

Rechargeable Batteries, Old and New

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

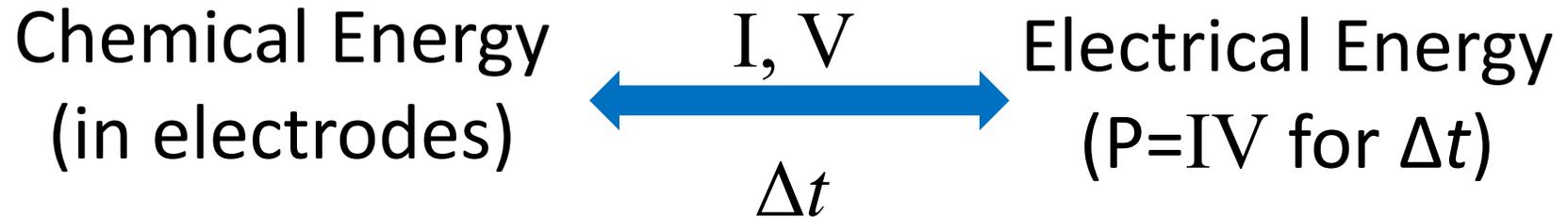
Unsustainable Cost

- 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?

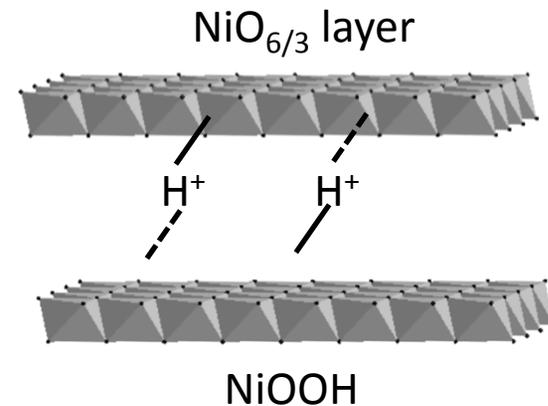
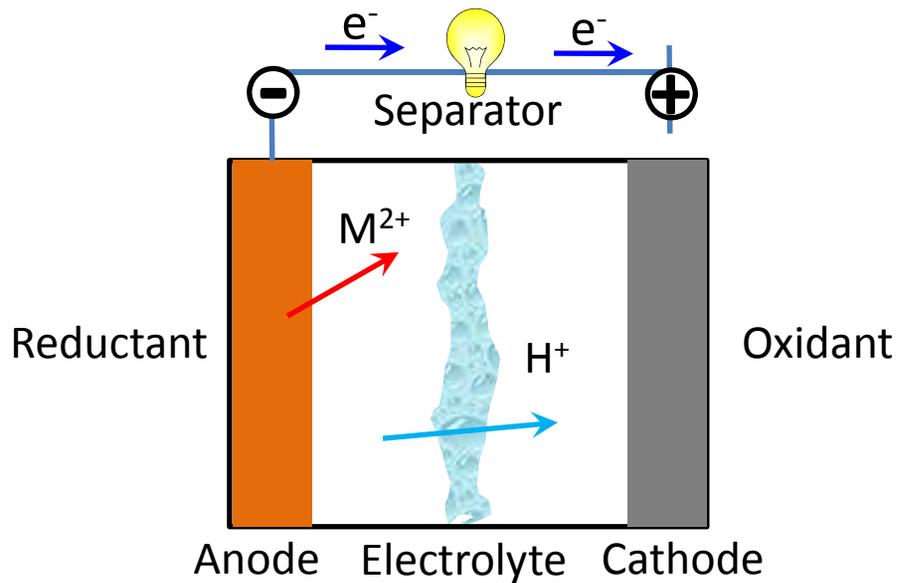
Battery Principle



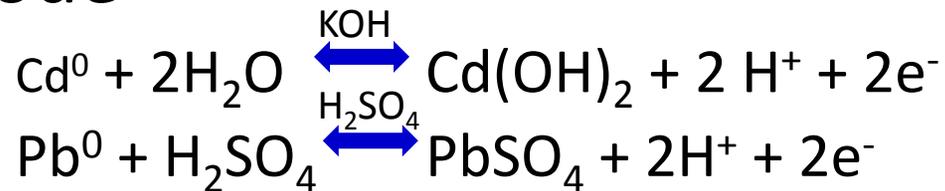
Rechargeable Electrochemical Cell: $P_{\text{charge}} > P_{\text{discharge}}$

