Solid Electrolyte Batteries

John B. Goodenough and Youngsik Kim

Texas Materials Institute
The University of Texas at Austin

DOE Vehicle Technologies Annual Merit Review Meeting

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Project ID: **ES060**

Overview

Timeline

- Project Start Date – Oct. 2009
- Project End Date – Sept. 2010
- Percent Complete – 50 % complete

Barriers

- Design of the battery cell containing a solid electrolyte
- Search for a solid electrolyte that has a high Li-ion conductivity ($\sigma \geq 10^{-3}$ S/cm) and a wide electrochemical window (0 – 9 V vs. Li^+/Li^0)

Budget

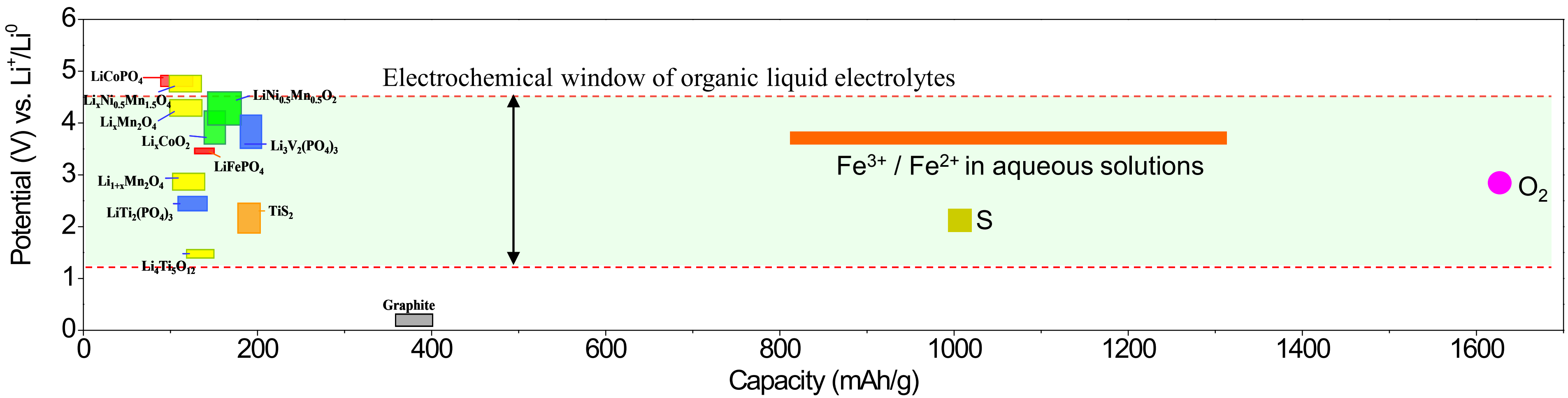
- Funding received in FY09
  – $ 315 K
- Funding received in FY10
  – $ 315 K

Partners

Milestones

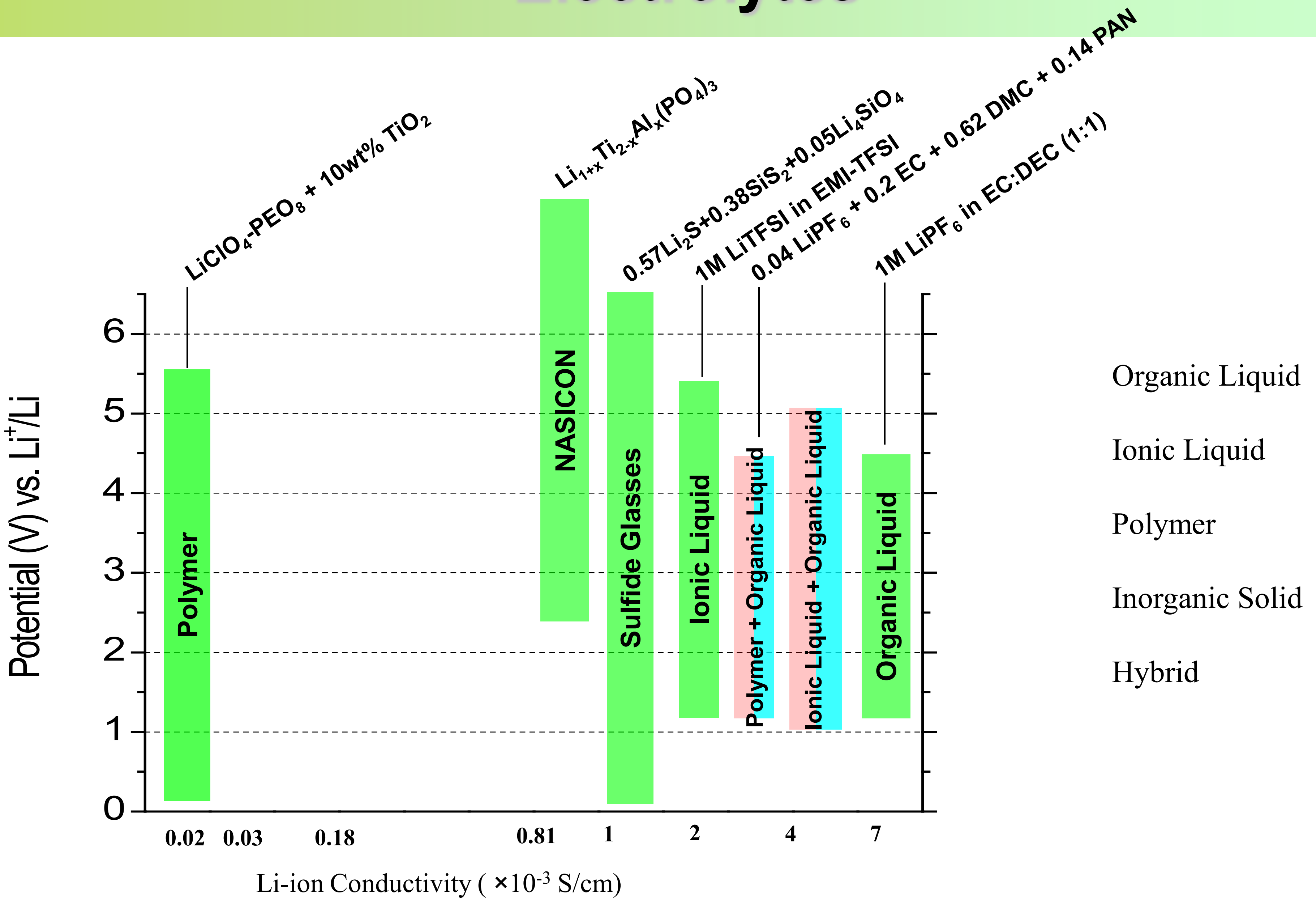
- Develop and test a suitable test cell (Jan. 10): **Complete**
- Optimize components of the cell (Apr. 10) **Complete**
- Develop a Li/Air cell (July. 10)
- Test alternative cathode catalysts (Sept. 10).
- Comparison of performance test of cells with that of the best reported Li-Air cell (Oct. 10)

