid Electrolytes
## (Carbonates and Ethers)

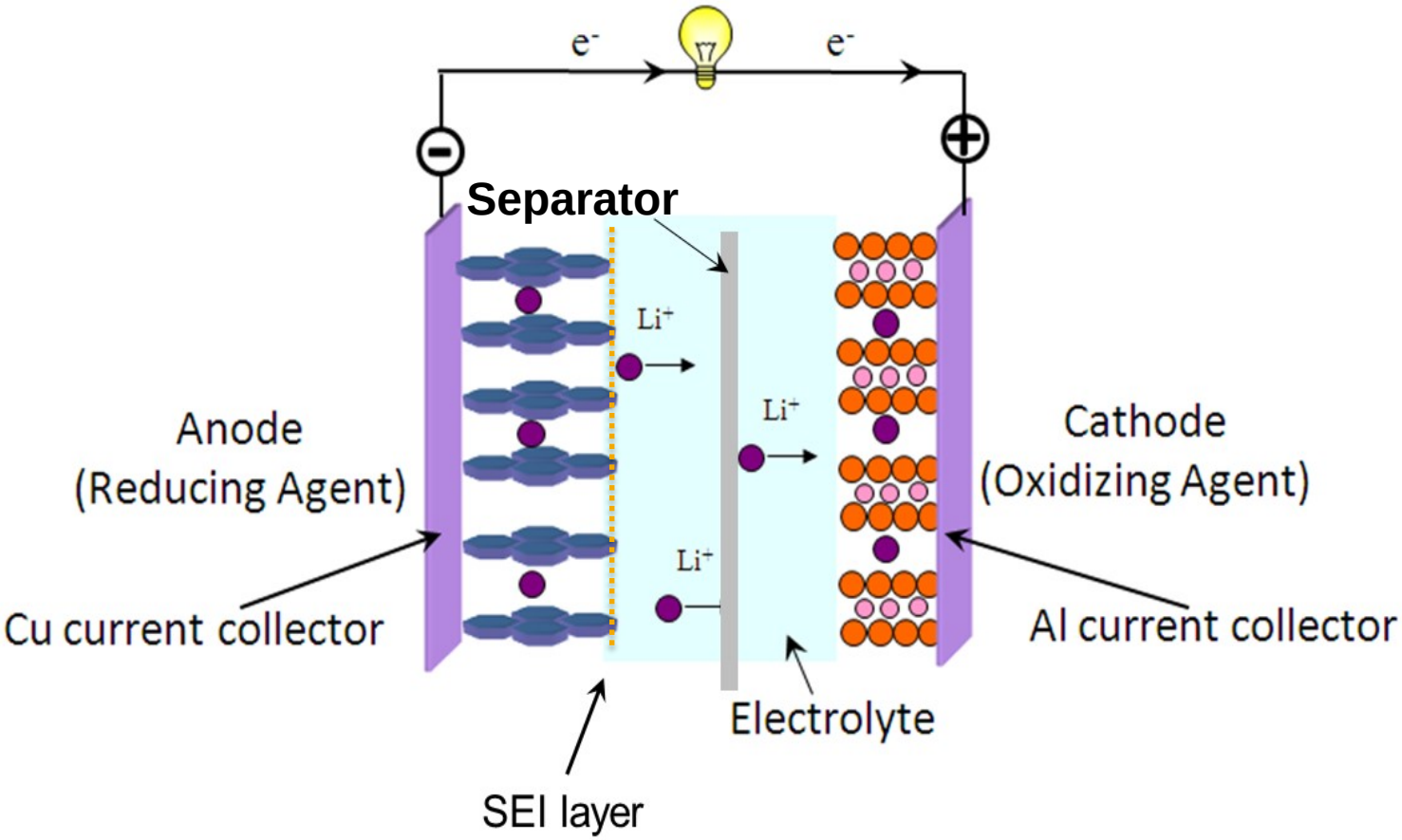
### Advantages

- $Li^+$, $Na^+$, $K^+$ ionic conductors
- $\sigma_i \approx 5 \times 10^{-2}$ S cm$^{-1}$
- Accommodates electrode volume changes

### Limitations (carbonates)

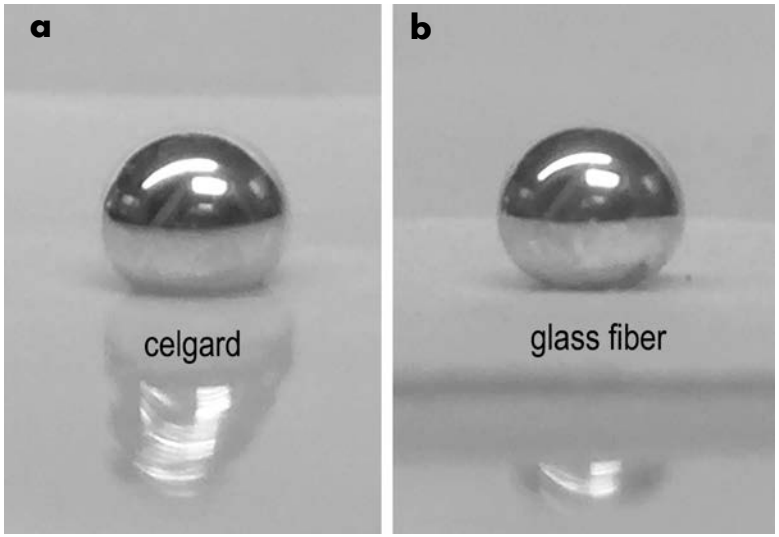
- $E_g \approx 3\ eV$ not matched to high-voltage $V_{oc}$
  LUMO ≃ 1.2, HOMO ≃ 4.2 eV versus lithium
- $V_{oc} > 3\ V$ with SEI passivation, but limits cycle life
- $LiFePO_4/Li_4Ti_5O_{12}$ for stationary storage ($\langle V(q) \rangle \cong 2$ eV)