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

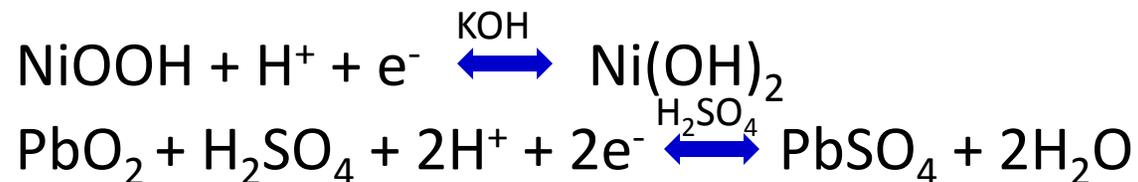
Traditional Rechargeable Cells



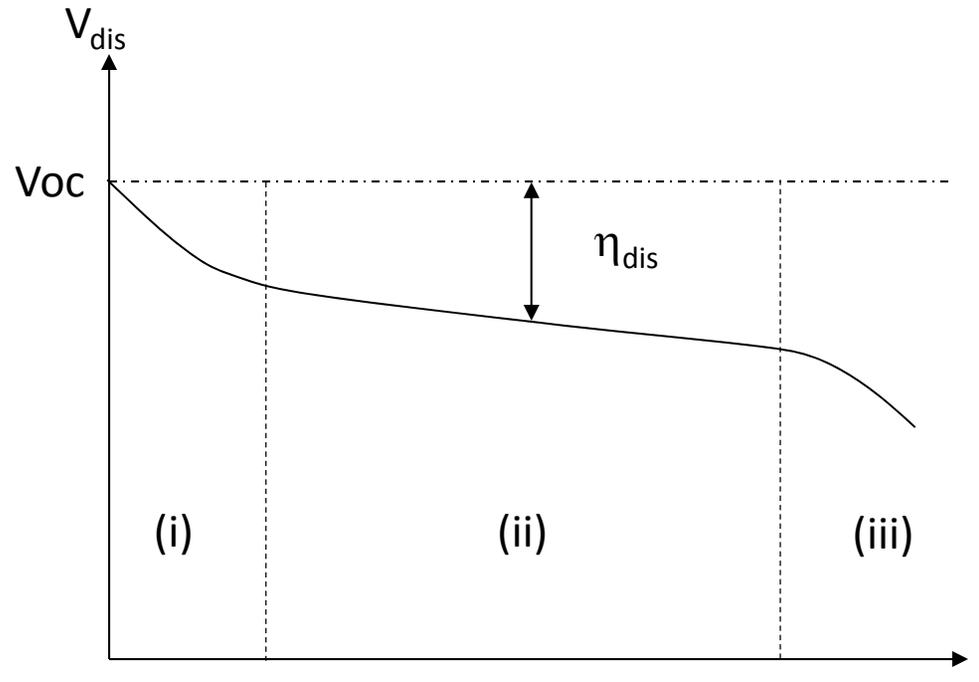
□ Anode



□ Cathode



TYPICAL BATTERY DISCHARGE



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

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

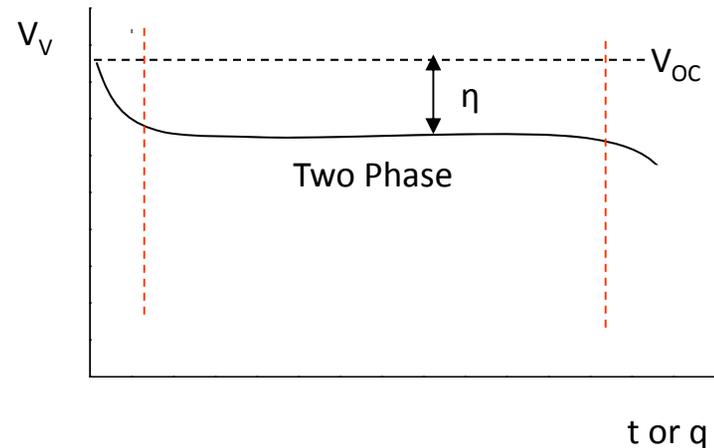
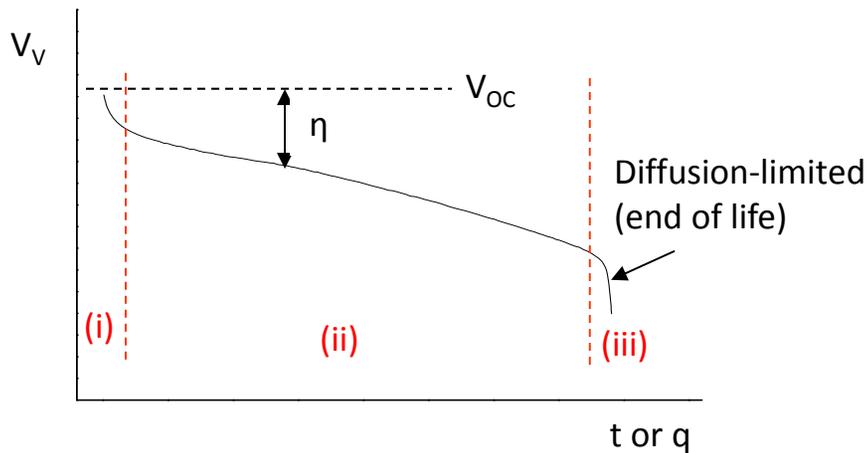
$$V_{\text{ch}} = V_{\text{oc}} + \eta_{\text{ch}}(I, q)$$

Cell Energy at Constant $I = dq/dt$

$$\text{Energy} = \int_0^{\Delta t} IV(q)dt = \int_0^{Q(I)} V(q)dq; \quad Q(I) = \int_0^{\Delta t} Idt = \int_0^{Q(I)} dq$$

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

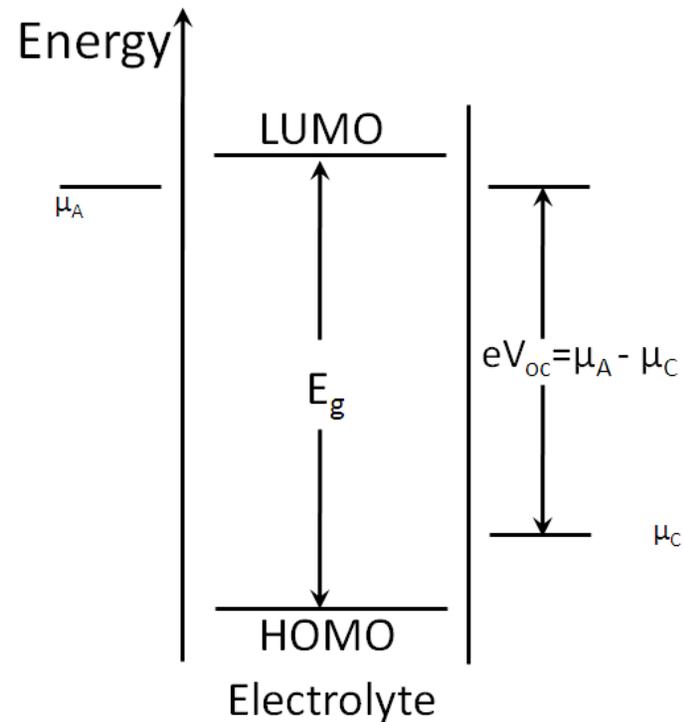
$$V(q) = V_{OC} - \eta(q, I); \quad V_{OC} = (\mu_A - \mu_C)/e \leq \text{electrolyte } E_g$$



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

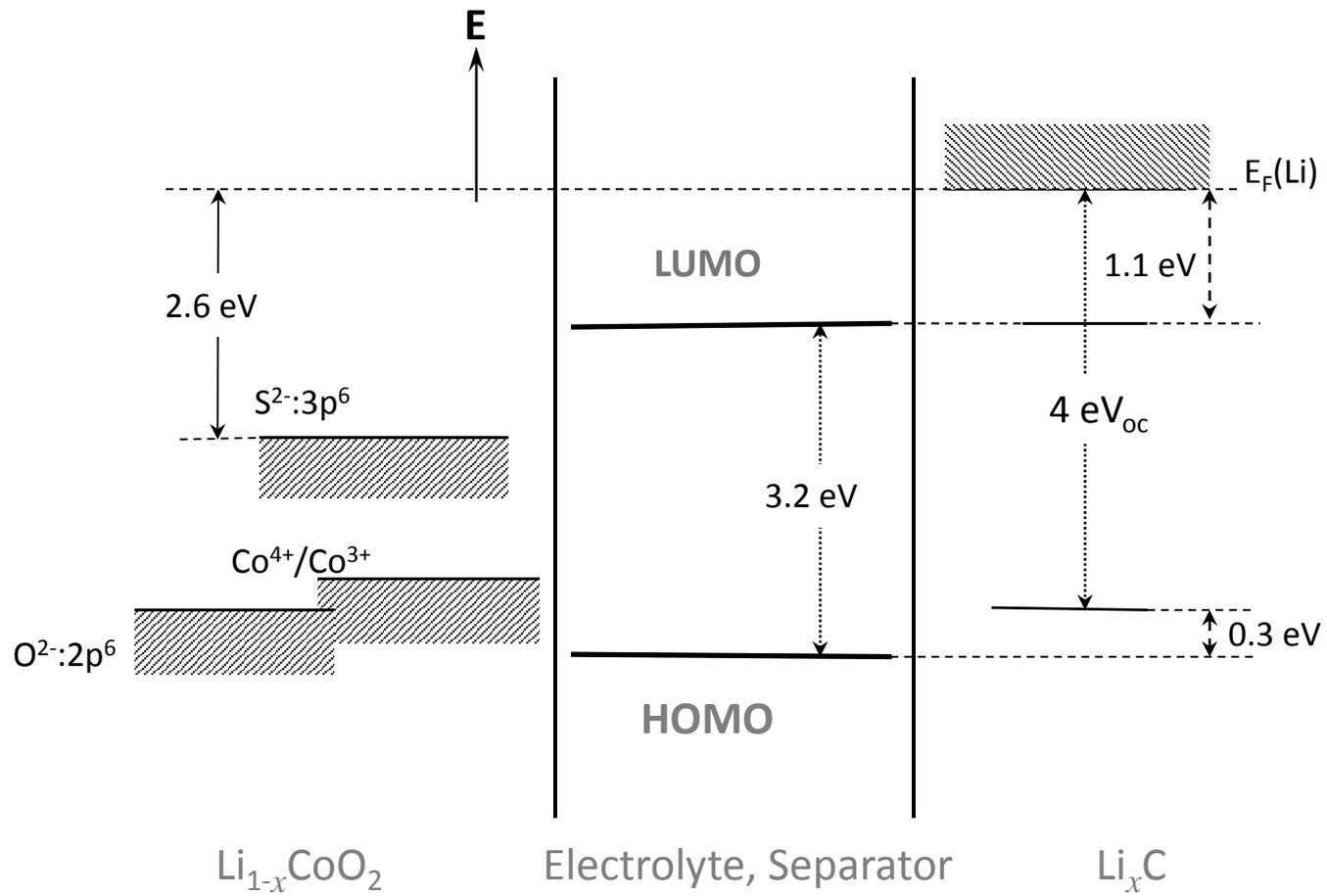
Problem: Maximize V_{OC} , $Q(I)$ and # cycles to $Q/Q_0 = 0.8$; minimize η