Problems with the Present Li-ion Batteries



- Insertion compounds have limited capacity
- Li / Air batteries are inefficient if used for electrical energy storage
- Li / S batteries have too low a voltage and need a new electrolyte and a better cycle life
- Liquid cathodes need a solid electrolyte stable against Li and H_2O with $\sigma > 10^{-4}$ S/cm

Electrolytes



The Use of Inorganic Solid Electrolyte for Li Batteries

- **Concept**

Li | Organic Liquid | Inorganic Solid | Air (Primary) / Aqueous (Primary or Secondary)

- **Present Practice** (Visco, PolyPlus Battery Company)

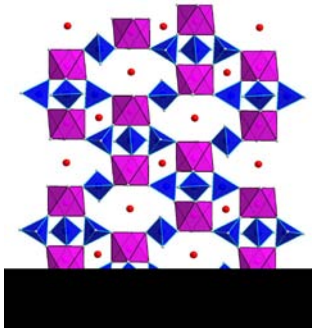
Li | 1M $LiPF_6$ in EC/DEC || $Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$ | Sea Water

Li_3N

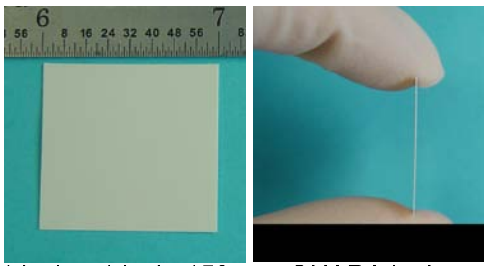
- **Proposed Practice**