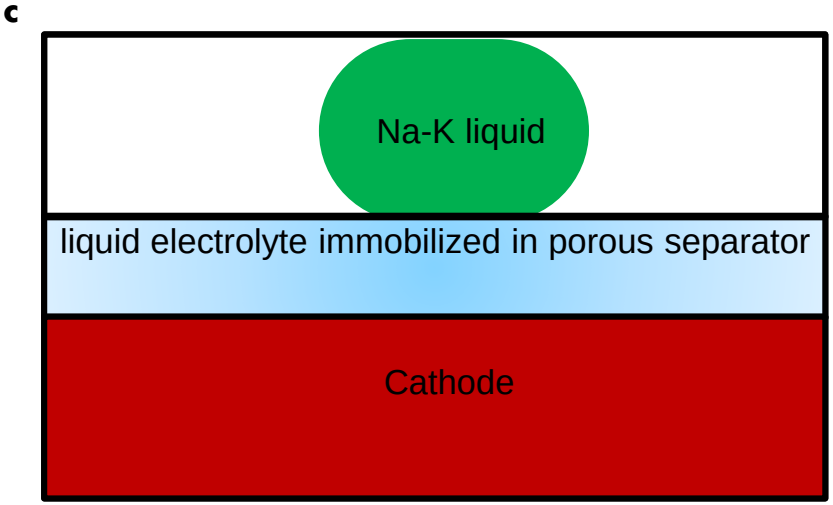
# The Li-Ion Battery

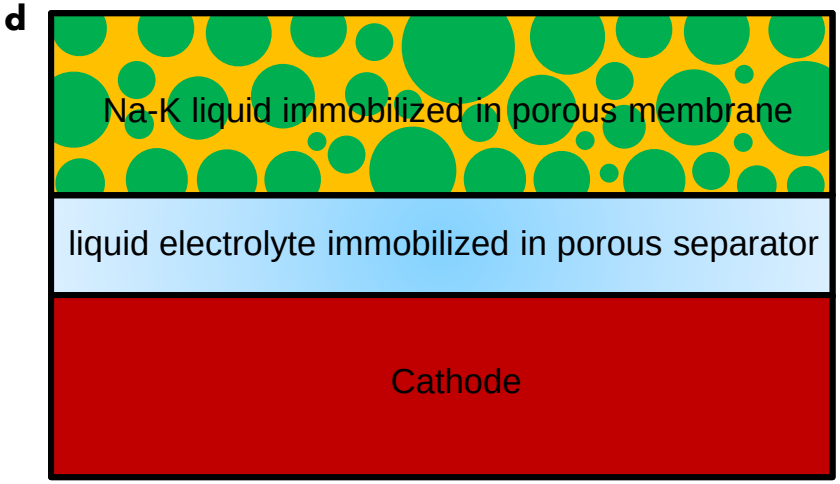



Limited safe $<V_{dis}>$ $Q(I_{dis})$/volume

# Alkali-Metal Wetting




Leigang Xue *et al.*

# Solid Electrolytes
## ($\sigma_{Li}$ at 25°C)

- Crystalline ceramics:

  oxides: $\sigma_{Li} \lesssim 10^{-3}$ S cm$^{-1}$, $E_g > 5\ eV$

  sulfides: $\sigma_{Li} \cong 10^{-2}$ S cm$^{-1}$ $(E_F(Li) - E_c) = 3.5\ eV$
- Polymers: $\sigma_{Li} \approx 10^{-4}$ S cm$^{-1}$, $E_g > 5\ eV$, plastic
- Amorphous dielectric ceramic: $Li^+$ or $Na^+$ coexist with electric dipoles