Electrolyte

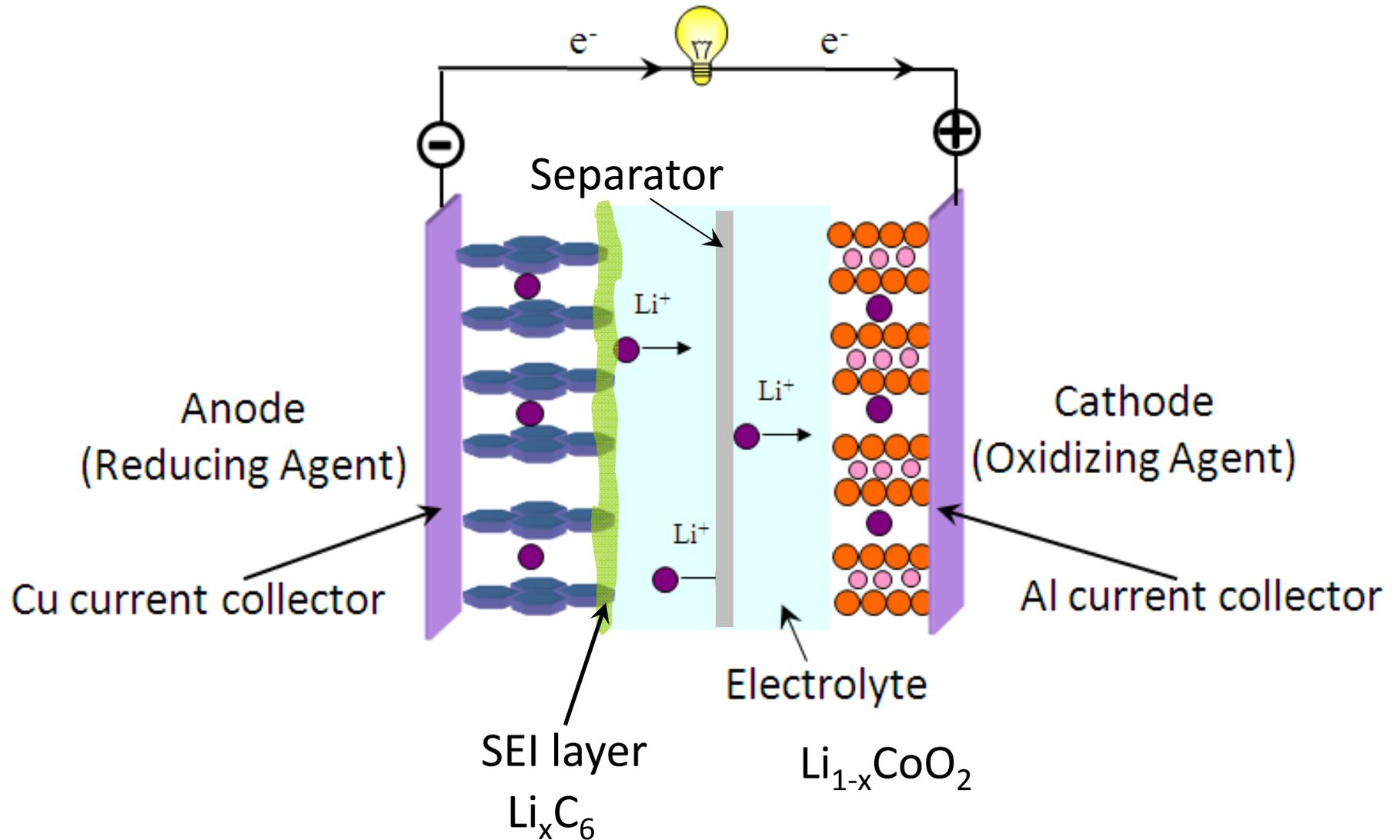


- ❑ Aqueous Electrolyte: $E_g = 1.23 \text{ eV}$
 - LUMO = $\text{H}_2\text{O}/\text{H}_2$; HOMO = $\text{O}_2/\text{H}_2\text{O}$
- ❑ Kinetic Stability
 - $\text{NiOOH}/\text{KOH}/\text{Cd}^0$ $V_{oc} = 1.5 \text{ V}$
- ❑ Limited Life
 - $\text{PbO}_2/\text{H}_2\text{SO}_4/\text{Pb}^0$ $V_{oc} = 2.0 \text{ V}$

