SOLID ELECTROLYTE BATTERIES

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This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Project Start Date-Oct. 2009
- Project End Date- Sept. 2010
- Percent complete: 100% complete

Barriers

- Lithium-ion solid electrolyte.
- Choice of redox couples.
- Flow-through- cathode cell design

Budget

- Funding received in FY09-FY10
  – $315K
- Funding received in FY10-FY11
  – $315K

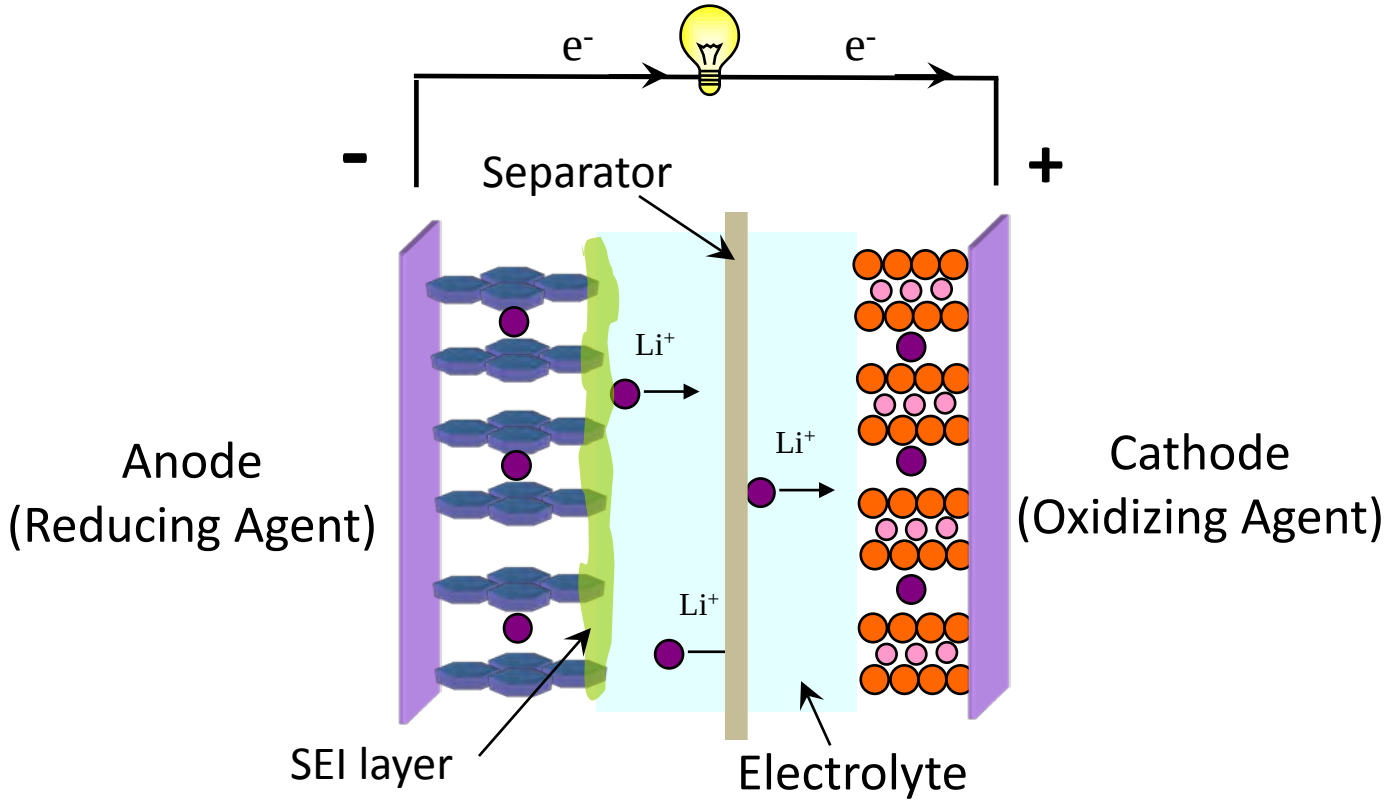
Partners

- Karim Zaghib of Hydro Quebec

Milestones

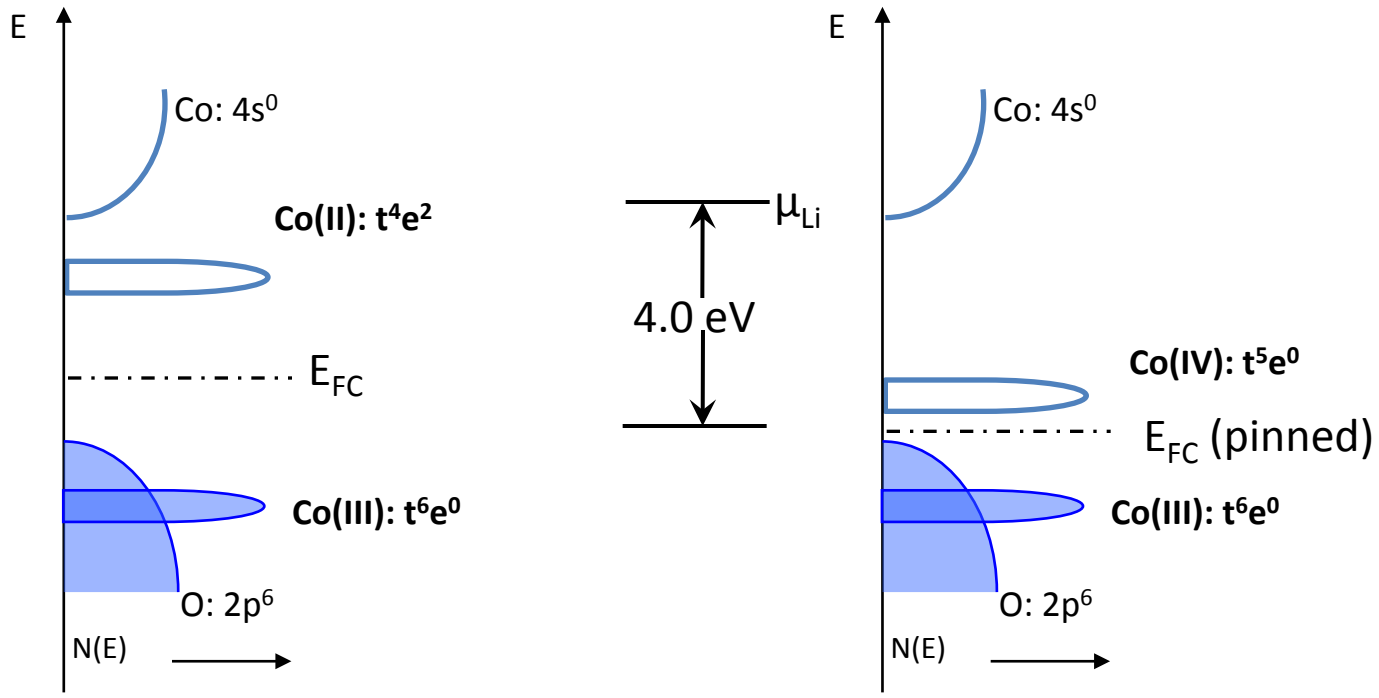
- Develop and test a suitable test cell. (Jan. 10) **Completed**
- Optimize components of the cell. (Apr. 10) **Completed**
- Develop a lithium/$Fe(NO_3)_3$ cell. (July. 10) **Completed**
- Design of a new cell (Sept. 10) **Completed**
- Test flow-through cell (Jan. 11) **Completed**

Typical Lithium Ion Battery (LIB) Cell



- Capacity limited by Li solid solution in cathode and loss in SEI layer
- Voltage limited by E_g of carbonate electrolyte.