Li | 1M $LiPF_6$ in EC/DEC | $Li_7Zr_2R_3O_{12}$ | $Fe(NO_3)_3$ / $Fe(NO_3)_2$

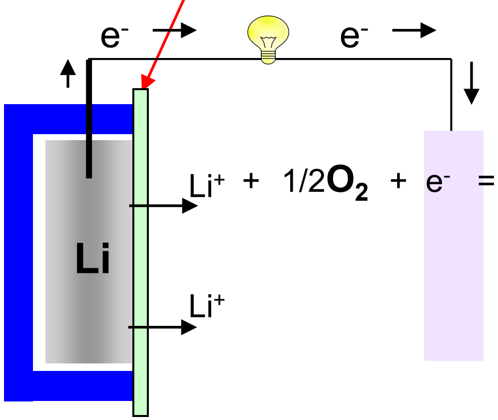
Present Li/Air Batteries



NASICON structure
$LiM_2(PO_4)_3$

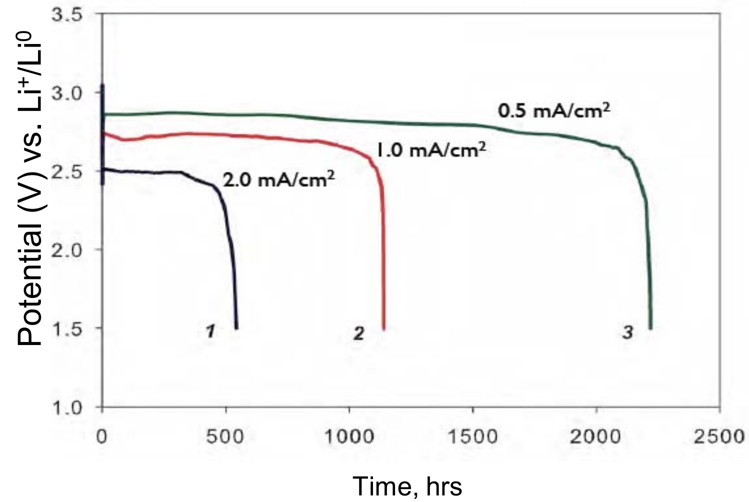


1 inch × 1 inch, 150 μm, OHARA in Japan

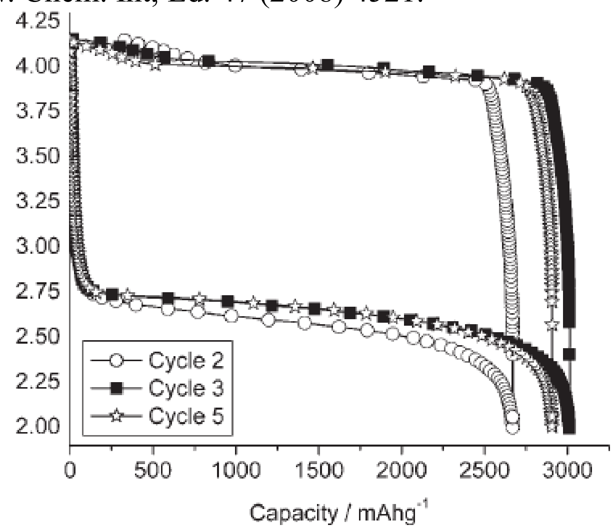


$Li^+ + 1/2O_2 + e^- = 1/2Li_2O_2$ E = 2.96 V

Steven J. Visco et. al. PolyPlus Battery Company



A. Debart, A.J. Paterson, J. Bao, P.G. Bruce, Angew. Chem. Int, Ed. 47 (2008) 4521.

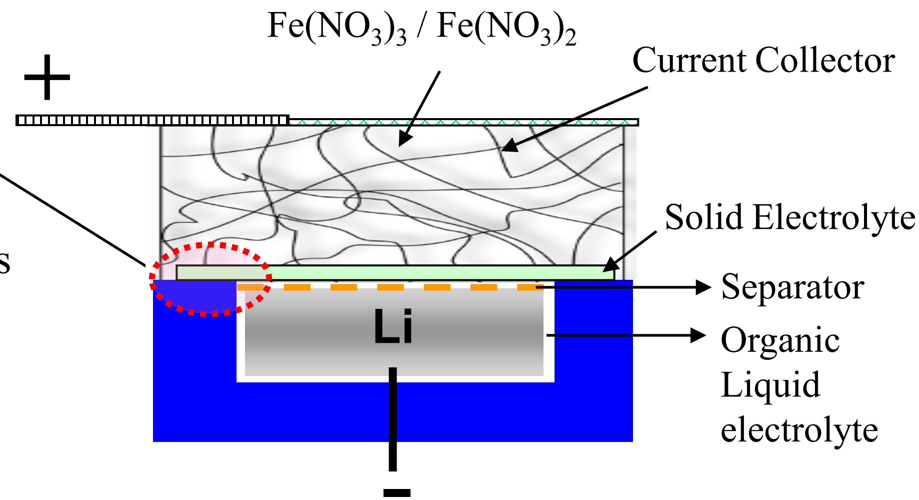


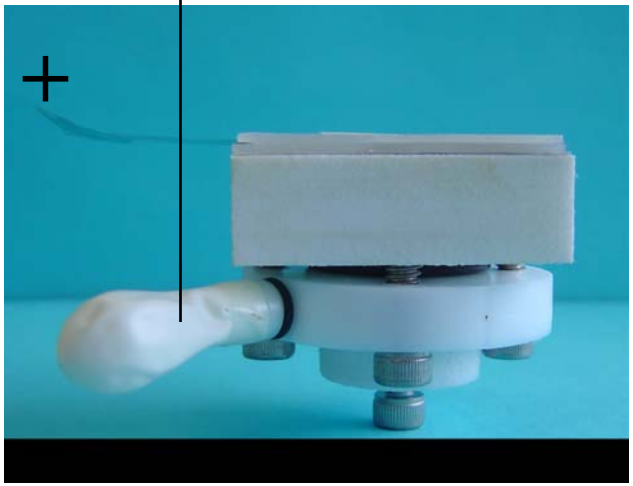
Design of Test Cell

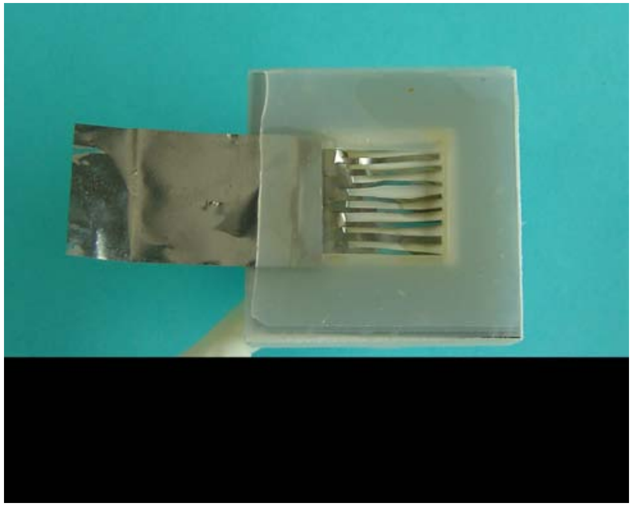
Two design challenges

(1) to find sealing agents stable in both highly reducing and oxidizing environments

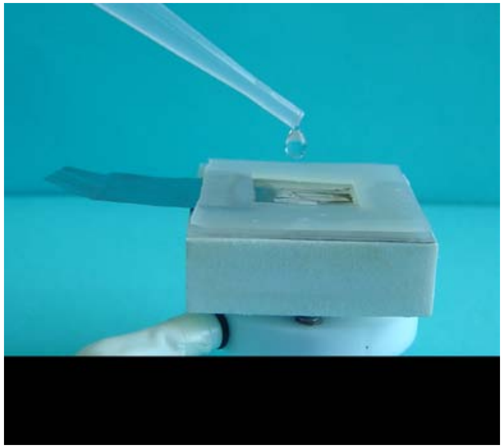
(2) to accommodate the electrode volume changes during cycling