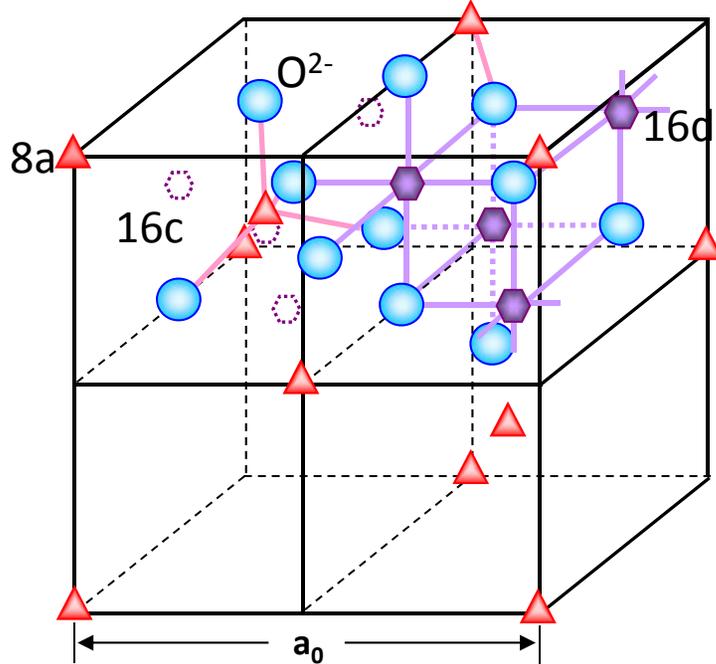
First Li-ion Battery



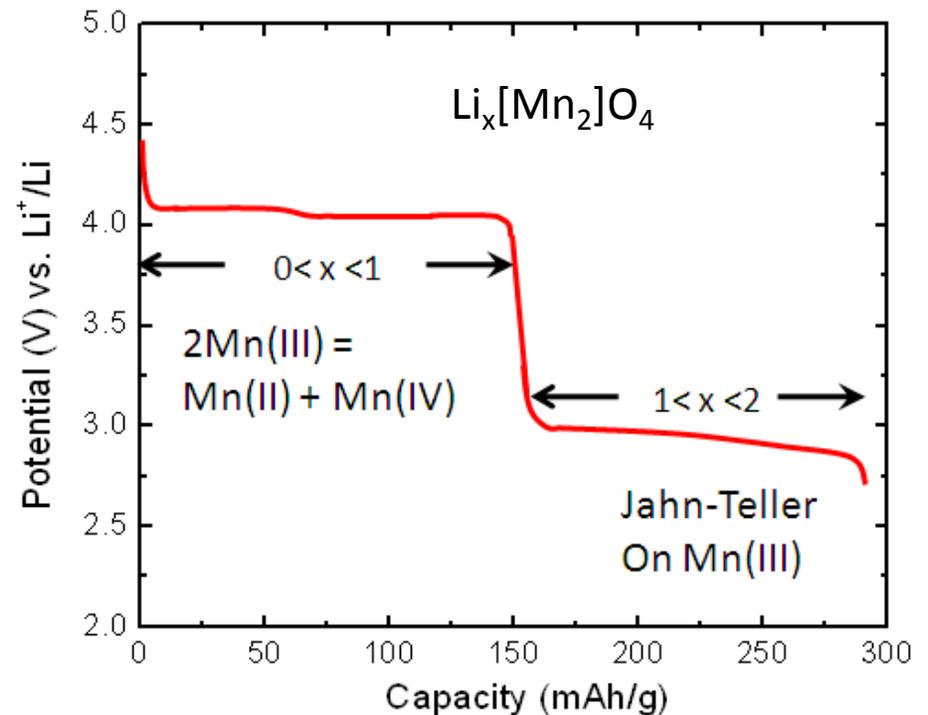
LiCoO₂//C Cell



$\text{Li}_x[\text{M}_2]\text{O}_4$ Spinel Electrodes

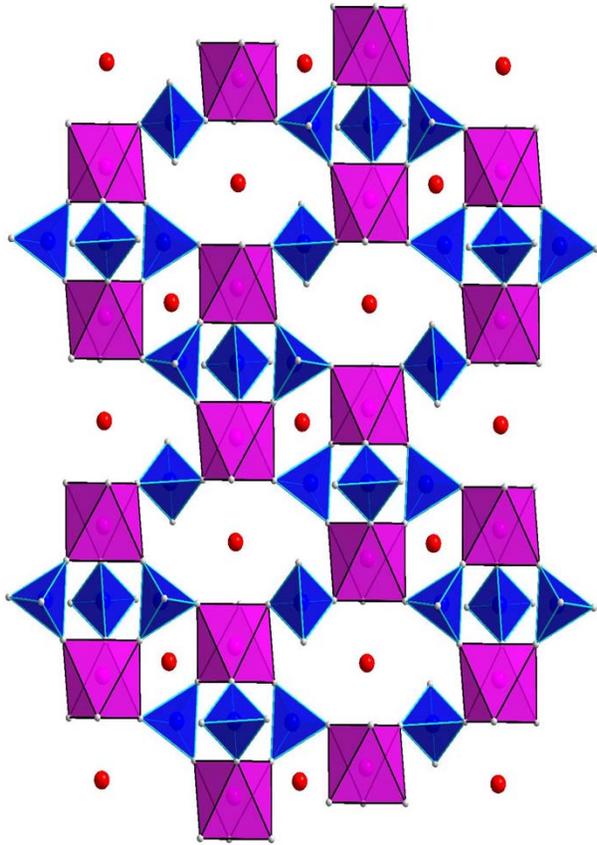


2 quadrants of structure
 Edge-shared $\text{MO}_{6/5}$ octahedra
 3D Li^+ insertion into close-packed oxygen array

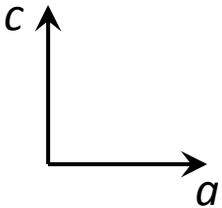
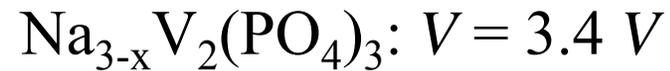
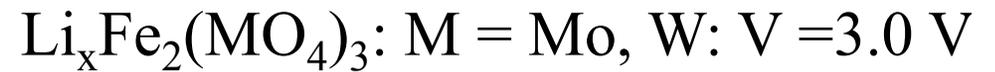
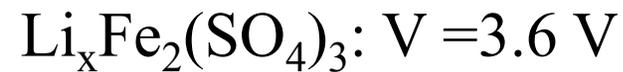


Note: $\text{Li}_{1+x}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$: $V=1.5$ V
 $\text{Li}_{1-x}[\text{Ni}_{0.5}\text{Mn}_{1.5}]\text{O}_4$: $V=4.7$ V
 $\text{Ni(II)} \rightarrow \text{Ni(IV)}$ with little step

NASICON Framework

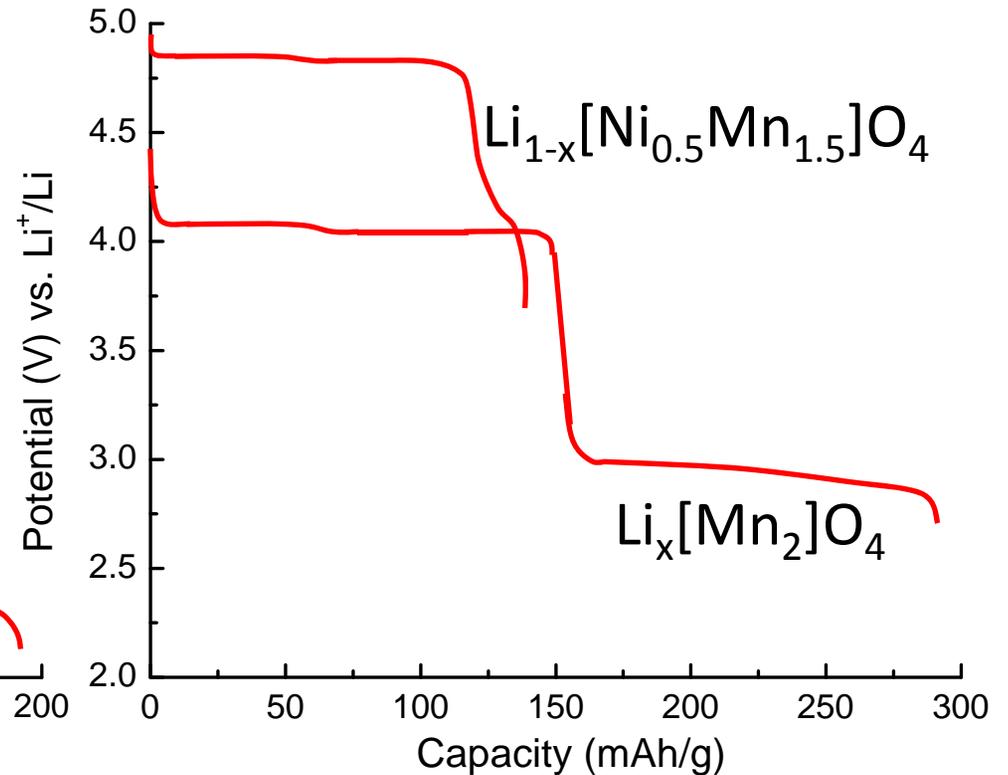
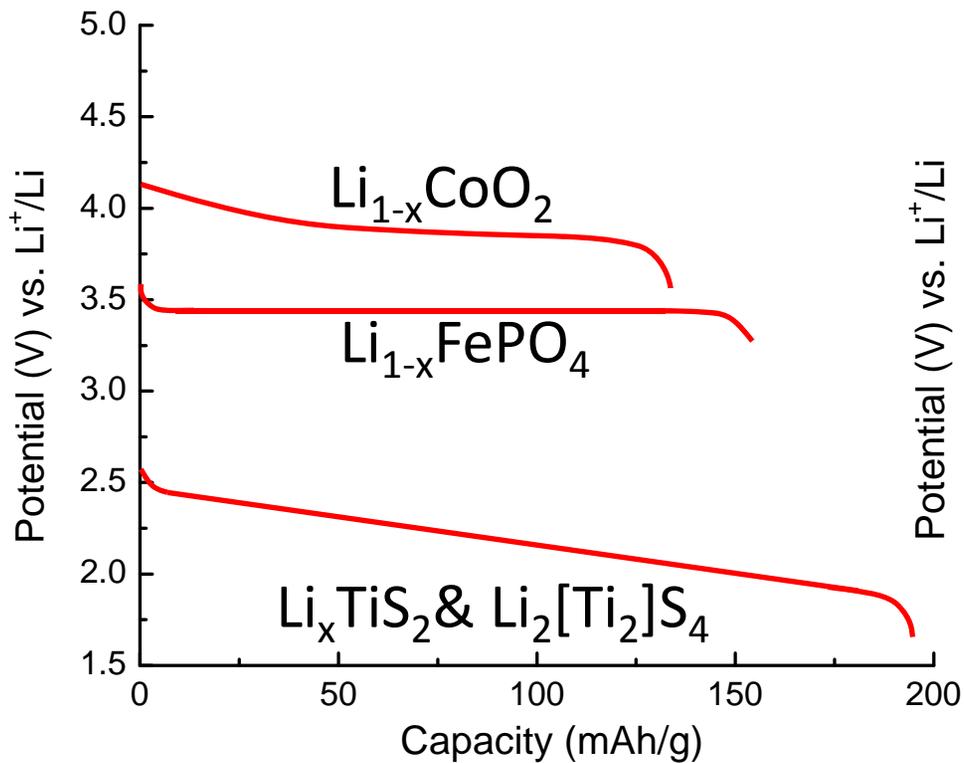