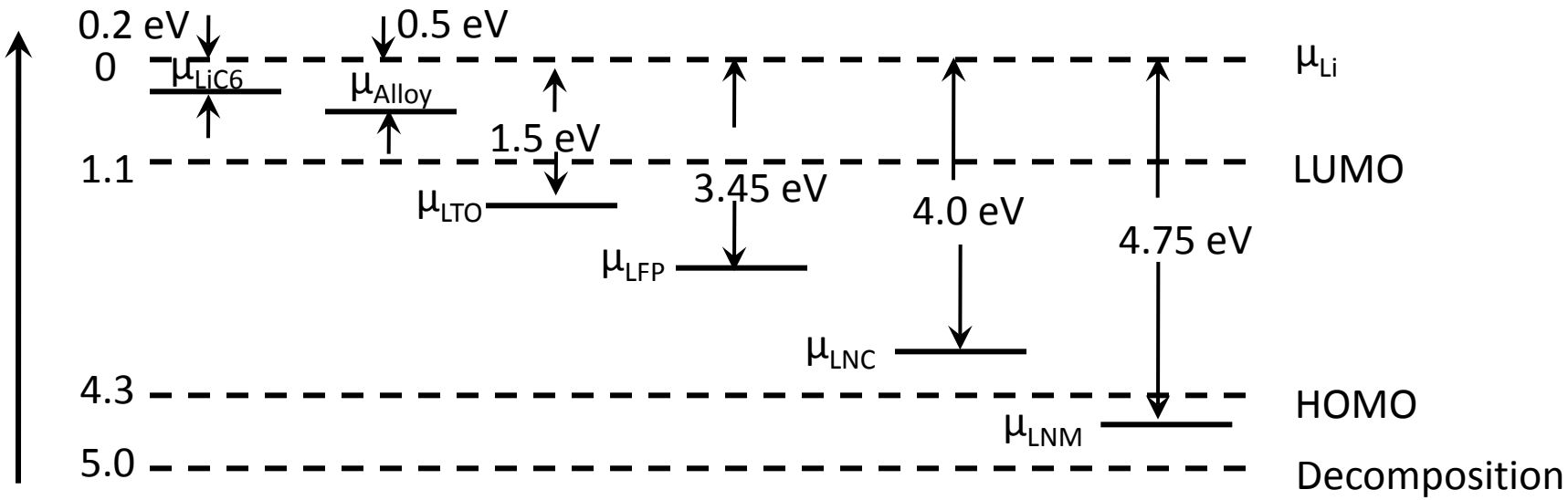
Why Oxides?



$LiCoO_2$ $Li_{1-x}CoO_2$ (0<x<0.55)

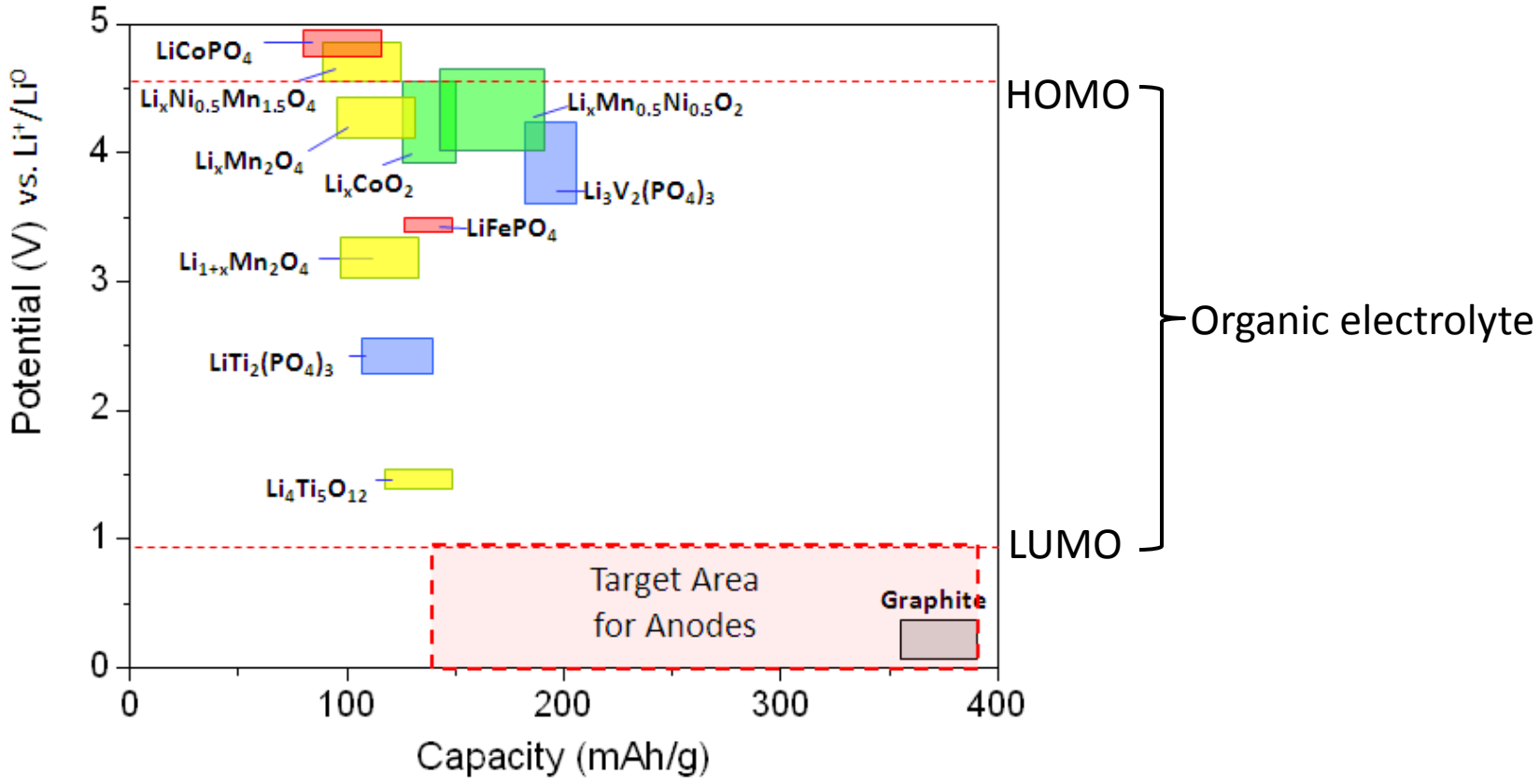
- Holes form peroxide $(O_2)^{2-}$ for x> 0.55 or H^+ inserted from electrolyte.
- At surface, $2(O_2)^{2-} = 2O^{2-} + O_2\uparrow$
- Note: $Li_{1-x}(Co_{0.15}Ni_{0.85})O_2$ (0<x<0.8) at 3.8 V versus Li^0.
- Note: Introduction of Mn(IV) stabilizes top of O: $2p^6$ bands to above 4.7 V versus Li^0.

