Modern Society is enabled by the chemical energy stored in fossil fuels.

**Unsustainable Cost**

- National vulnerabilities from uneven, finite distribution
- Spoiled environment by extraction
- Air pollution and global warming by use
Sustainable Energy Supply

- Generation of electrical energy by wind, solar, nuclear, and other sources
- Storage of electrical energy at an acceptable cost
- What is the status of rechargeable batteries? Electrochemical capacitors?
Battery Principle

Rechargeable Electrochemical Cell: $P_{\text{charge}} > P_{\text{discharge}}$

- Battery=Stack of cells connected in series to increase $V$, in parallel (or electrode area) to increase $I=dq/dt$ and/or $\Delta t$.
- Challenges: Cost, Safety, Energy Density, Life, Rate.
Traditional Rechargeable Cells

- **Anode**
  
  \[
  \begin{align*}
  \text{Cd}^0 + 2\text{H}_2\text{O} & \rightarrow \text{Cd(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \\
  \text{Pb}^0 + \text{H}_2\text{SO}_4 & \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^- 
  \end{align*}
  \]

- **Cathode**
  
  \[
  \begin{align*}
  \text{NiOOH} + \text{H}^+ + \text{e}^- & \rightarrow \text{Ni(OH)}_2 \\
  \text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}
  \end{align*}
  \]
TYPICAL BATTERY DISCHARGE

\[ V_{\text{dis}} = V_{\text{oc}} - \eta_{\text{dis}}(I,q) \]

\[ R_{\text{electrolyte}} = (dV/dI)_{ii} \]

\[ V_{\text{ch}} = V_{\text{oc}} + \eta_{\text{ch}}(I,q) \]
Cell Energy at Constant $\frac{dQ}{dt}$

Energy $= \int_0^{\Delta t} I V(q)\,dt = \int_0^{Q(I)} V(q)\,dq$; $Q(I) = \int_0^{\Delta t} I\,dt = \int_0^{Q(I)} dq$

$Q(I)/\text{wt or vol} = \text{specific or volumetric capacity}$

$V(q) = V_{OC} - \eta(q, I)$; $V_{OC} = (\mu_A - \mu_C)/e \leq \text{electrolyte } E_g$

$\eta(q, I)$ increases with resistance to working-ion current

**Problem:** Maximize $V_{OC}$, $Q(I)$ and # cycles to $Q/Q_0 = 0.8$; minimize $\eta$
Electrolyte

- **Aqueous Electrolyte**: \( E_g = 1.23 \text{ eV} \)
  - LUMO = \( \text{H}_2\text{O}/\text{H}_2 \); HOMO = \( \text{O}_2/\text{H}_2\text{O} \)
- **Kinetic Stability**
  - \( \text{NiOOH/KOH/Cd}^\circ \) \( V_{oc} = 1.5 \text{ V} \)
- **Limited Life**
  - \( \text{PbO}_2/\text{H}_2\text{SO}_4/\text{Pb}^\circ \) \( V_{oc} = 2.0 \text{ V} \)
First Li-ion Battery

$E_{F(Li)}$

LUMO

HOMO

$E_{F(Li)}$

2.6 eV

$S^{2-}:3p^6$

$Co^{4+/Co^{3+}}$

$O^{2-}:2p^6$

$Li_{1-x}CoO_2$

Electrolyte, Separator

$Li_xC$

$4 eV_{oc}$

3.2 eV

1.1 eV

0.3 eV
LiCoO$_2$//C Cell

Li$_{1-x}$CoO$_2$

Li$_x$C$_6$

Anode (Reducing Agent)

Cathode (Oxidizing Agent)

Electrolyte

Separator

Cu current collector

Al current collector
Li$_x$[M$_2$]O$_4$ Spinel Electrodes

2 quadrants of structure
Edge-shared MO$_{6/5}$ octahedra
3D Li$^+$ insertion into close-packed oxygen array

Note: Li$_{1+x}$[Li$_{1/3}$Ti$_{5/3}$]O$_4$: V=1.5 V
Li$_{1-x}$[Ni$_{0.5}$Mn$_{1.5}$]O$_4$: V=4.7 V
Ni(II) $\rightarrow$ Ni(IV) with little step
NASICON Framework

\[ \text{Na}_{1+3x}\text{Zr}_2(\text{P}_{1-x}\text{Si}_x\text{O}_4)_3 \]

\[ \text{Li}_x\text{Fe}_2(\text{SO}_4)_3: V = 3.6 \text{ V} \]

\[ \text{Li}_x\text{Fe}_2(\text{MO}_4)_3: M = \text{Mo}, \text{W}: V = 3.0 \text{ V} \]

\[ \text{Na}_{3-x}\text{V}_2(\text{PO}_4)_3: V = 3.4 \text{ V} \]
Capacity Challenge

(Limited specific capacity further reduced by anode SEI layer)

![Graph showing potential (V) vs. Li/Li⁺ and capacity (mAh/g) for different lithium compounds.