NASICON

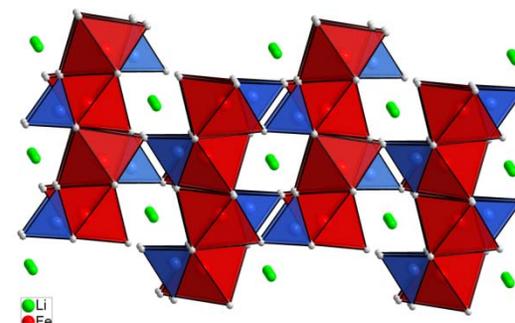
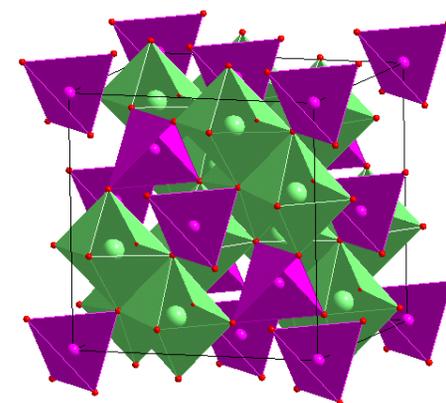
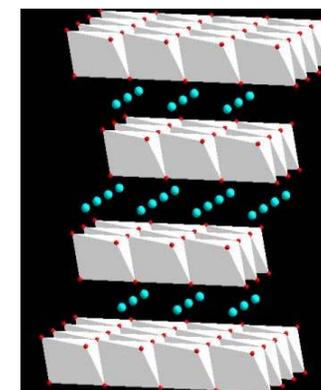
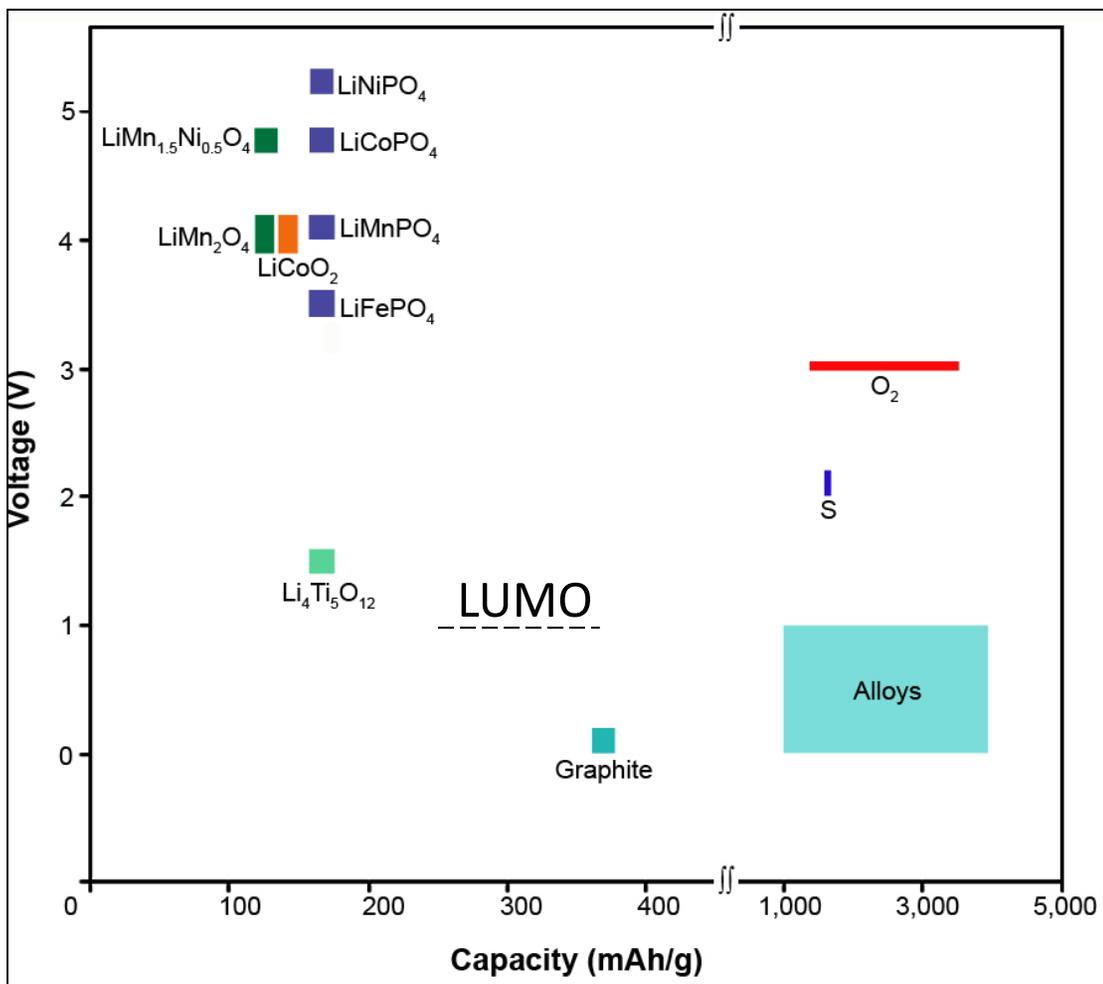


Capacity Challenge

(Limited specific capacity further reduced by anode SEI layer)