Carbonate Electrolyte



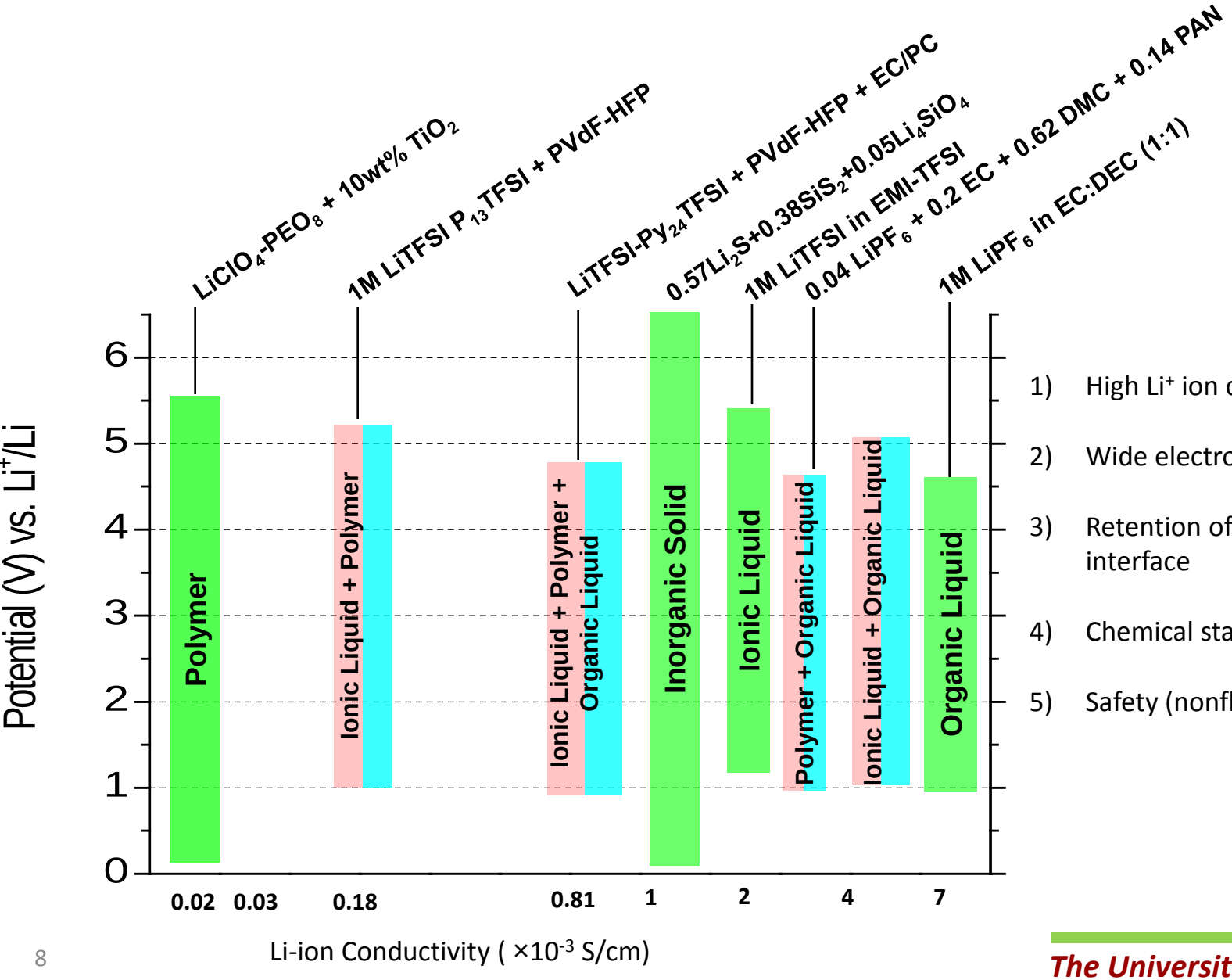
- $Li^0 - e^- = Li^+$; dentrites on recharge because of SEI layer.
- $LiC_6 - e^- = 6C + Li^+$; SEI layer prevents rapid charge, consumes Li from cathode.
- Alloy anodes undergo displacement reactions, which give large volume change.
- Can be buffered by C and have voltages allowing fast charge, but SEI layer if V<1 V.
- Need μ_C matched to HOMO or, with Li^+-permeable SEI layer, to decomposition voltage.

Existing Insertion Compound Electrodes



- Lithium metal has the highest specific energy of 3860 mAh/g. No cathode materials can match the capacity.
- Can we use lithium anode and develop a cathode with a capacity to match?

Existing Electrolytes



1) High Li^+ ion conductivity
2) Wide electrochemical window
3) Retention of electrode/electrolyte interface
4) Chemical stability
5) Safety (nonflammable)

Li Batteries Using a Solid Electrolyte Separator

- Concept

Li	Organic Liquid Or nothing	Inorganic Solid	Air or S_8 Aqueous (Fe^{3+}/Fe^{2+}) flow through

- Present Practice (Visco, PolyPlus Battery Company)

Li	1M $LiPF_6$ in EC/DEC	$Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$	Sea Water

Li_3N

- Proposed Practice

Li	1M $LiPF_6$ in EC/DEC	$Li_7Zr_2R_3O_{12}$	$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ flow through

$$Li + Fe(CN)_6^{3-}(aq) = Li^+ + Fe(CN)_6^{4-}(aq); \quad E=3.40\ V$$

Solid Electrolytes

- All Solid-State Cell

(+) All solid-state cell would simplify and lighten packaging

Sulfides offer large E_g and σ_{Li}> 10^{-3} S/cm

(-) Insertion compounds change volume on cycling, so cycle life of solid/solid interfaces is problematic