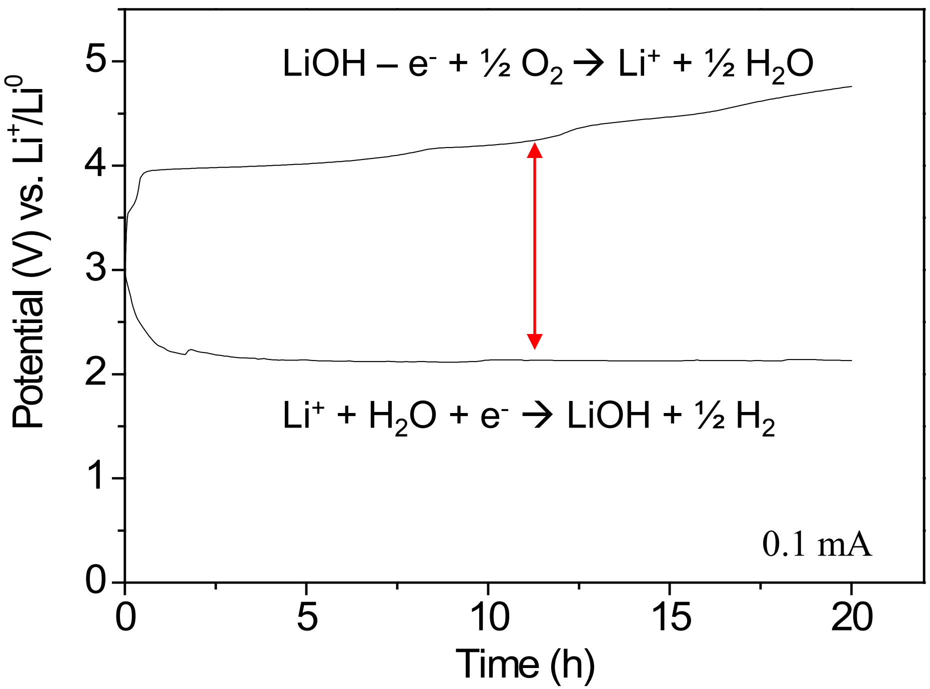


Water as Cathode

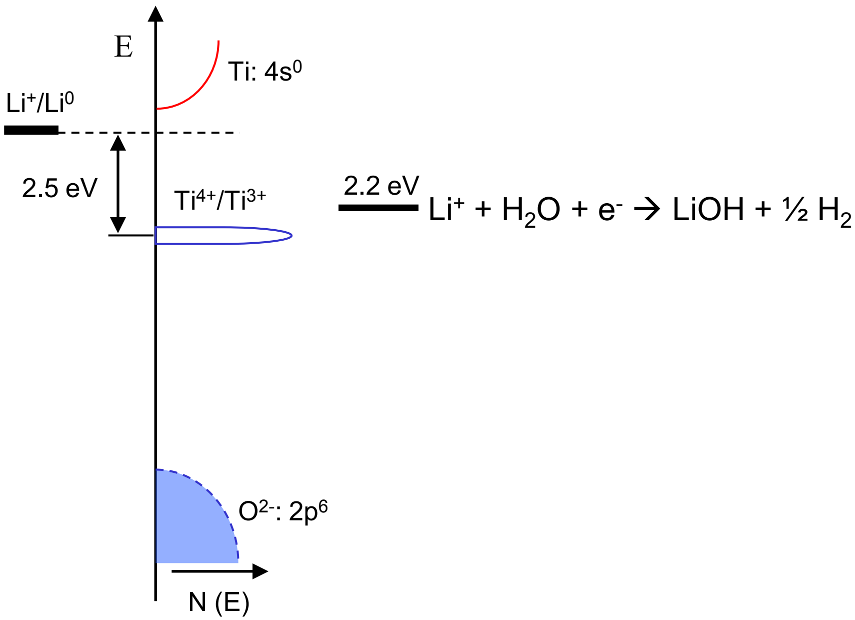


	Theoretical Capacity
O_2	1675 mAh/g
H_2O	1489 mAh/g

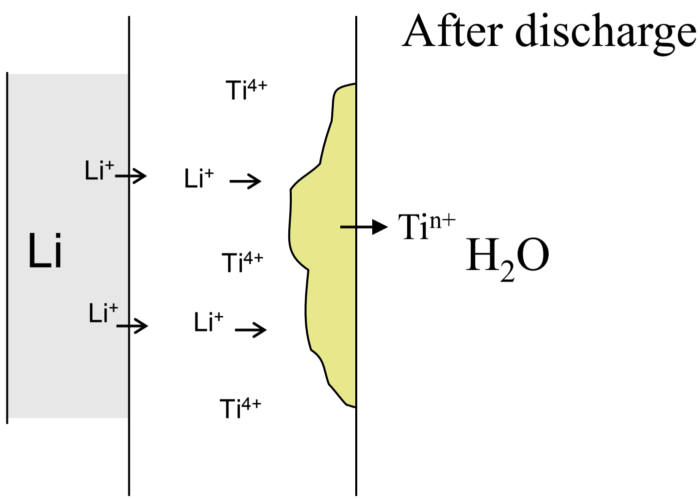
Poor charge efficiency, Poor cycle life



Problems with NASICON Solid Electrolyte for Water Cathode



$Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$