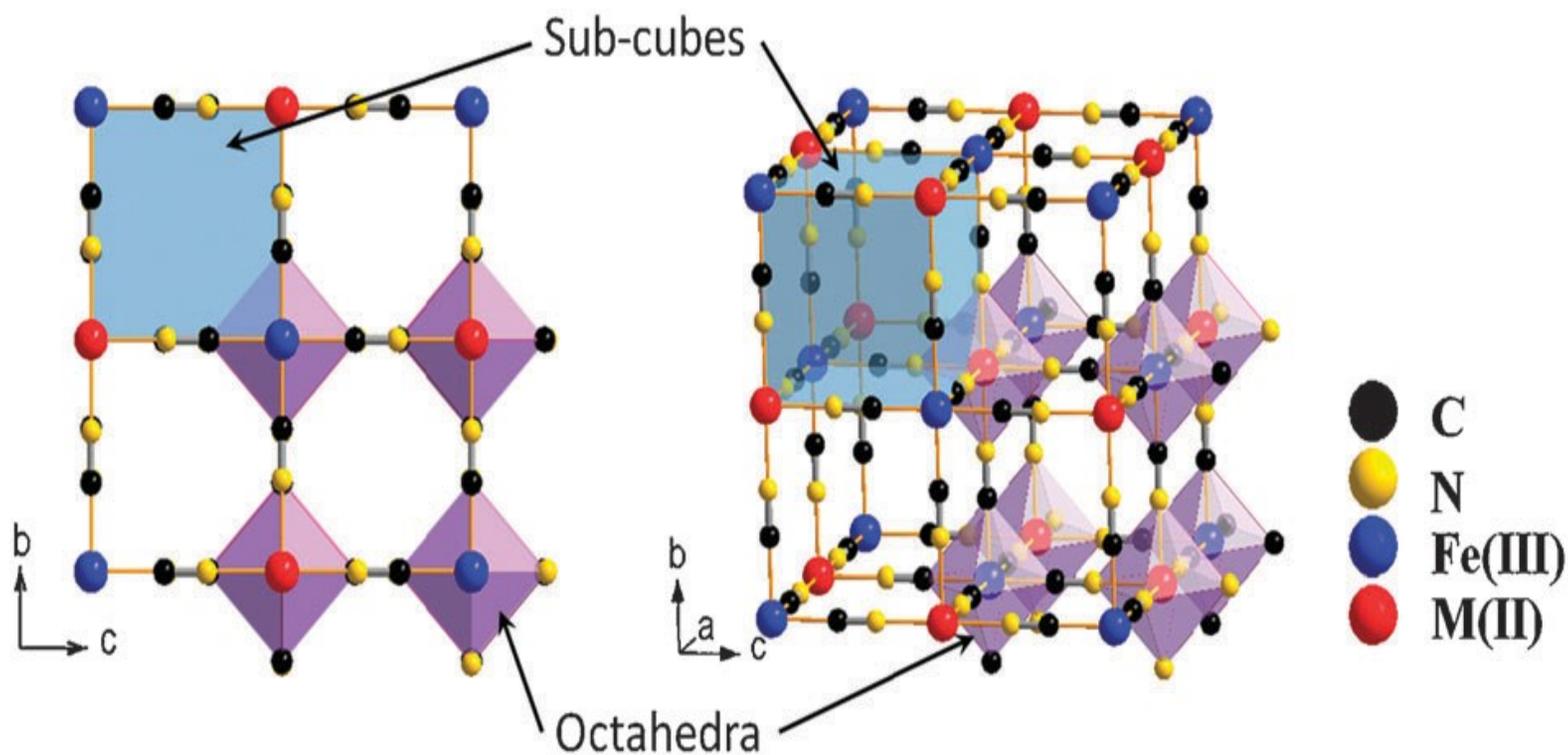


ELECTRODE MATERIALS



$\text{Na}_2\text{MnFe}(\text{CN})_6$ and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$:
 $V \approx 3.4 \text{ V}$, $Q(10\text{C}) > 100 \text{ mAh/g}$

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 $V_{\text{Ch}} < V_{\text{plate}}$, 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)

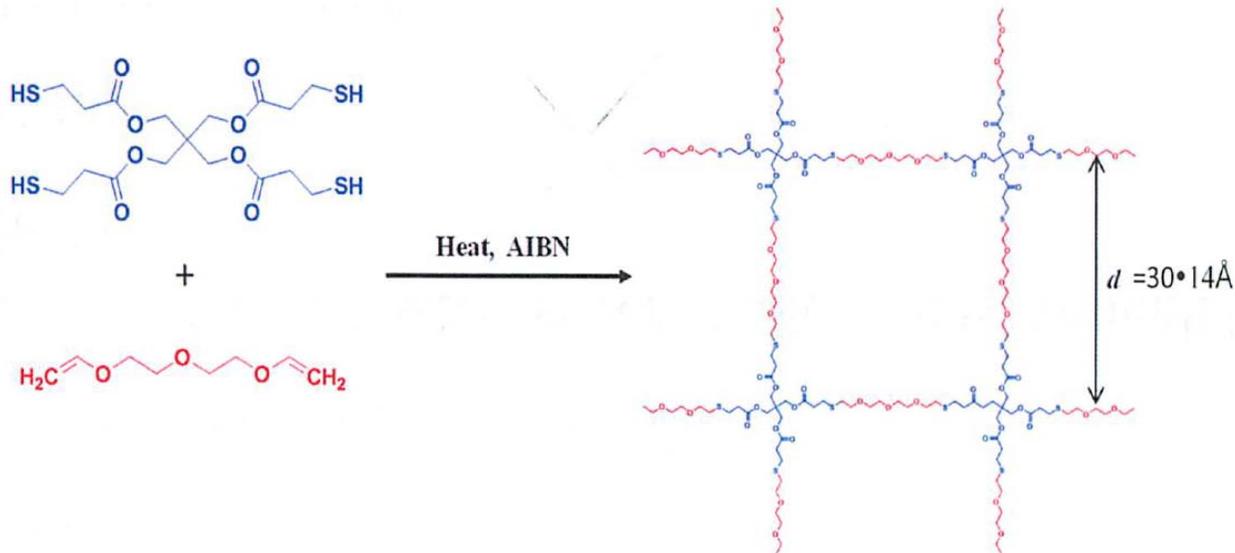
Oxide: Dried (400°C) Al₂O₃ Powder (300-400nm)

Polymer: DEGDVE = Di(ethyleneglycol) divinylether with ethyleneoxide (EO) units

PETT = tetrathiol crosslinker

Preparation: AIBN = thermal initiator (80°C, 4h)

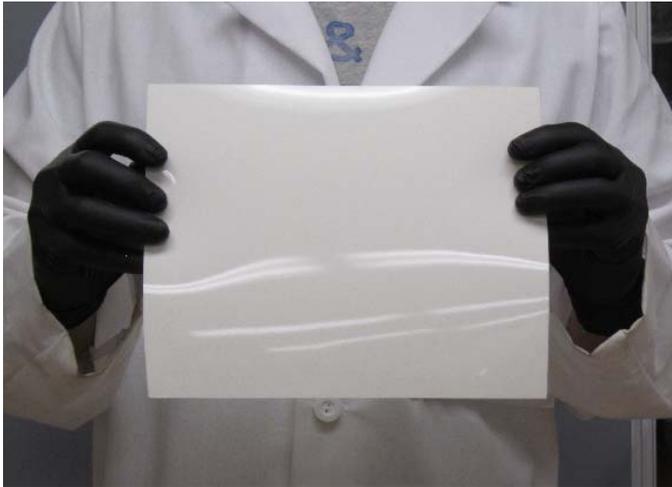
Yield: Quantitative, homogeneous network



AIBN = Azobisisobutyronitrile

PEO/ Al_2O_3 Composite-Membrane Separator

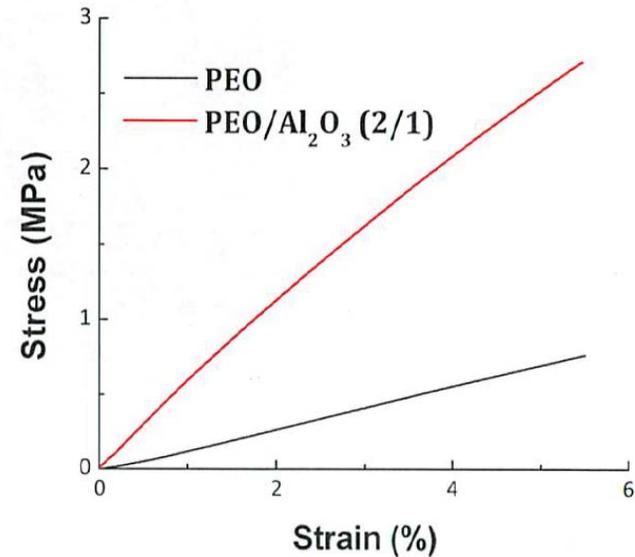
K. Park *et al.*



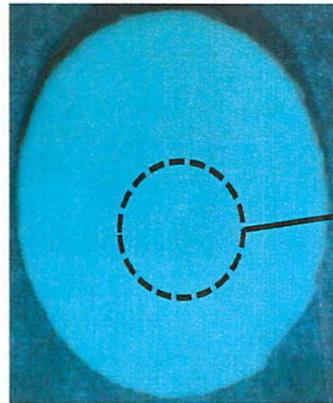
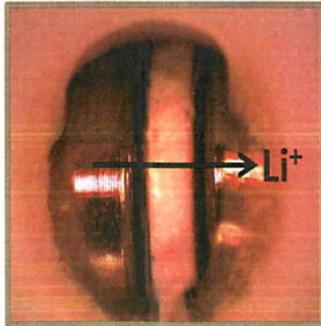
Photographs of a PEO/ Al_2O_3 (2/1 in weight) composite membrane ($25 \times 20 \text{ cm}^2$)