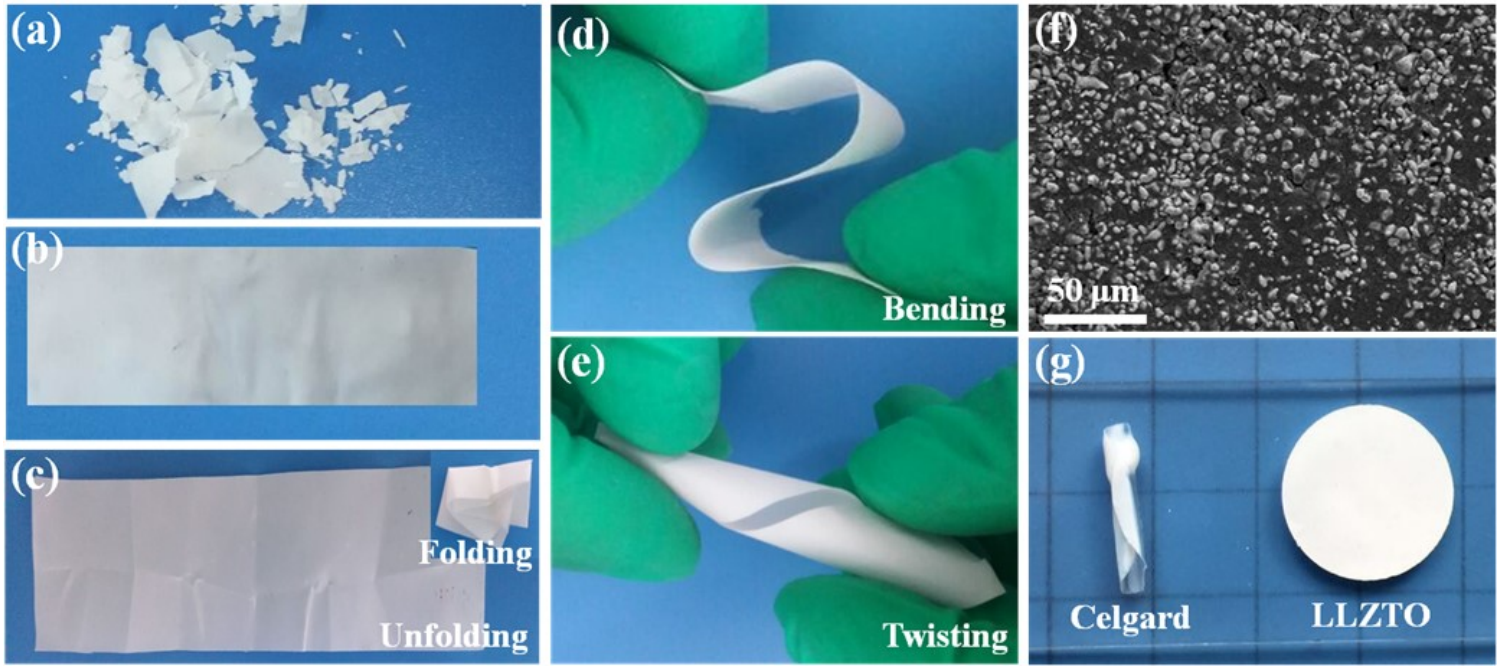
  $\sigma_{Li} \approx 10^{-2}$ S cm$^{-1}$, $E_g > 8\ eV$

# Ceramic Garnet $Li^+$ Electrolyte

Yutao Li

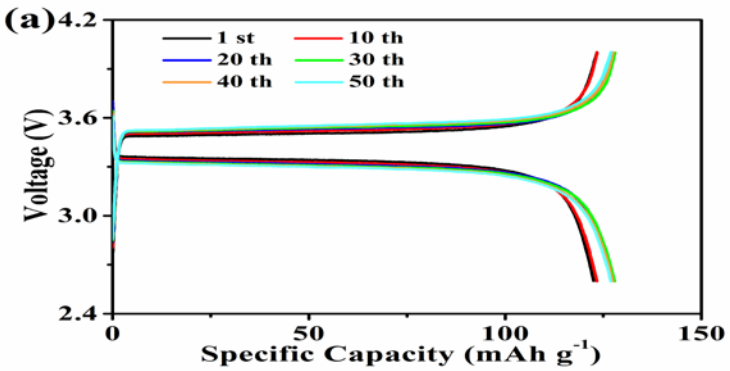
- $Li_{7-x}Lr_3Zr_{2-x}Ta_xO_{12}$ not reduced by $Li^0$ anode
- 3D interstitial space: Tet bridged by Oct.
- $10^{-4} \leq \sigma_{Li} \leq 10^{-3}$ S $cm^{-1}$ for $0 \leq x \leq 0.5$
- $T_{op} \gtrsim 55°C$ for thin ceramic film
- Air exposure gives $Li_2CO_3$ on surface

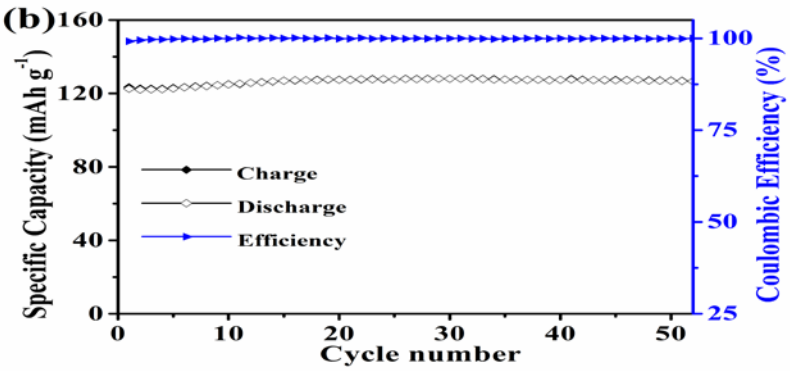
# All-Solid-State Li/$LiFePO_4$ Batteries with $Li_2CO_3$-Free Garnet