- Solid-Electrolyte Separator

(+) Would allow a lithium anode

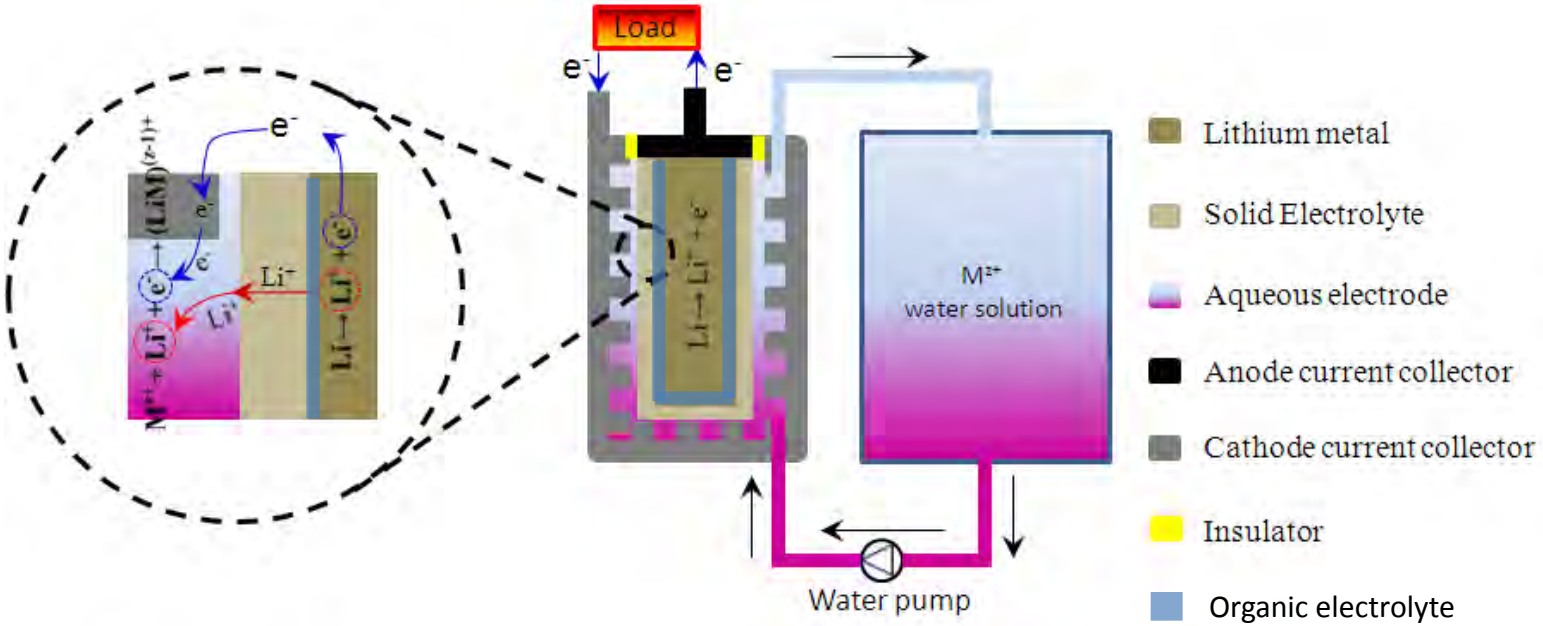
Would block dendrites from a lithium anode or a Li/solid-electrolyte interface

Would allow alternative cathodes, e.g. air, S_8, or Fe^{3+}/Fe^{2+} (aq) flow through

(-) For an aqueous cathode, need an oxide separator: σ_{Li}(oxide) ≈ 10^{-4} S/cm fabricated thin and dense on a support; and not reduced by lithium

Approach:

An Alkali-Metal/Aqueous Cathode Cell



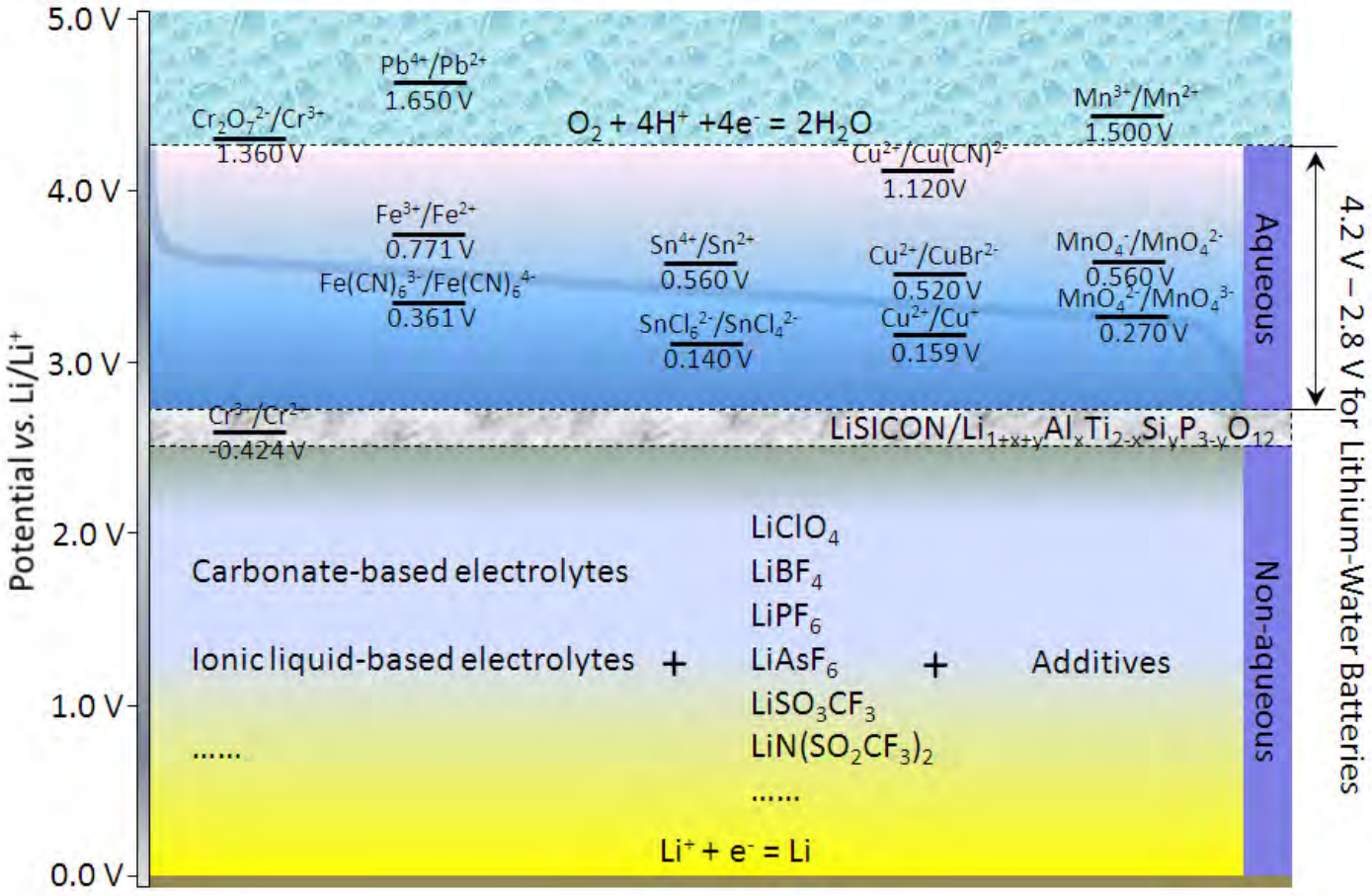
Anode reaction: $nA \rightarrow nA^{+} + ne^{-}$; (A=Li or Na)

Cathode Reaction: $M^{z+}(aq) + ne^{-} \rightarrow M^{(z-n)+}(aq)$;

Overall reaction: $nA + M^{z+}(aq) = nA^{+} + M^{(z-n)+}(aq)$; $(1 \leq n < z)$.

- No phase change takes place in the cathode.
- No catalyst is needed in the cathode.
- The cell is rechargeable.
- The cell works at room temperature.
- The cell works in the voltage range of 2.8 to 4.2 V.