Mechanical Stability

- Tensile test shows a good mechanical stability, especially after Al_2O_3 incorporation.
- Stability against Li dendrite



Li|PEO/Al₂O₃(2/1)|Li
- Ch. behavior -

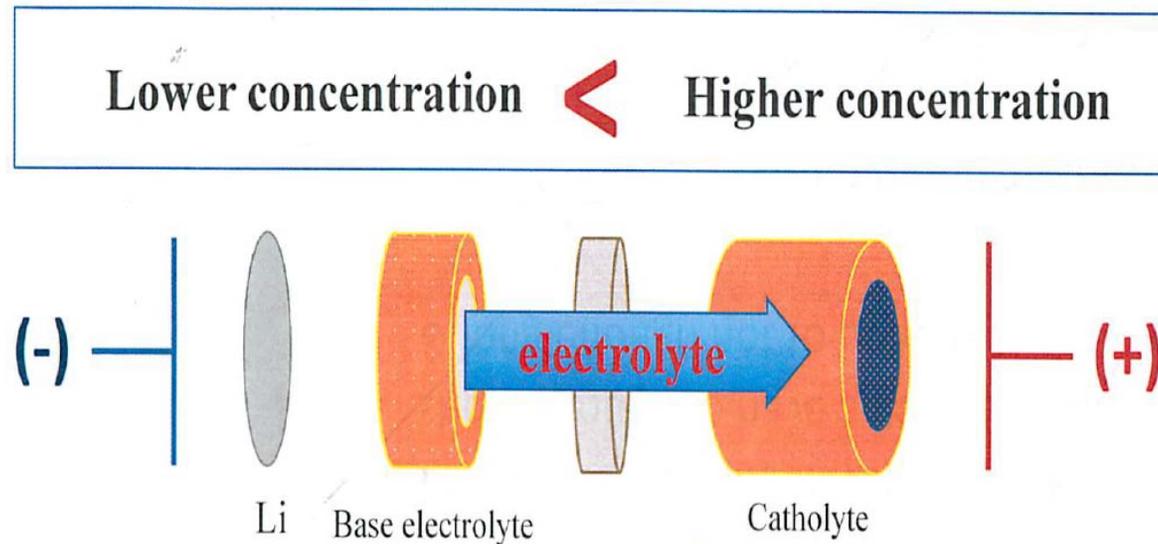


Minor surface dent by Li dendrite
After full charging

➡ It blocks Li dendrite.

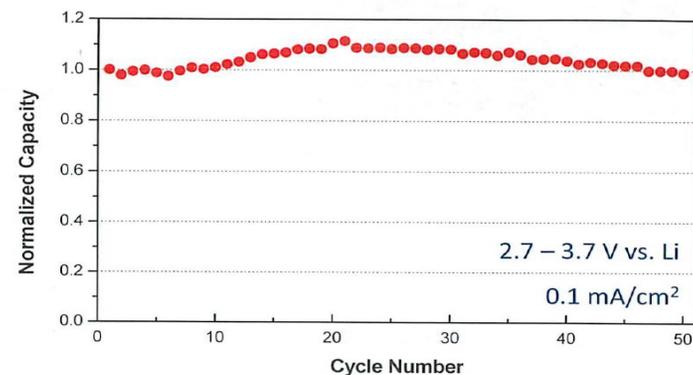
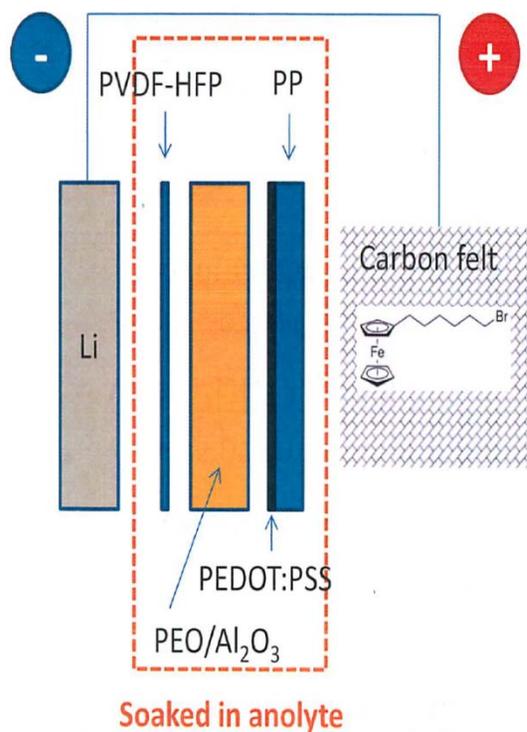
Presence of Osmosis

- Presence of concentration gradient of a redox-molecule across the PEO/ Al_2O_3 membrane

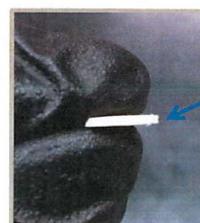


- Balancing the concentrations between catholyte and anolyte is necessary, for example, with high-molecular-weight Ionic liquids and PEGDME.

Charge/Discharge Cycle Property



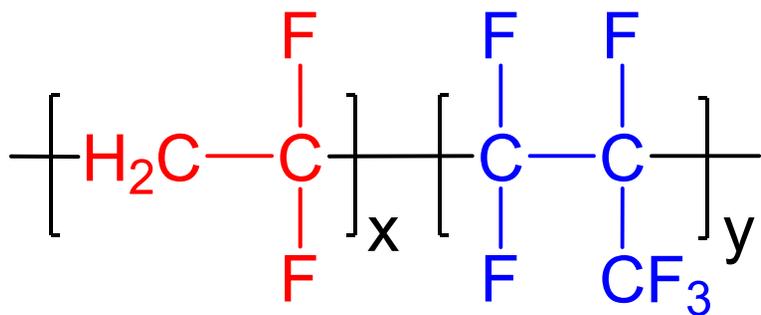
Center fragment of PEO/Al₂O₃ after cycling



Clean and white cross-section w/o color change!

Anolyte: 1M LiTFSI in EC/DEC w/0.1M PEGDME 500

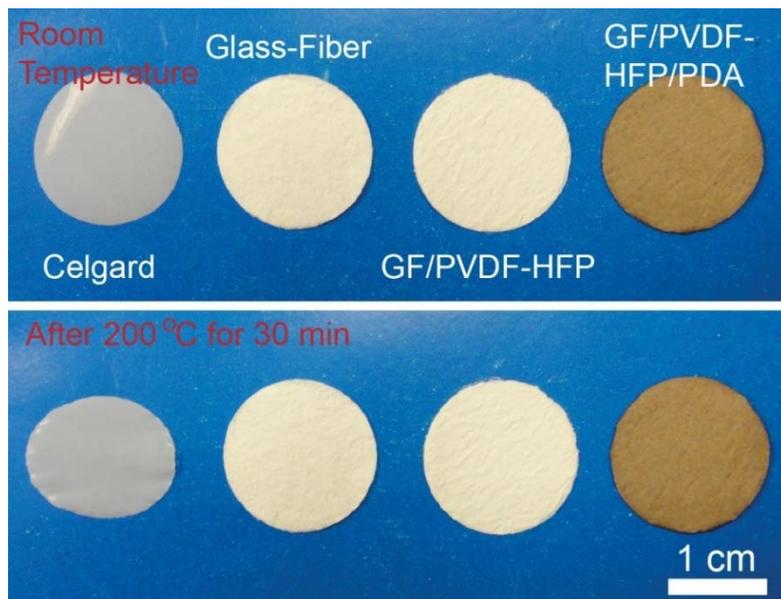
Catholyte: 1M LiTFSI in EC/DEC w/0.1M 6-Bromohexyl ferrocene