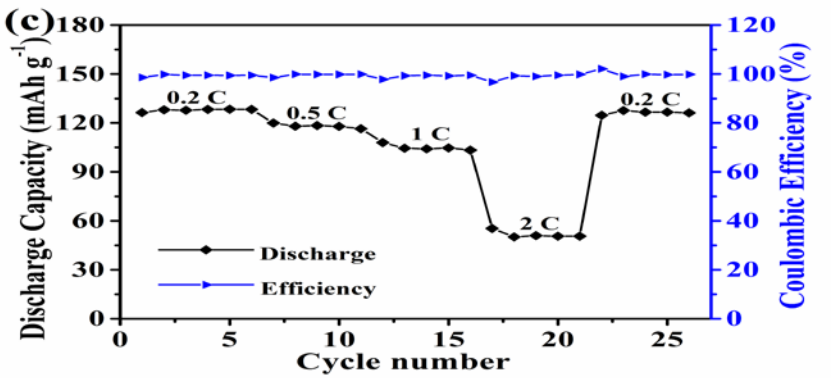


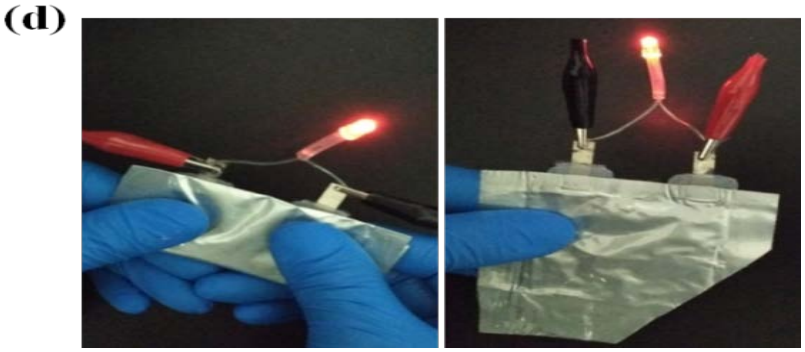

Photographs of the ceramic–based composite membranes: (a) without PEG; (b) with 5 wt% PEG; photographs of PEO–LLZTO–PEG membrane (the weight ratio of PEO:LLZTO:PEG is 10:85:5) showing the (c) structural integrity after cutting corner; (d–e) the self–standing and flexibility; (f) SEM image; (g) thermal stability at 140 $^{o}$C for 30 min.