Selection of Aqueous Cathode with Existing Solid Electrolyte

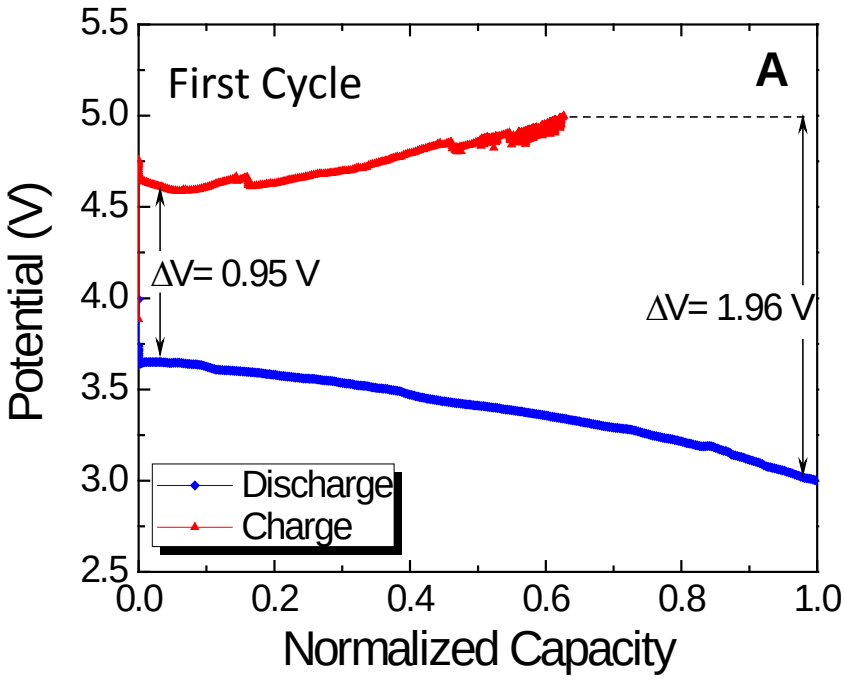


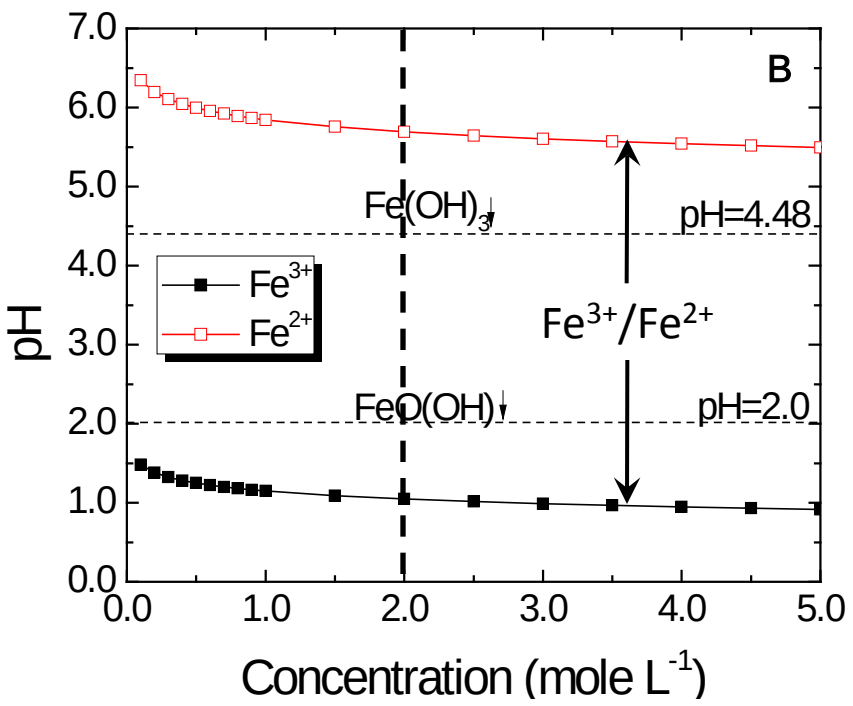
- Aqueous electrodes will depend on electrolyte and must have:

  1) proper redox potentials; 2) no side reactions; 3) good stability in water; 4) good reversibility; 5) reliable safety; 6) no toxicity and 7) low cost.

Accomplishments:

A Lithium|$Fe(NO_3)_3$ (aq) Cell

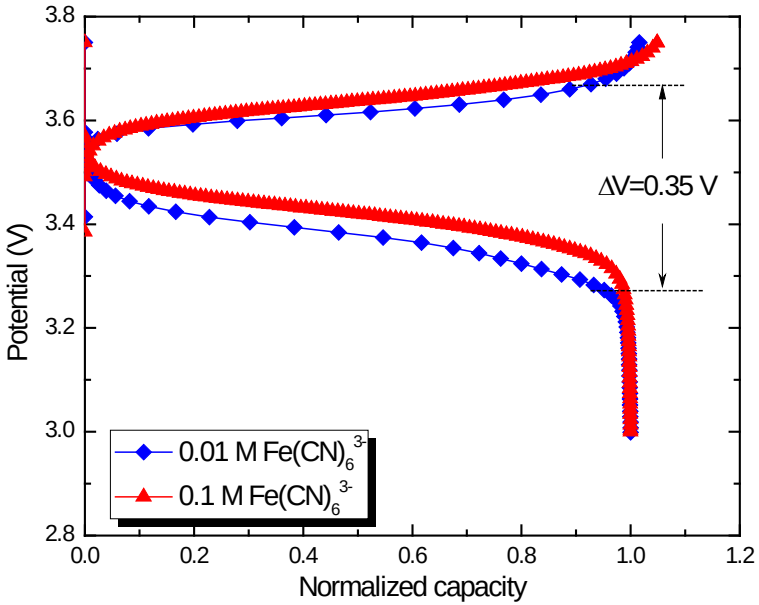


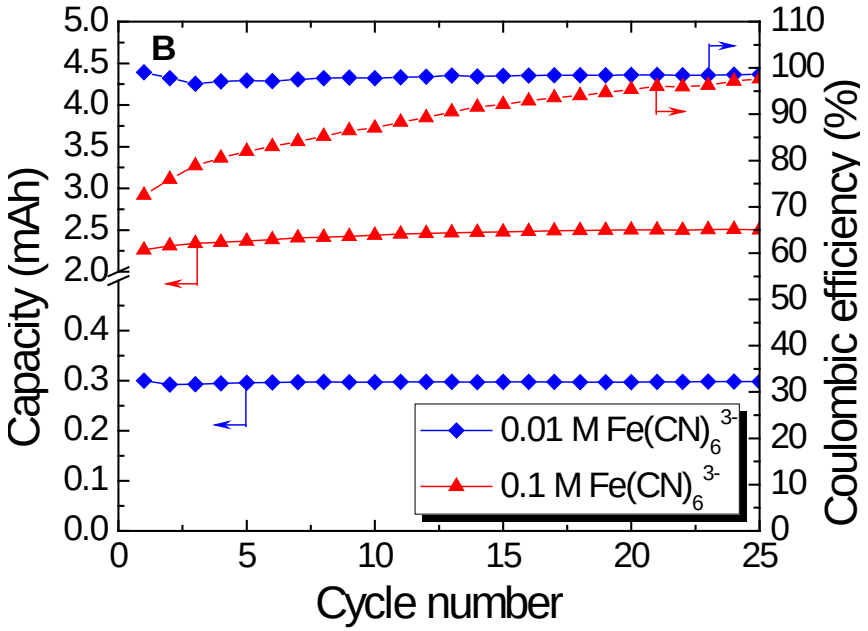


- The open circuit voltage of the battery is 3.99 V. Its initial discharge voltage is 3.74 V at a current of 0.5 mA.
- After discharge Its initial charge voltage is 4.73 V at the current of 0.5 mA.
- Hydrolyzation of Fe(III) results in precipitates of FeO(OH) for pH>2 and $Fe(OH)_3$ for pH>4.8 when pH of the aqueous electrode solution increases with cell discharge.

