Battery Power for All-Electric Road Vehicles
John B. Goodenough and M. Helena Braga
The University of Texas at Austin, and of Porto, Portugal

• 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:

$$\int_0^{\Delta t} P_{dis} \, dt = <V_{dis}> \cdot Q(I_{dis})$$
Components of a Battery Cell

Anode(−)|M⁺-Electrolyte| Cathode (+)

$\mu_A | \Delta l | \mu_C$

- Electrolyte is $M^+$ conductor, $e^-$ insulator
- Cell delivers $P_{\text{dis}} = I_{\text{dis}} V_{\text{dis}}$
  
  \[ V_{\text{oc}} = (\mu_A - \mu_C)/e \]
  
  \[ I_{\text{dis}} \sim \sigma_M A/\Delta l \] (neglecting interface resistance)
Electrolyte $E_g$ Restricts $V_{\text{dis}}$

- $\mu_A > \text{LUMO}$ or
- $\mu_C < \text{HOMO}$ 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 $-30^\circ C$

Range:   300 miles between charges: volumetric
         $<V_{dis}(q)> \cdot Q(I_{dis})$
Electrolyte Requirements
(Liquids versus Solids)

• Retain electrode/electrolyte contact during electrode volume change
• Dendrite-free plating/stripping of alkali-metal anode
• $\sigma_M > 10^{-2} \text{ S cm}^{-1}$ 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: $\text{H}^+$

- Electrolyte $E_g = 1.23$ eV: $V_{oc} \lesssim 1.5$ V

- Need large $Q(I)$ of air cathode for large $<V_{dis}> = Q(I_{dis})$
Organic-Liquid Electrolytes
(Carbonates and Ethers)

Advantages

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

Limitations (carbonates)

- \(E_g \approx 3 \text{ eV}\) not matched to high-voltage \(V_{oc}\)
  - LUMO \(\approx 1.2\), HOMO \(\approx 4.2 \text{ eV}\) versus lithium
- \(V_{oc} > 3 \text{ V}\) with SEI passivation, but limits cycle life
- LiFePO\(_4\)/Li\(_4\)Ti\(_5\)O\(_{12}\) for stationary storage (\(<V(q)> \approx 2 \text{ eV}\)
The Li-Ion Battery

Limited safe $<V_{dis}> \frac{Q(I_{dis})}{\text{volume}}$
Alkali-Metal Wetting

Leigang Xue et al.
Solid Electrolytes
\((\sigma_{Li} \text{ at } 25^\circ\text{C})\)

- Crystalline ceramics:
  - oxides: \(\sigma_{Li} \lesssim 10^{-3} \text{ S cm}^{-1}, E_g > 5 \text{ eV}\)
  - sulfides: \(\sigma_{Li} \equiv 10^{-2} \text{ S cm}^{-1} (E_{F}(\text{Li}) - E_c) = 3.5 \text{ eV}\)
- Polymers: \(\sigma_{Li} \approx 10^{-4} \text{ S cm}^{-1}, E_g > 5 \text{ eV}, \text{ plastic}\)
- Amorphous dielectric ceramic: \(\text{Li}^+\) or \(\text{Na}^+\) coexist with electric dipoles
  \(\sigma_{Li} \approx 10^{-2} \text{ S cm}^{-1}, E_g > 8 \text{ eV}\)
Ceramic Garnet Li$^+$ Electrolyte

Yutao Li

- $\text{Li}_{7-x}\text{Lr}_3\text{Zr}_{2-x}\text{Ta}_x\text{O}_{12}$ not reduced by $\text{Li}^0$ anode
- 3D interstitial space: Tet bridged by Oct.
- $10^{-4} \leq \sigma_{\text{Li}} \leq 10^{-3}$ S cm$^{-1}$ for $0 \leq x \leq 0.5$
- $T_{\text{op}} \geq 55^\circ\text{C}$ for thin ceramic film
- Air exposure gives $\text{Li}_2\text{CO}_3$ on surface
All-Solid-State Li/LiFePO₄ Batteries with Li₂CO₃-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 °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$^+$ \textit{ac} conductivity and permittivity at 1000 Hz of a Li-glass

M. Helena Braga
Symmetric Li/Li-glass/Li cell
(Glass $\sigma_{\text{Li}} = 15 \times 10^{-2}$ S cm$^{-1}$ at 25°C)

$\sigma_{\text{cell}} = 5$-10 mS.cm$^{-1}$
$I = 3$ mA.cm$^{-2}$

SS/Cu/Li//Li-glass in matrix//Li/Cu/SS
$A = 0.45$ cm$^2$
$d = 80$ µm

$\Delta T \downarrow \Rightarrow R \downarrow \Rightarrow ~8 \Omega$
$3.1 \Omega$
$5.7 \Omega$
Li/Li$^+$-Glass/S + C + Cu

$E_F(\text{Li}) = -1.39 \text{ eV}, E_F(S_8) = -4 \text{ eV}$ versus vacuum. Therefore $[V_{OC} = E_F(\text{Li}) - E_F(S_8)]/e \approx 2.6 \text{ V}$
Self-Charge, Self Cycling  
(Found with Li-glass, Na-glass)  

\[
\mu_A(Al) - \mu_C(Cu) \approx 2.2 \text{ eV}; \mu_A(Li) - \mu_C(Cu) \approx 3.5 \text{ eV}
\]
Al/Na\(^+\)-glass + polymer/Cu

A Relaxation Oscillator
Succinonitrile (SN)

Terahertz vibrational modes of the rigid crystal phase of succinonitrile.
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

Compete 2020 and FCT
PTDC-CTM-ENE-2391-2014