# All-Solid-State Li/$LiFePO_4$ Pouch Cell at 55°C with PEG, PEO-in-Garnet Electrolyte

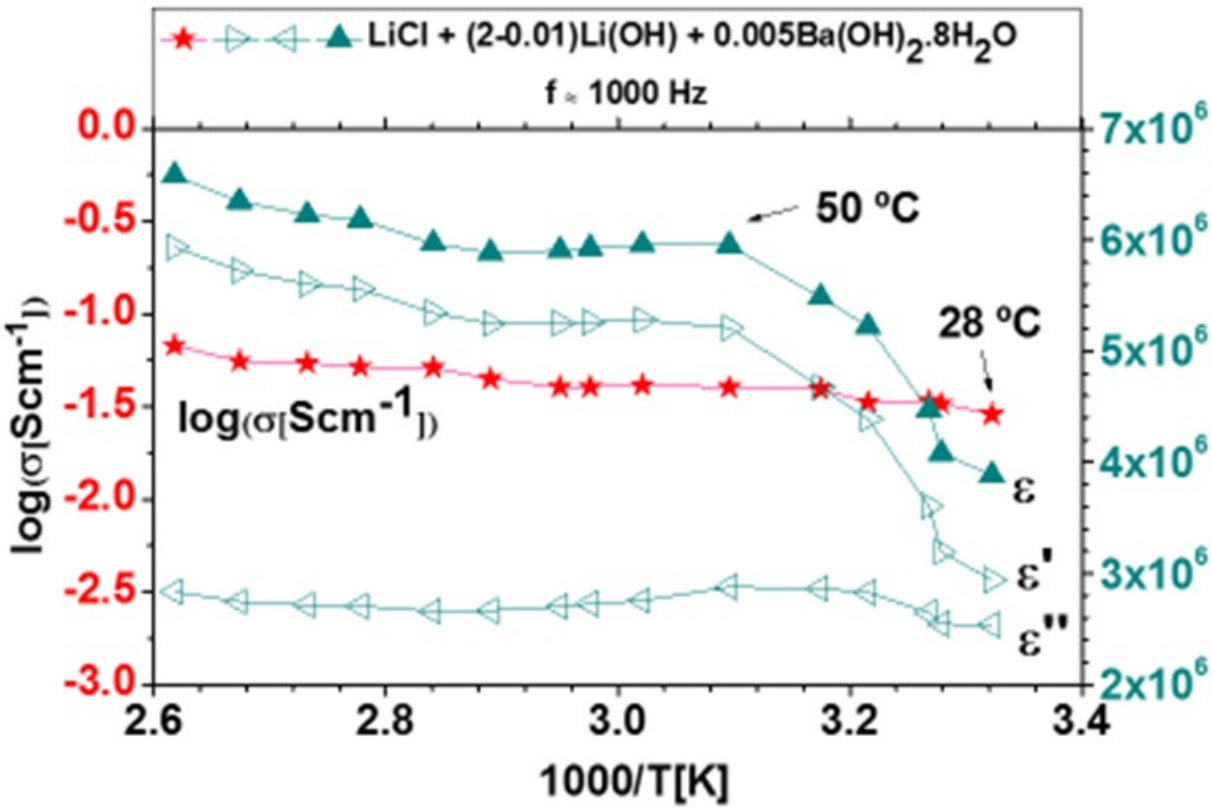


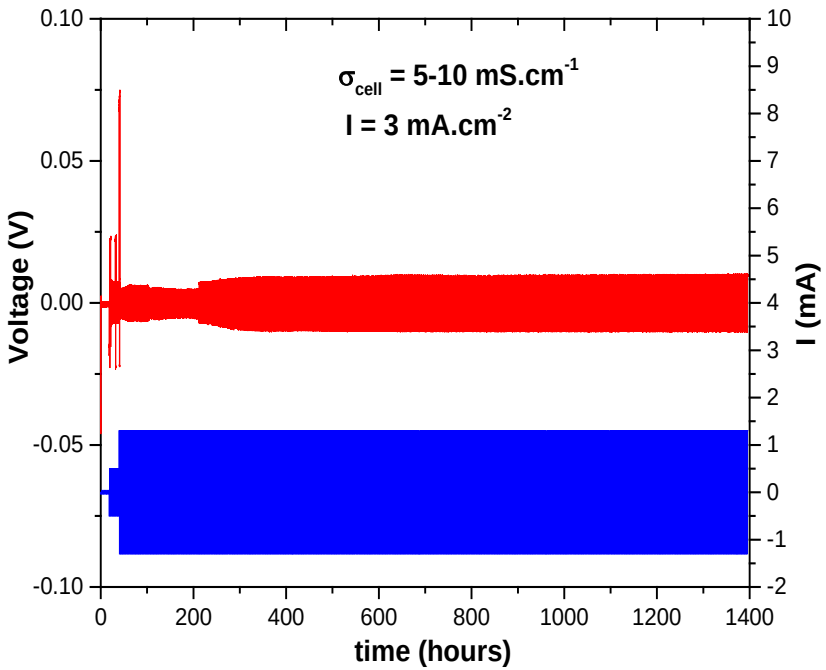



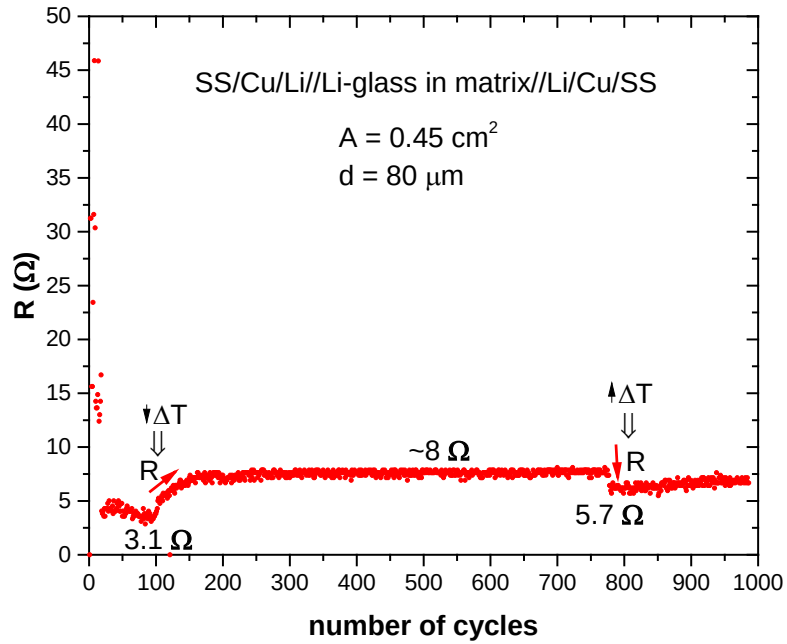
# Arrhenius Plots of $Li^+$ *ac* conductivity and permittivity at 1000 Hz of a Li-glass