Accomplishments:

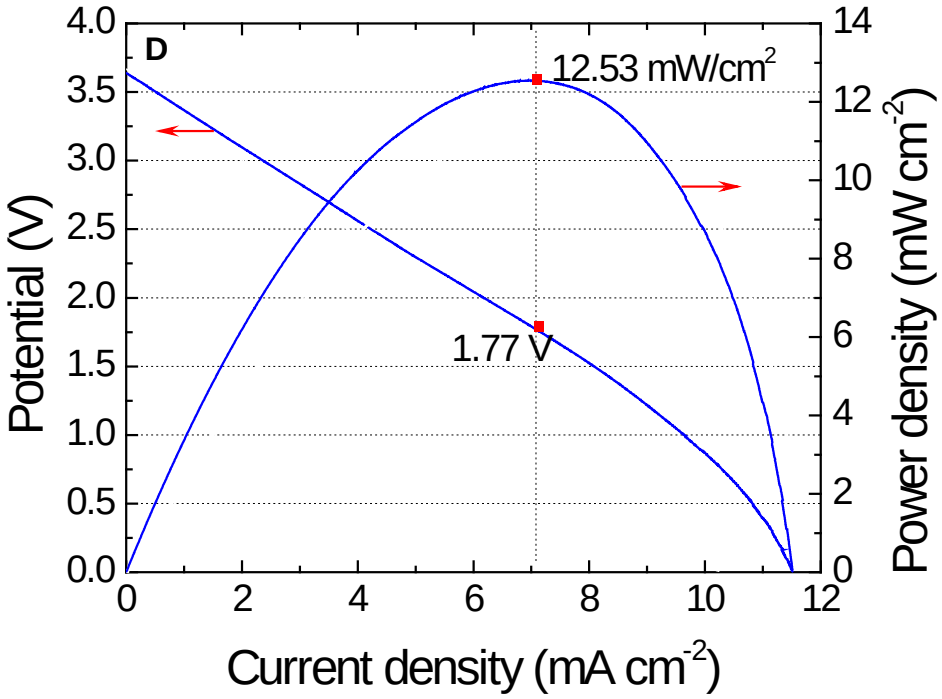
Lithium| $Fe(CN)_6^{3-}$ (aq) Cells

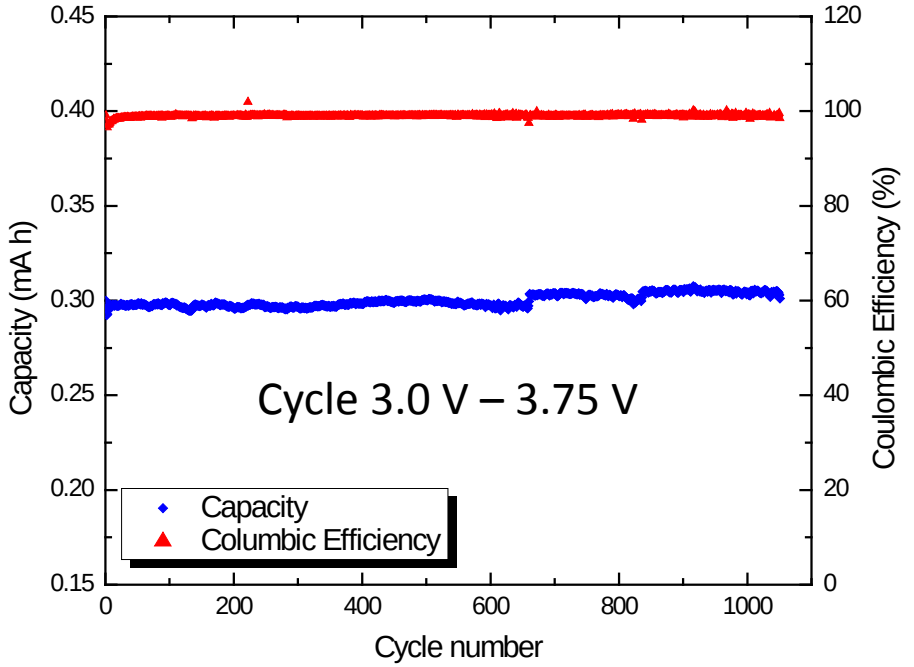




- No hydrolyzation of Fe(III)
- The theoretical voltage of the battery is 3.40 V.
- Its effective voltage with the commercial solid electrolyte distributes between 3.33 V and 3.68 V.
- Different concentrations of the redox couple in the aqueous electrode slightly affect the normalized discharge/charge curves.
- The battery shows a high coulombic efficiency.

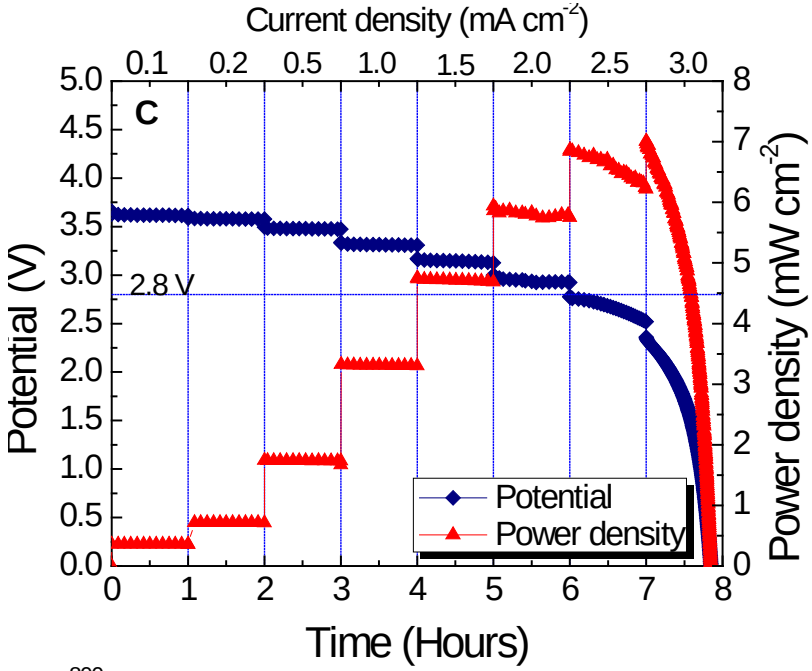
Power Density and Reversibility of Li|$Fe(CN)_6^{3-}$ (aq) Cells