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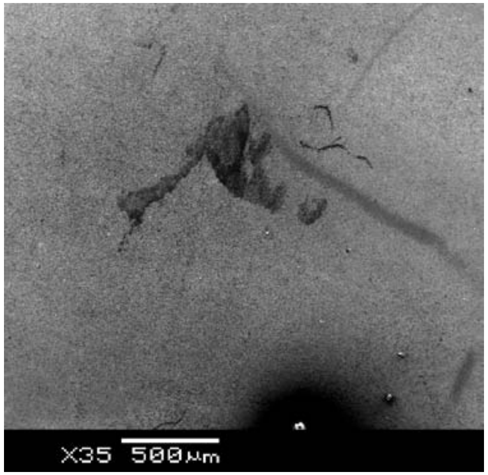
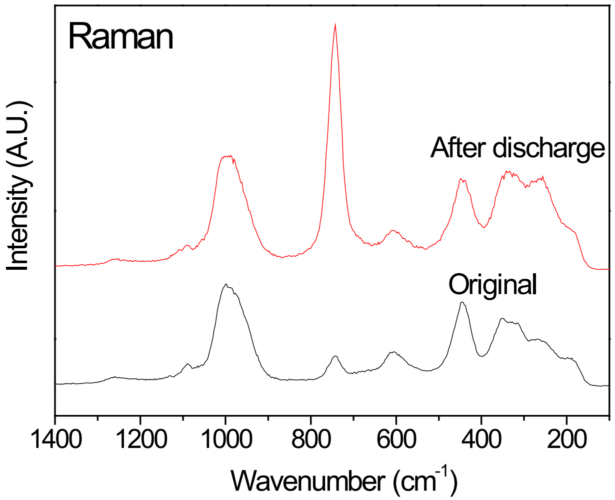
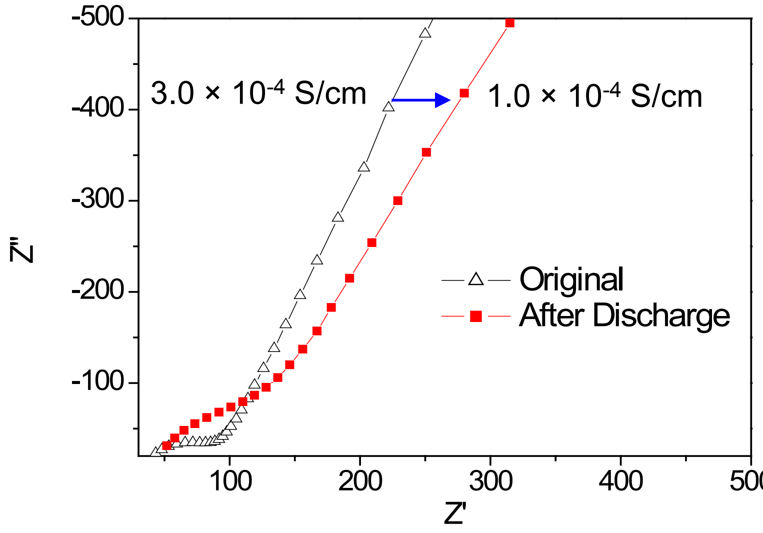
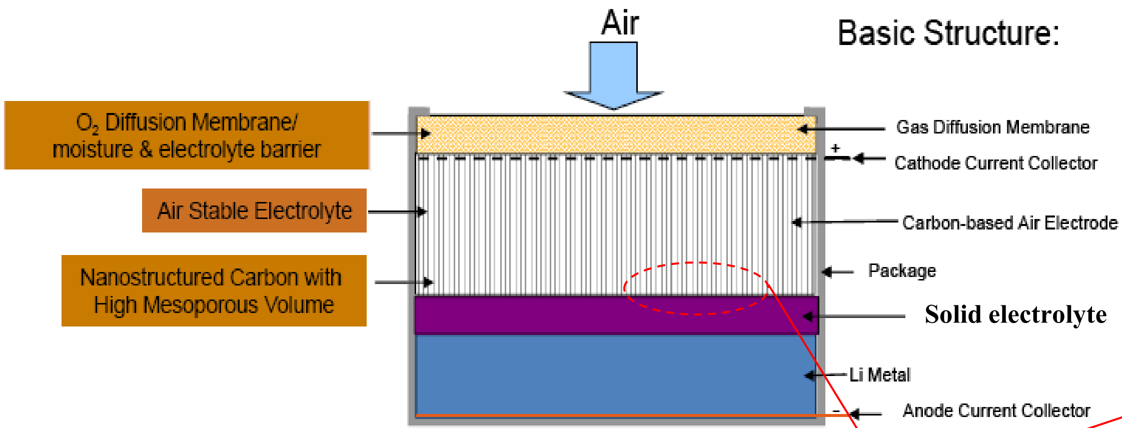




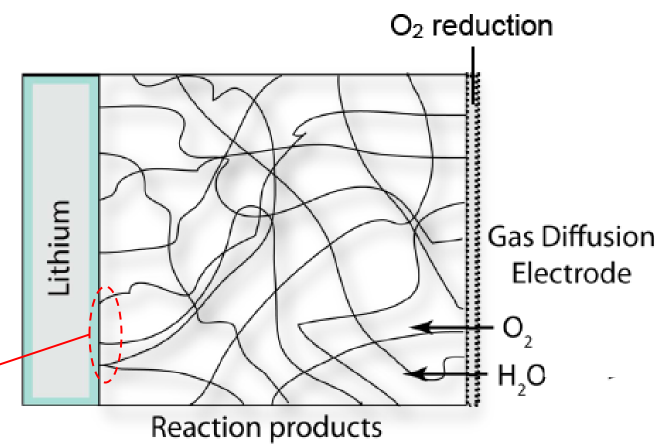


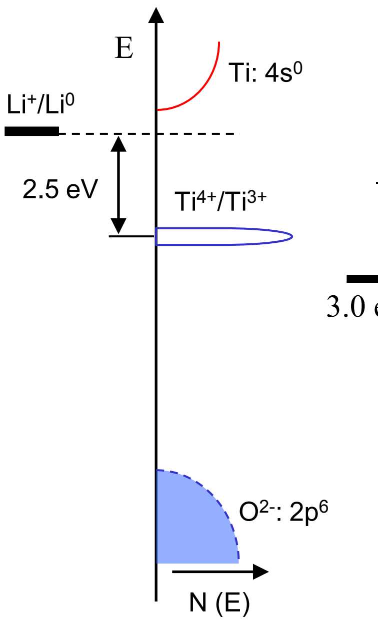
Problems of NASICON Electrolyte with Cell Designs for Air Cathode