- \( \text{Li}_{1-x}\text{CoO}_2 \)
- \( \text{Li}_{1-x}\text{FePO}_4 \)
- \( \text{Li}_x\text{Ti}_2\text{S}_2 \& \text{Li}_2[\text{Ti}_2]\text{S}_4 \)
- \( \text{Li}_{1-x}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4 \)
- \( \text{Li}_x[\text{Mn}_2]\text{O}_4 \)
**ELECTRODE MATERIALS**

Na$_2$MnFe(CN)$_6$ and Na$_3$V$_2$(PO$_4$)$_3$:
$V \approx 3.4$ V, $Q(10C) > 100$ mAh/g
Framework of Prussian Blue Analogues
Anode Problem with Organic Liquid Electrolyte

- An $E_F$ (Anode) > LUMO requires an SEI
- SEI on Li$^0$ or Na$^0$ creates dendrites, so C anode
- Need $V_{Ch} < V_{\text{plate}}$, so C-buffered alloys
- Need SEI permeable to Li$^+$ or Na$^+$: if Li$^+$, Na$^+$ come from cathode, get capacity loss on initial charge.
- Reforming SEI gives capacity fade limiting cycle life
- SEI slows Li$^+$ or Na$^+$ transfer
Separators

- Celgard membrane: penetrated by dendrites; insertion-compound cathode
- Polymer-gel membranes: blocks dendrites; adds choice of liquid flow-through cathode
- Anode/Solid-electrolyte interface: prevents dendrites, allows choice of sulfur or liquid flow-through and air cathode if solid electrolyte stable in alkaline water
Al₂O₃/PEO Separator
(K.S. Park, J.-H. Cho, C.J. Ellison)

Oxide: Dried (400°C) Al₂O₃ Powder (300-400nm)
Polymer: DEGDVE = Di(ethyleneglycol) divinylether with ethylene oxide (EO) units
     PETT = tetrathiol crosslinker
Preparation: AIBN = thermal initiator (80°C, 4h)
Yield: Quantitative, homogeneous network

AIBN = Azobisisobutyronitrile
PEO/Al$_2$O$_3$ Composite-Membrane Separator
K. Park et al.

Photographs of a PEO/Al$_2$O$_3$ (2/1 in weight) composite membrane (25 × 20 cm$^2$)
Mechanical Stability

- Tensile test shows a good mechanical stability, especially after Al$_2$O$_3$ incorporation.
- Stability against Li dendrite
Presence of Osmosis

- Presence of concentration gradient of a redox-molecule across the PEO/Al$_2$O$_3$ membrane

- Balancing the concentrations between catholyte and anolyte is necessary, for example, with high-molecular-weight Ionic liquids and PEGDME.
Anolyte: 1M LiTFSI in EC.DEC w/0.1M PEGDME 500
Catholyte: 1M LiTFSI in EC/DEC w/0.1M 6-Bromohexyl ferrocene
PVDF-HFP: Widely used as host for gel-polymer electrolytes
But with unsatisfactory mechanical strength
Glass-fiber paper: Used to enhance the mechanical properties

The composite membranes have good thermal stability and mechanical strength.

Polydopamine: Biomimetic polymer of mussel adhesive protein
Polymerized at room temperature in aqueous solution
Modify the surface properties of PVDF-HFP

Gel-polymer electrolytes: Improve rate and cycle performance of air-dried cathode of Na₂MnFe(CN)₆

Strategy for an Alkali-Metal Anode

- Cathode
- Li⁺/Na⁺
- Separator membrane
- Current collector
- Solid electrolyte
- Current collector
- Separator membrane
Cost Targets

• Cycle Life $N > 10,000$; calendar life 10 years

• Simple processing of inexpensive materials.

• Increased VQ(I) to reduce number of cells.

• Simplify battery management
Lithium-Sulfur Batteries

\[ S + 2\text{Li}^+ + 2\text{e}^- \leftrightarrow \text{Li}_2\text{S} \]

2 electron reaction
1,672 Ah/kg
2,500 Wh/kg