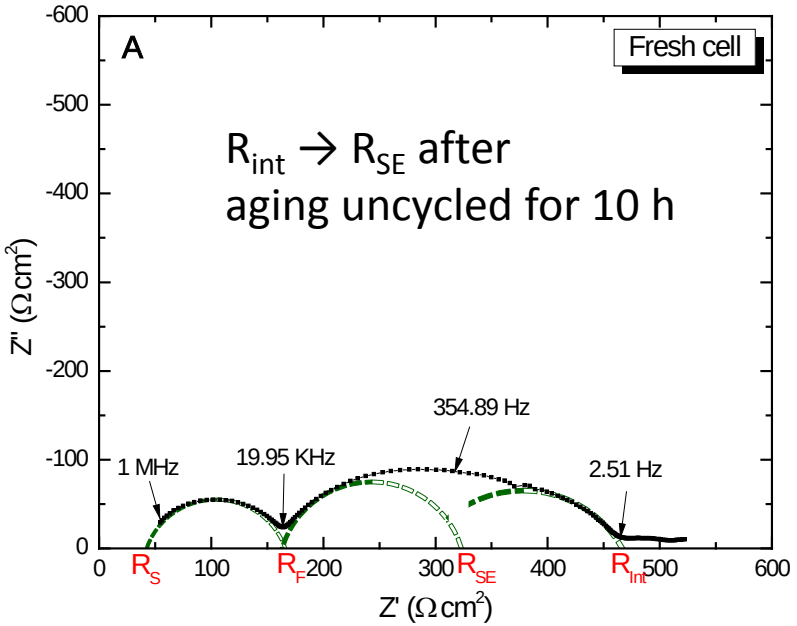


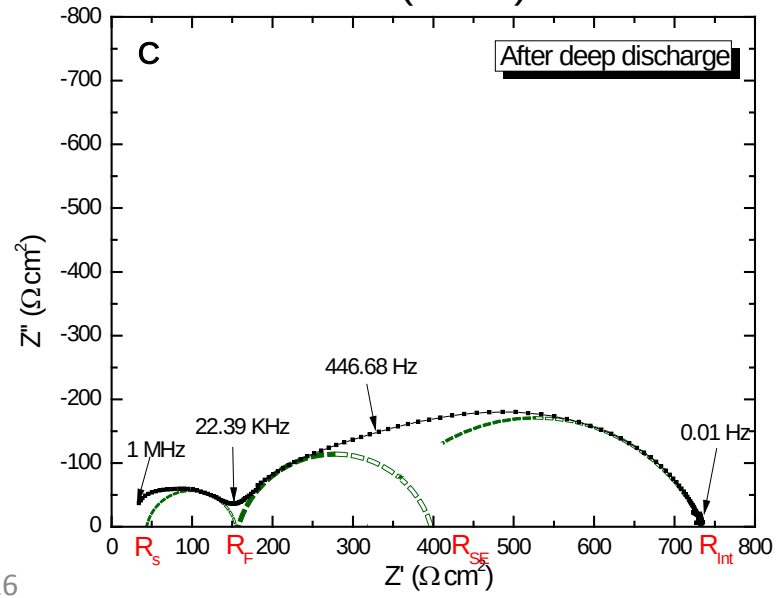


- The cell demonstrates a maximum power density of 12.53 mW/cm^2, which is competitive with a direct methanol fuel cell of similar active area.
- Due to no cathode phase change in the charge/discharge, the cell shows a good reversibility. No capacity loss was observed over 1000 cycles.