Pacific Northwest National Laboratory



PolyPlus Battery Company





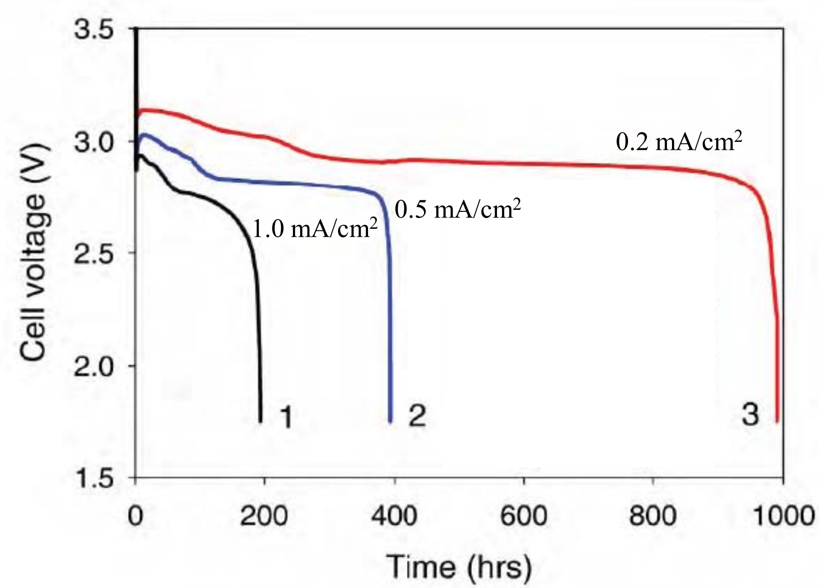
$Li_{1.3}Ti_{1.7}Al_{0.3}(PO_4)_3$

End of discharge

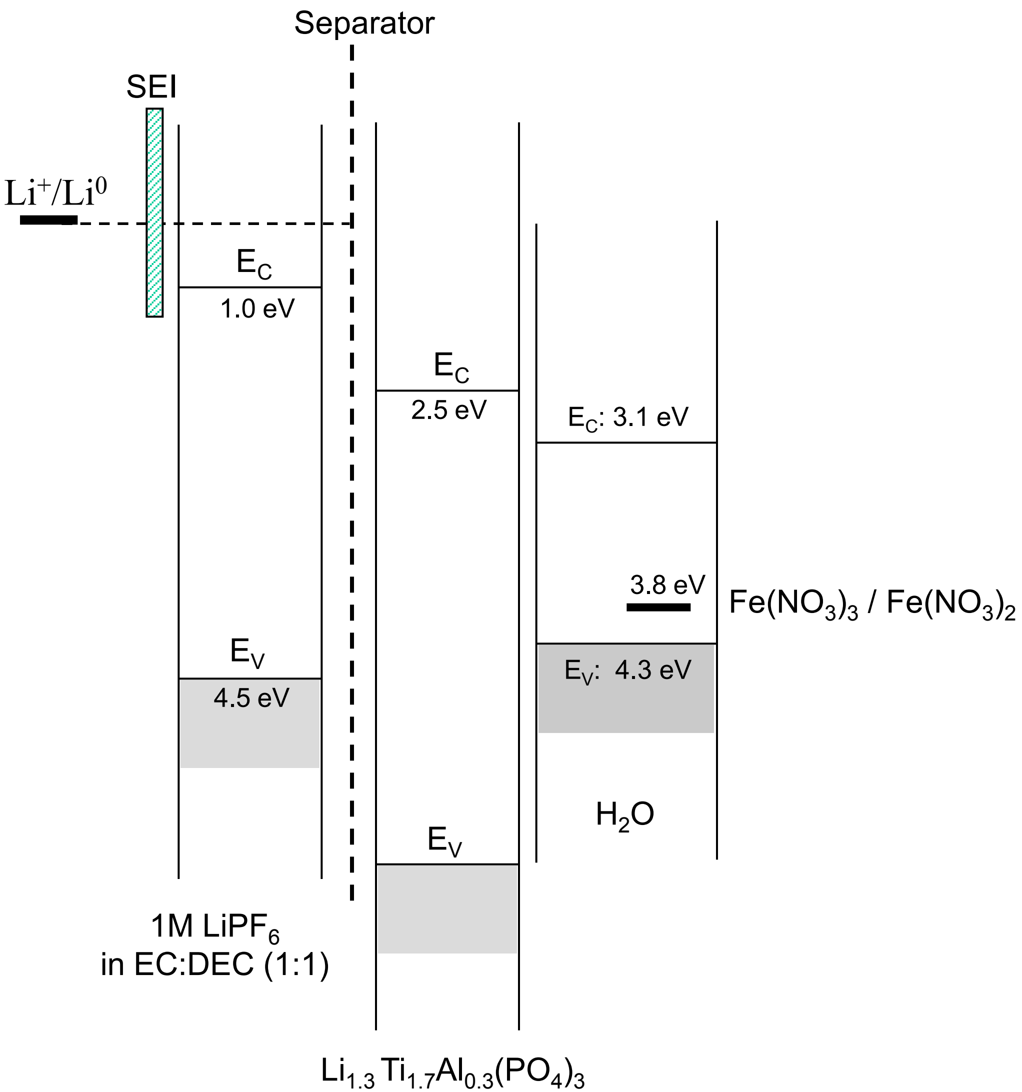
3.0 eV $\quad 2Li^+ + O_2 + e^- \rightarrow Li_2O_2$

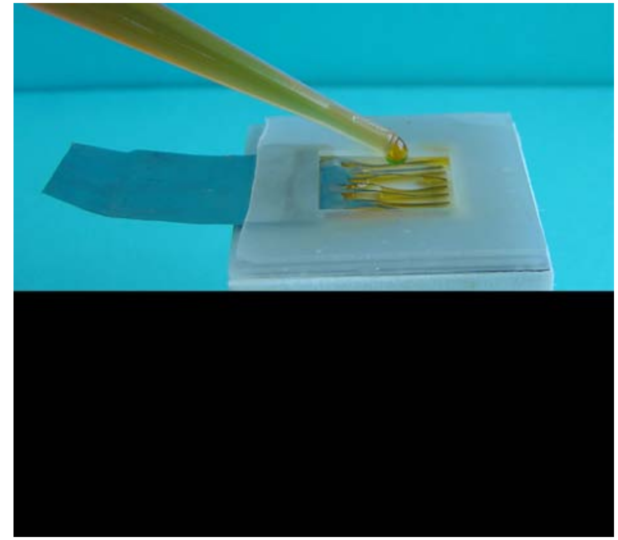
The current collectors reduce Ti^{4+} to Ti^{3+}