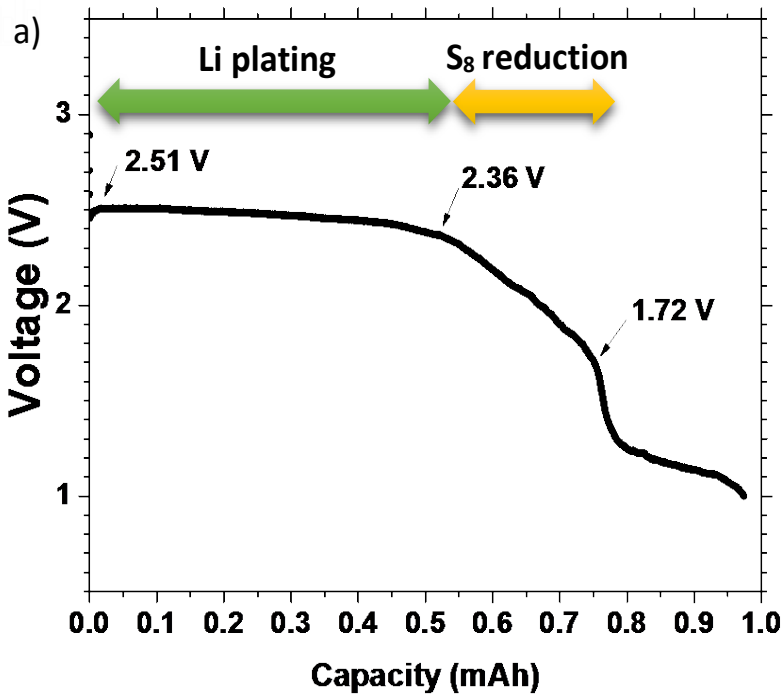

M. Helena Braga

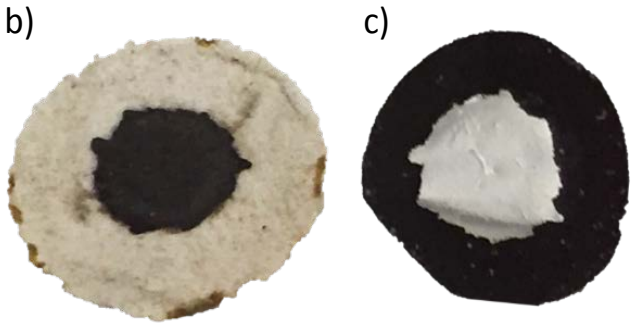
# Symmetric Li/Li-glass/Li cell (Glass $\sigma_{Li}$ = 15 × $10^{-2}$ S $cm^{-1}$ at 25°C)



# Li/Li$^+$-Glass/S + C + Cu



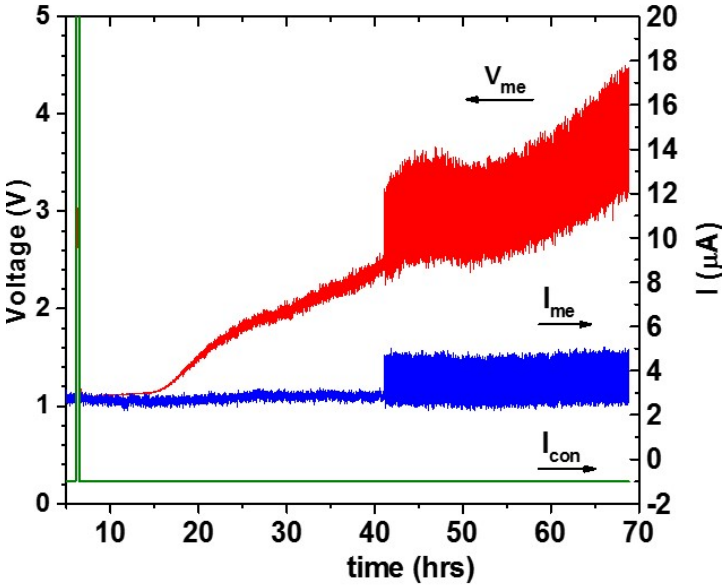

$E_F(Li) = -1.39$ eV, $E_F(S_8) = -4$ eV versus vacuum.

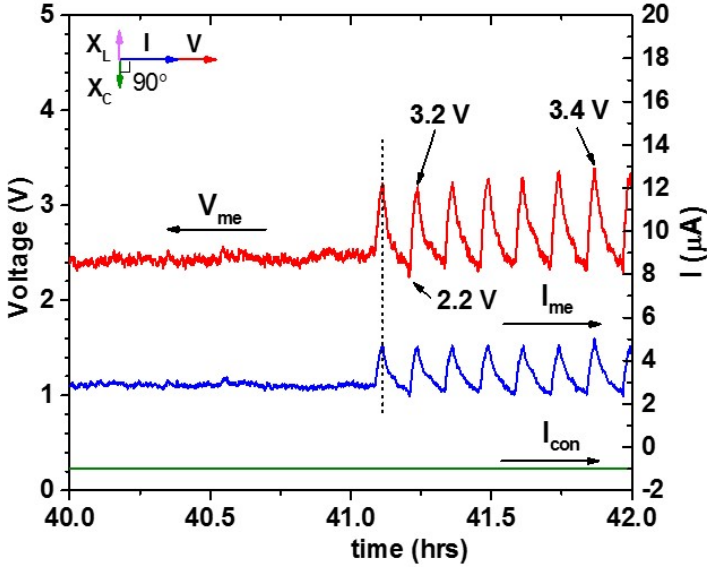
Therefore $[V_{OC} = E_F(Li) - E_F(S_8)]/e \approx 2.6$ V