Stability of Li|$Fe(CN)_6^{3-}$ (aq) Cells with Existing Electrolyte

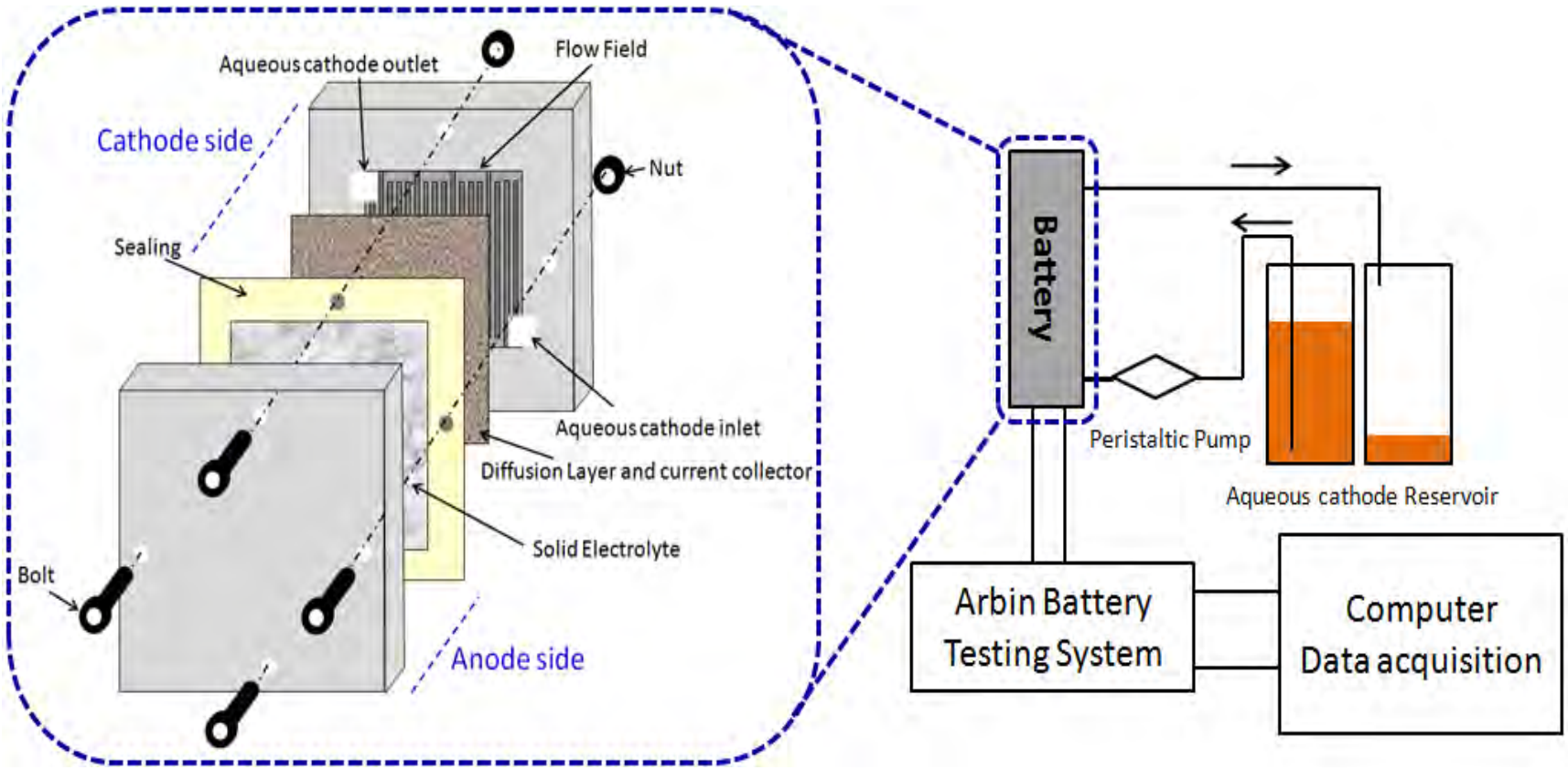






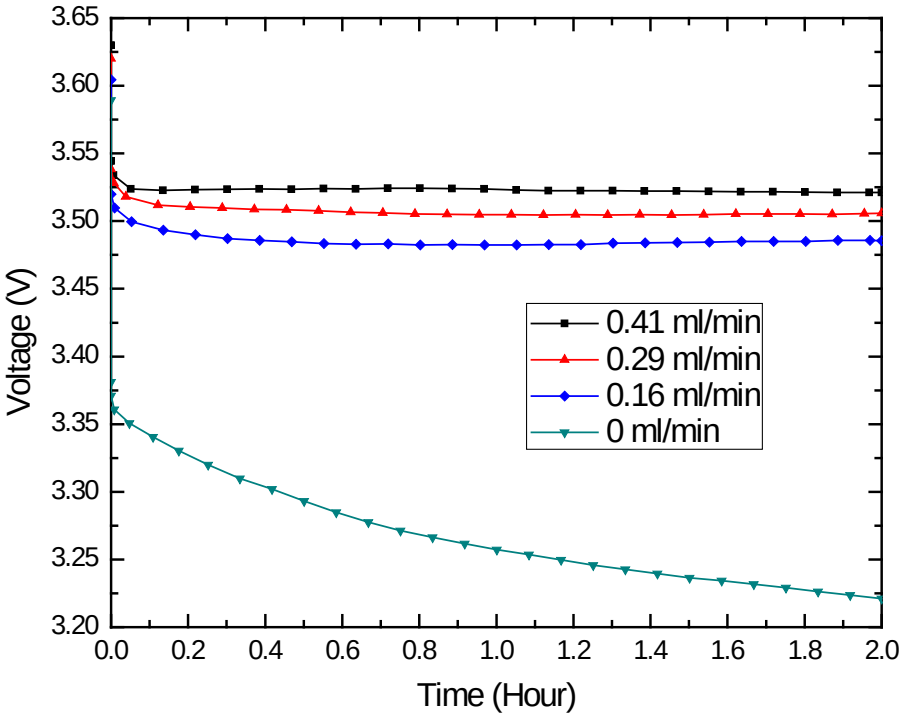
	A	C
R_S (solution)	42.46	43.79
R_F (charge transfer)	120.52	115.62
R_{SE}(solid electrolyte)	160.24	237.84
R_{Int}(interface)	143.34	346.33

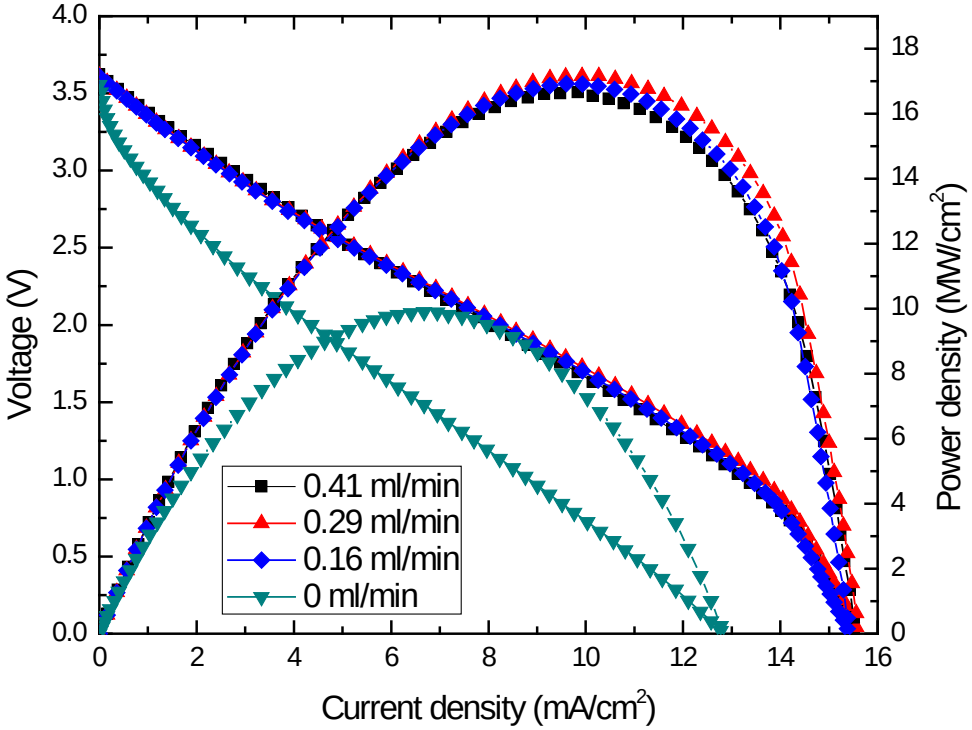
Rechargeable Lithium|Cathode-Flow Battery (RLCFB)



- The aqueous cathode in a flow-through mode can be individually stored in a “fuel” tank, which reduces the volume of the battery and increases the design flexibility of the battery structure.
- Recycling of aqueous cathode can match the large capacity of lithium metal.

Behavior of RLCFB





- The maximum power density of the battery with existing electrolyte is about 17 mW/cm^2.
- Flow rates of the aqueous cathode don't influence significantly the power density of the battery.
- Development of a thinner solid-electrolyte separator with a higher Li^+-ion conductivity would provide commercially viable room-temperature EES for energy sources alternative to fossil fuels.

Summary

- The study demonstrates the feasibility of a Lithium|water battery utilizing lithium metal as anode and a redox couple soluble in aqueous solution as the cathode.
- This new strategy represents a third-generation lithium-ion battery promising lower cost than the conventional lithium-ion rechargeable battery, safe operation, and having a columbic efficiency and voltage greater than that of a Li/air battery with, in principle a comparable capacity.
- A flow-through mode of the aqueous cathode can provide a full and efficient match of the capacity of a lithium-metal anode. The flow of the aqueous solution continuously brings heat out of the battery system and keeps the battery working near a mild condition.
- Flow rates of the aqueous cathode in the study don't influence significantly the power density of the battery.
- The demonstrated power output is limited by the commercially available solid electrolyte separating an organic-liquid or polymer anolyte and the aqueous cathode; the fabrication of a superior solid electrolyte is clearly needed.
- The new strategy promises to be applicable to both the electric-vehicle market and the problem of electrical energy storage for the grid.

Future Work

- By stabilizing the existing electrolyte against degradation, which we have shown to be due to the presence of Ti(IV), we will obtain data on the specific capacity versus molar fraction of the Fe(III)/Fe(II) couple in the cathode solution and how capacity is retained at higher discharge/charge rates.
- We will obtain data on the ability of seals to prevent water crossover into the anode compartment and whether a lithium/solid-electrolyte solid-solid interface can be maintained over a long cycle life.
- We will explore different cathode current-collector configurations.
- Alternative solid electrolytes will be identified and their fabrication into dense, durable films will be explored.
- The use of a Na rather than a Li anode with a Na^+-ion solid electrolyte will be investigated.