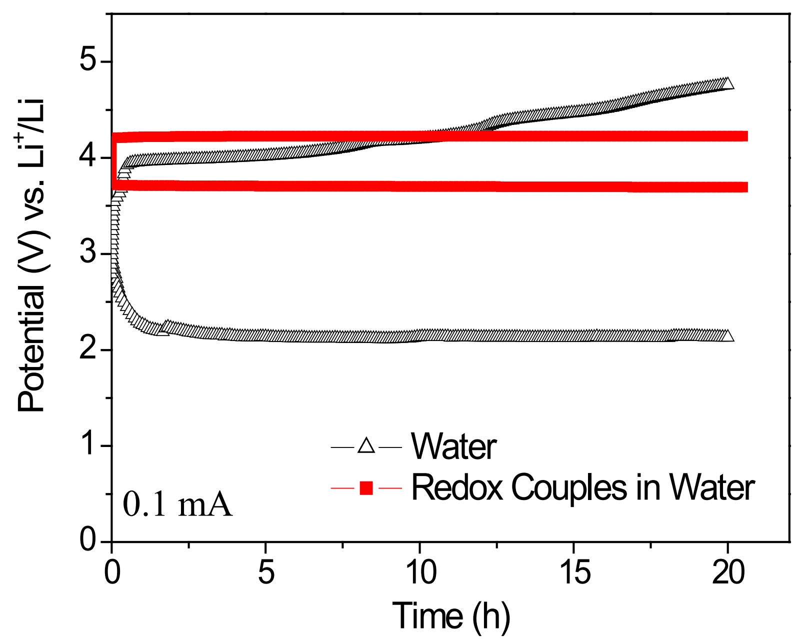
→ Not rechargeable



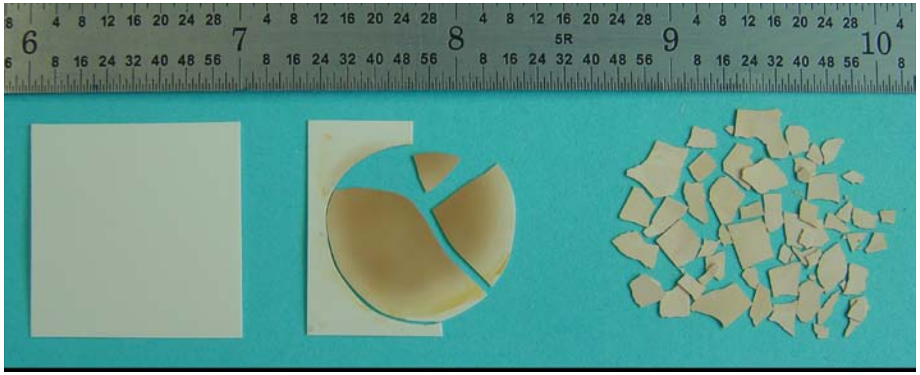
Transition-Metal Redox Couples in Aqueous Solutions