# Self-Charge, Self Cycling
## (Found with Li-glass, Na-glass)

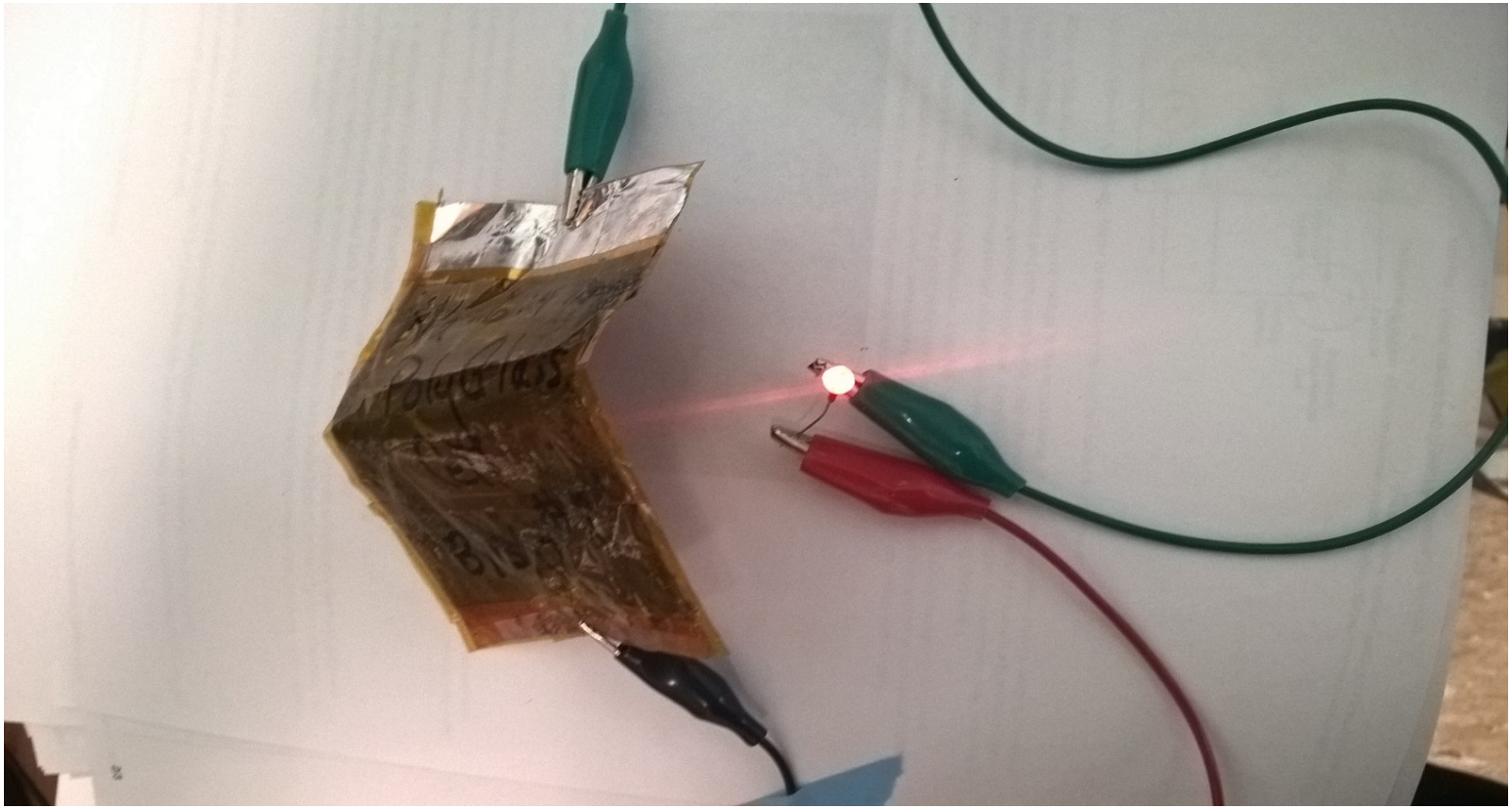
Cu/Li-glass/Al

$$\mu_A(Al) - \mu_C(Cu) \approx 2.2\ eV;\ \mu_A(Li) - \mu_C(Cu) \cong 3.5\ eV$$



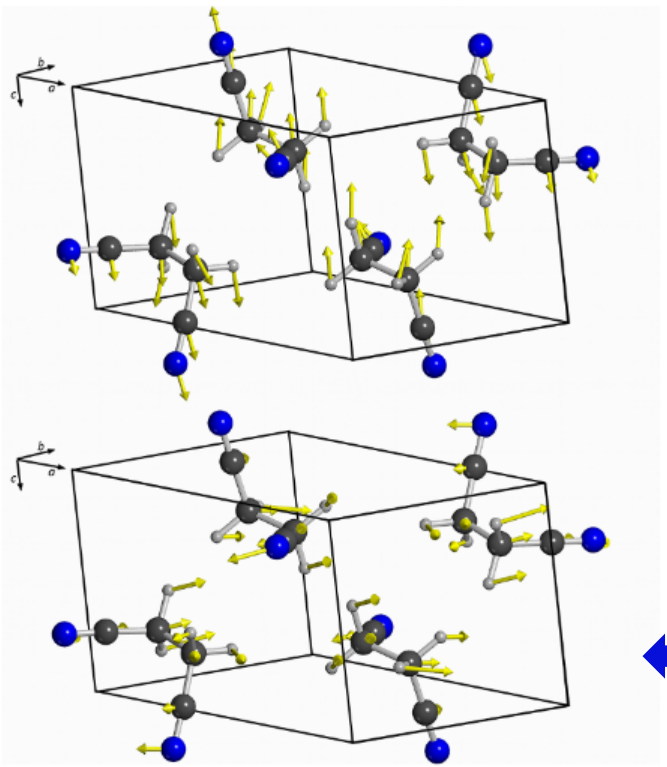



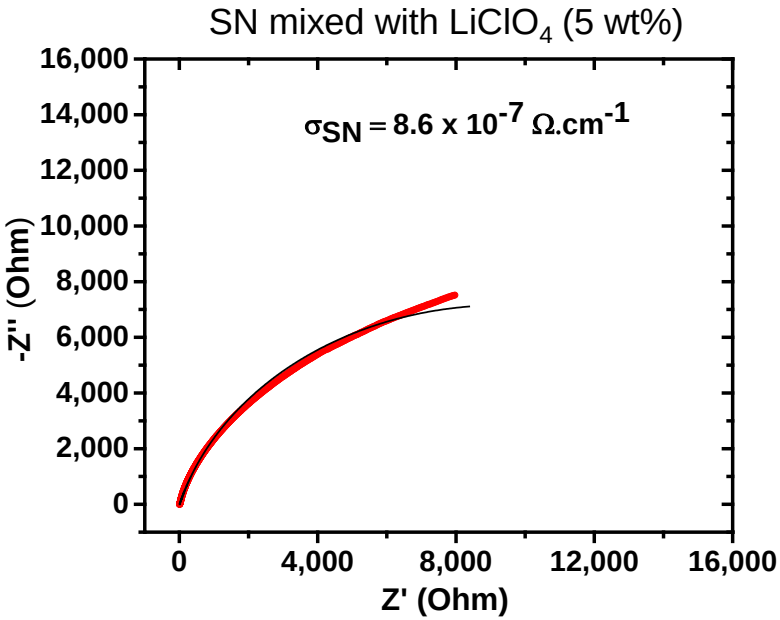
# Al/$Na^+$-glass + polymer/Cu



**A Relaxation Oscillator**

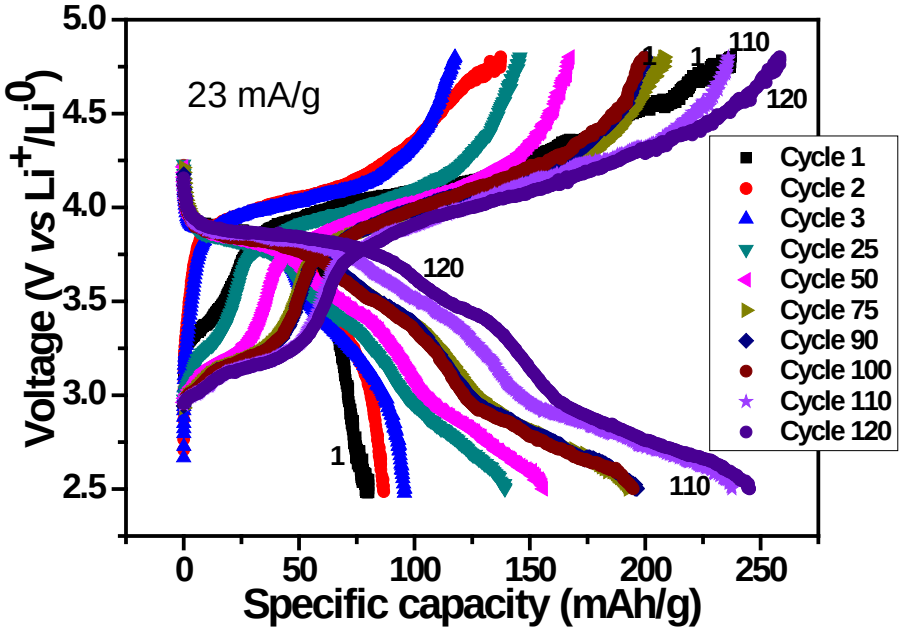
# Succinonitrile (SN)

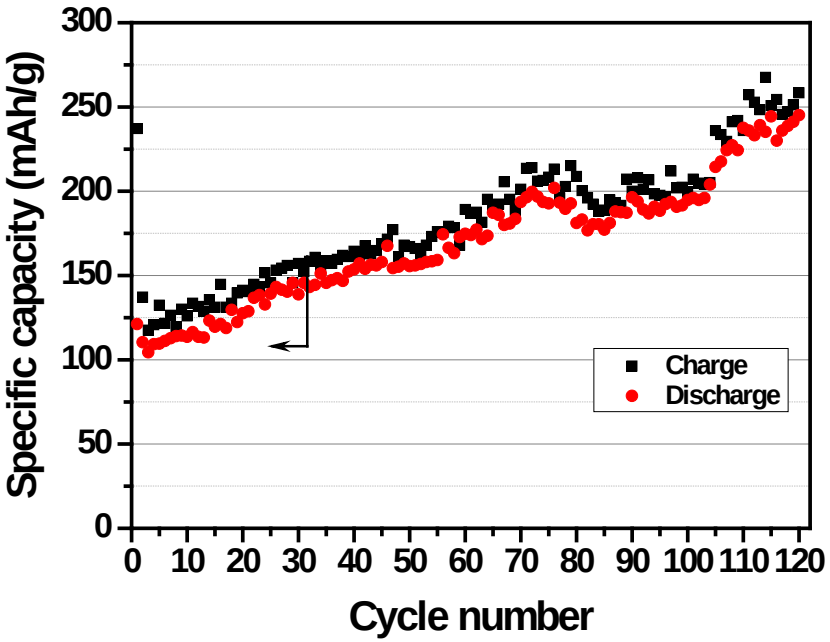





**Terahertz vibrational modes of the rigid crystal phase of succinonitrile.**
D. V. Nickel, S. P. Delaney, H. Bian, J. Zheng, T. M Korter, D. M Mittleman, The journal of physical chemistry. A, 2014

# Electrochemical Performance of Li-NMO/$Li^+$-glass/Li Cell




Cathode with PVDF and Super P Carbon (8:1:1 and blended with plasticizer (7:3); glass electrolyte in non-woven paper.

# Status of Battery-Cell Development

- Demonstration of new concepts has been completed with coin cells
- Easy scale-up to pouch-cell size has been made
- Transition of intellectual property to industry for product development is on-going

Reference: Les Nichols, Office of Technology Commercialization, The University of Texas at Austin, lnichols@otc.utexas.edu

# Acknowledgement of Support

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