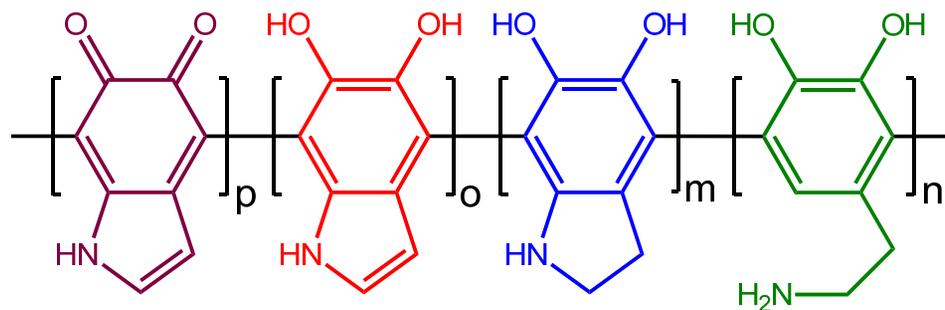
PVDF-HFP: Widely used as host for gel-polymer electrolytes

But with unsatisfactory mechanical strength

Glass-fiber paper: Used to enhance the mechanical properties



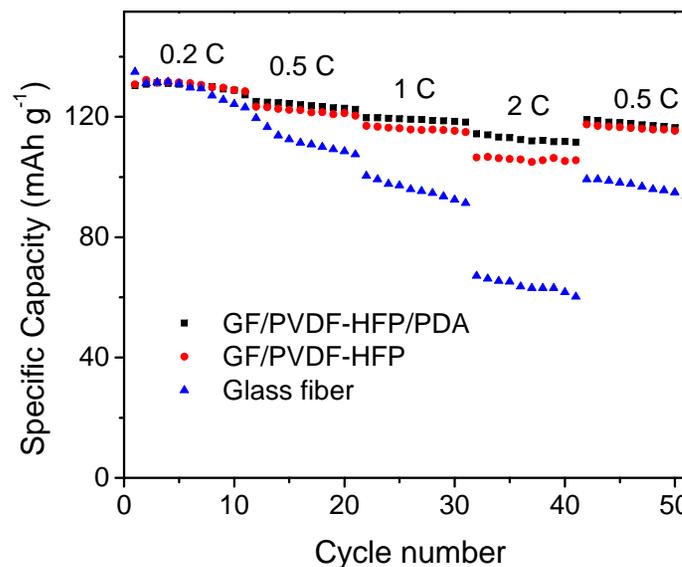
The composite membranes have good **thermal stability** and **mechanical strength**.



Polydopamine: Biomimetic polymer of mussel adhesive protein

Polymerized at room temperature in aqueous solution

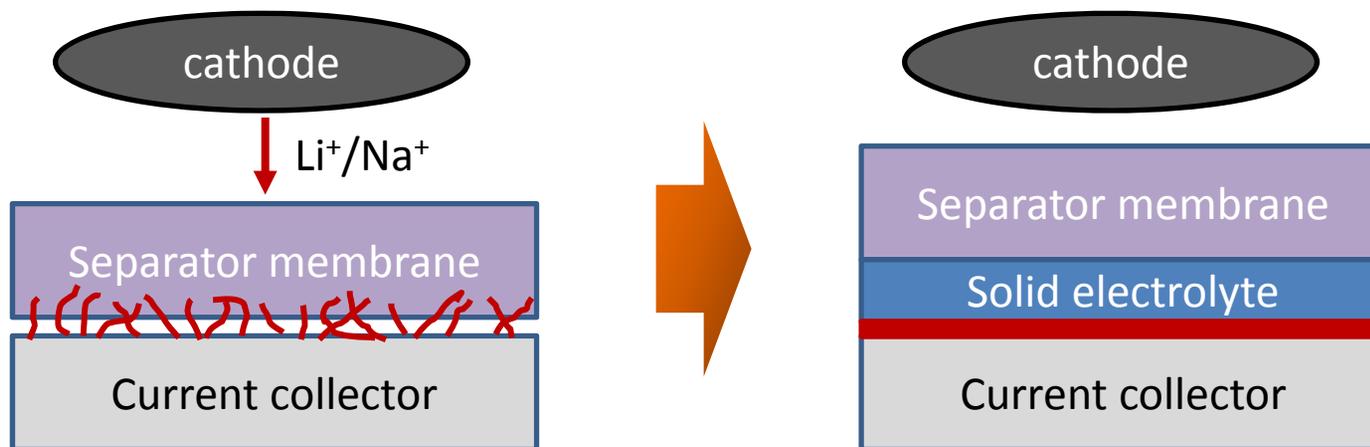
Modify the surface properties of PVDF-HFP



Gel-polymer electrolytes: Improve rate and cycle performance of air-dried cathode of $\text{Na}_2\text{MnFe}(\text{CN})_6$

Hongcai Gao, et al. Adv Energy Mater 2015

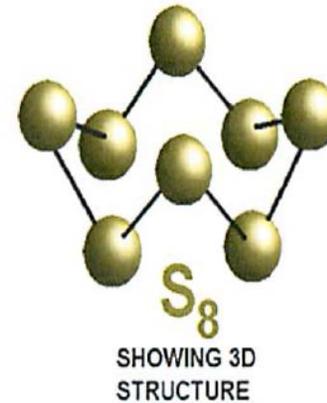
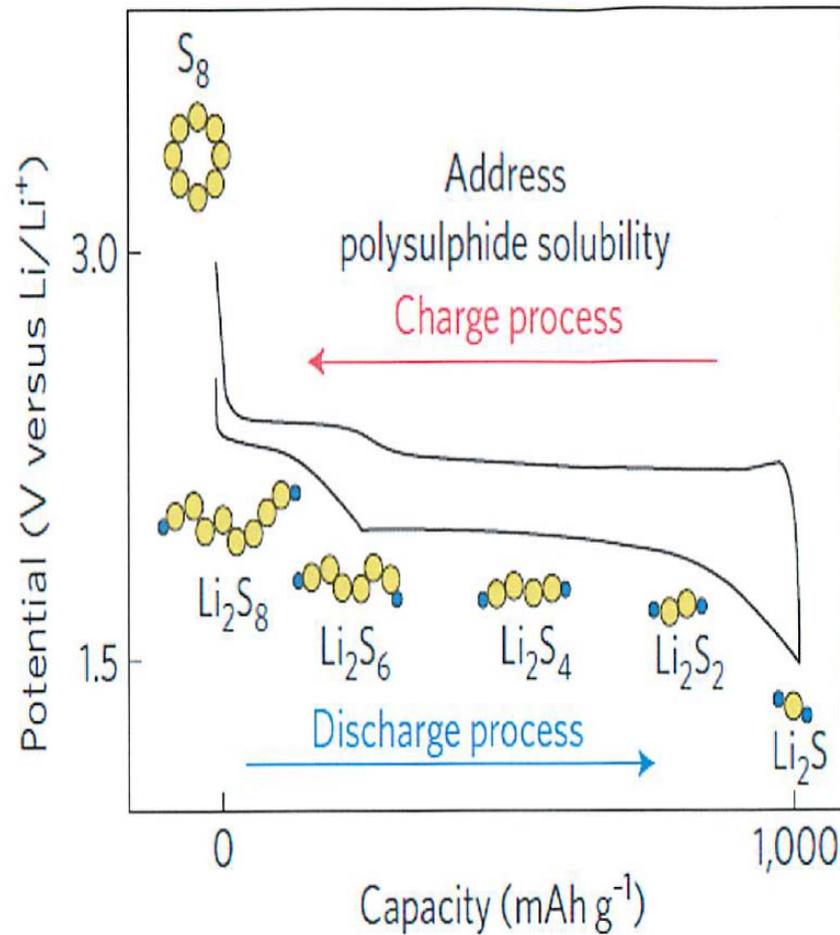
Strategy for an Alkali-Metal Anode



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



2 electron reaction

1,672 Ah/kg

2,500 Wh/kg