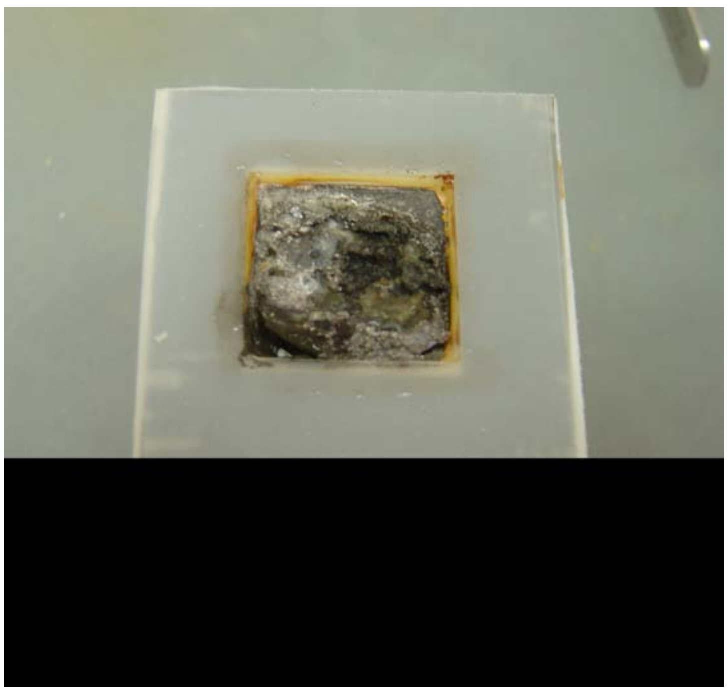






Instability of Solid Electrolytes in Acid Solution



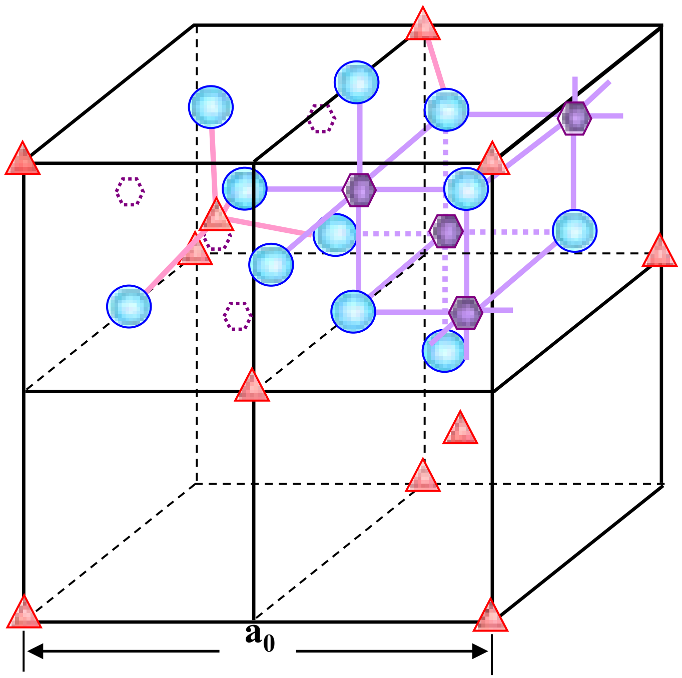


Future Work

Exploration of new solid electrolytes

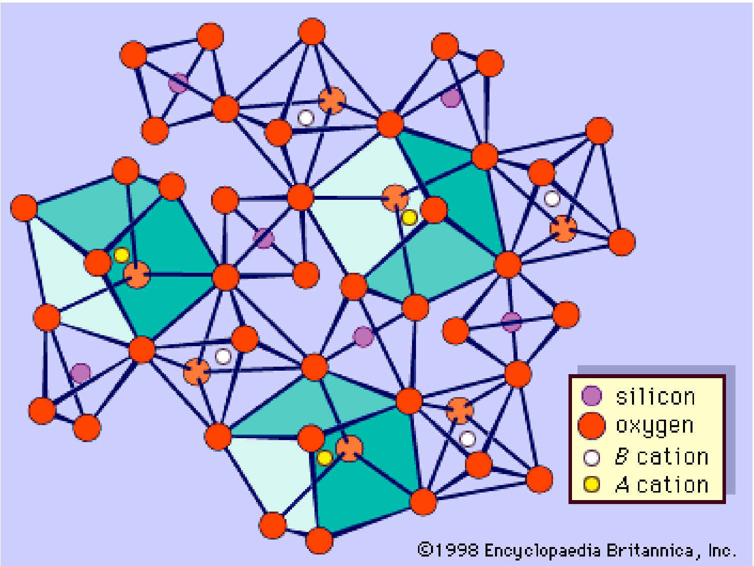
Closed packed O^{2-} framework

Spinel Structure



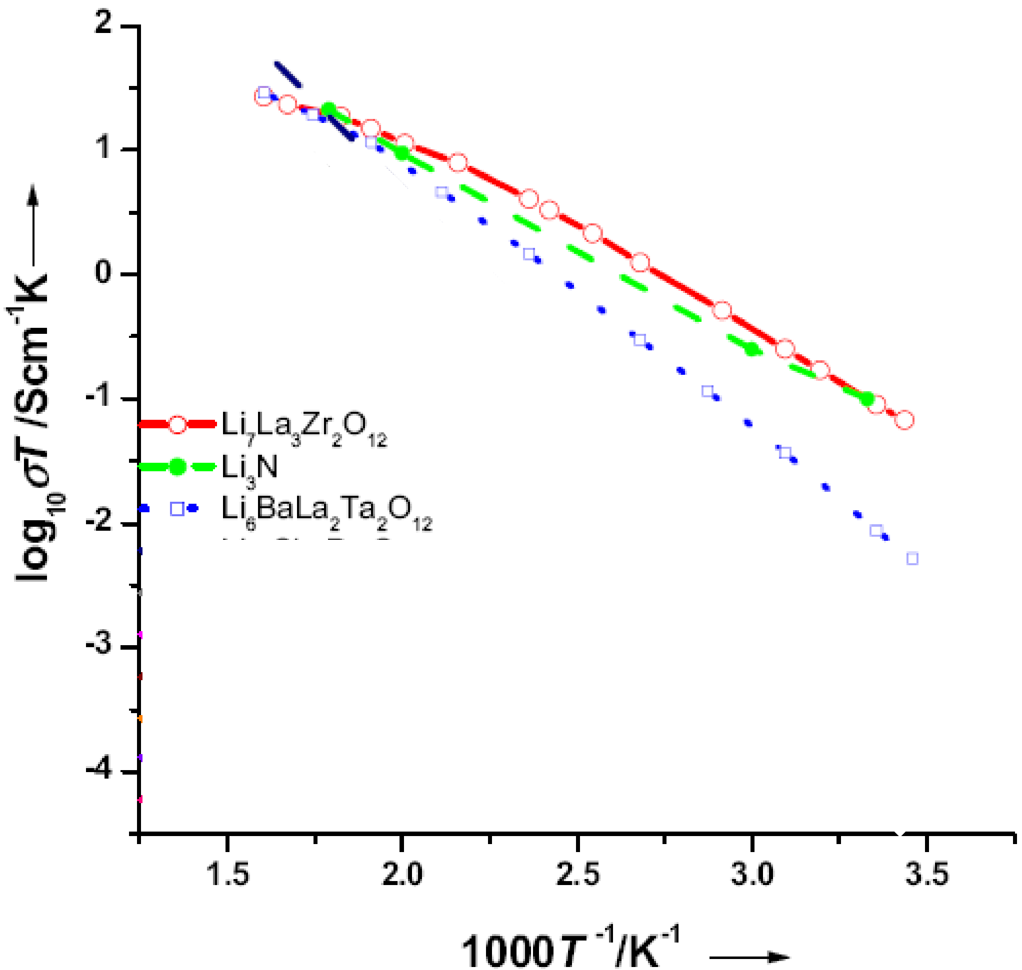
$A[B_2]O_4 = B_2(AO_4)$

Garnet Structure



$A_3B_2Si_3O_{12} = A_3B_2(SiO_4)_3$

Future Work



R. Murugan, V. Thangadurai, W. Weppner, Angew. Chem. Int. Ed. 46 (2007) 7778

Summary

- A Li / aqueous $Fe(NO_3)_3$ / $Fe(NO_3)_2$ battery has been shown to be feasible and to offer a capacity in excess of 1000 mAh/g compared to a Li/insertion cathode with a Q/W < 250 mAh/g.
- Commercial success of an aqueous cathode depends on development of a robust solid electrolyte with $\sigma_{Li} > 10^{-4}$ S/cm.
- The commercially available inorganic Li^+-ion solid electrolyte having $\sigma_{Li} \approx 10^{-4}$ S/cm is unstable with an acidic aqueous cathode.
- The inorganic solid electrolyte $Li_7Zr_2R_3O_{12}$ having $\sigma_{Li} \approx 10^{-4}$ S/cm shows promise.