Solid State Cell Chemistries and Designs

Sehee Lee
Department of Mechanical Engineering
University of Colorado at Boulder

Crash-Safe Energy Storage Systems For Electric Vehicles Workshop
Denver, CO November 12 & 13, 2012

Outline

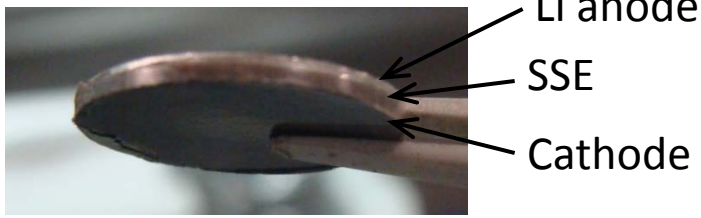
- History
- Basic theory (solid state electrolytes)
- SOA solid state batteries
- All-solid-state lithium secondary batteries
- Solid Power, Inc.

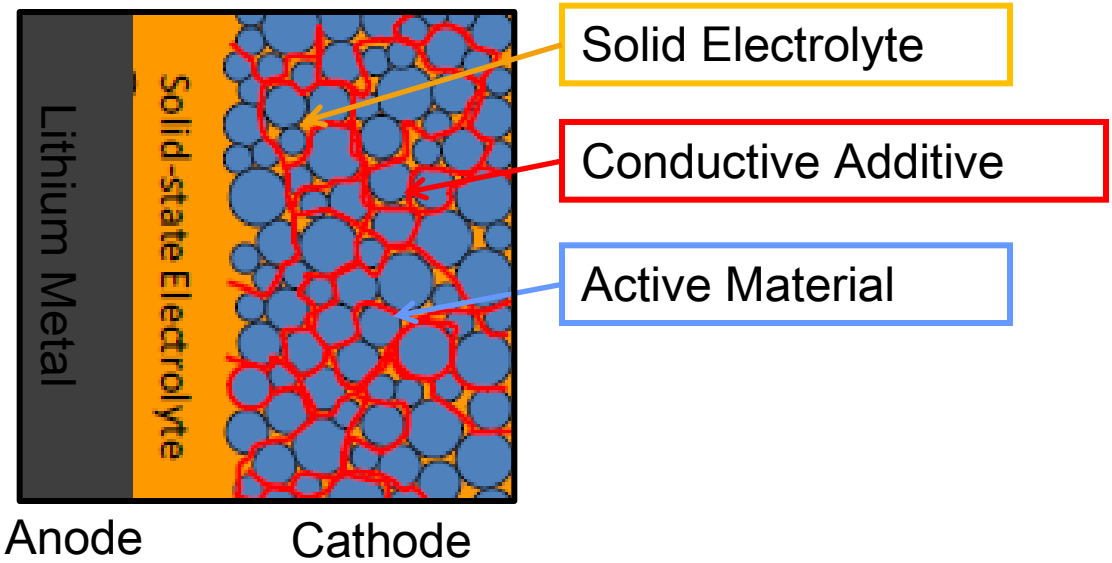
Why solid state battery?

Advantages	Disadvantages
No flammable liquid electrolyte → **Ultimate safety** → **No thermal runaway**	Slower kinetics due to • **Low ionic conductivity** • **High interfacial resistance** • **Poor interfacial contact**
High energy density	
No safety devices required	
Excellent cycling stability	
Excellent shelf life	

General Solid State Battery Construction

- **Two electrodes are separated by solid state electrolyte layer**
  - Electrolyte has high ionic conductivity and is electronically insulating
- **Composite electrodes**
  - Incorporate solid electrolyte into composite for fast ion transport
  - Incorporate conductive additive into composite for fast electron transport





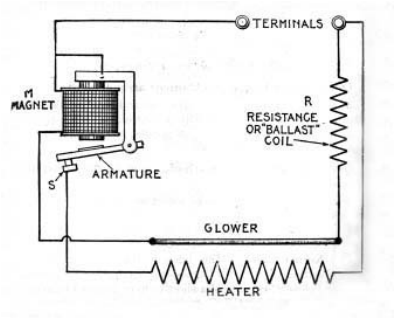
History

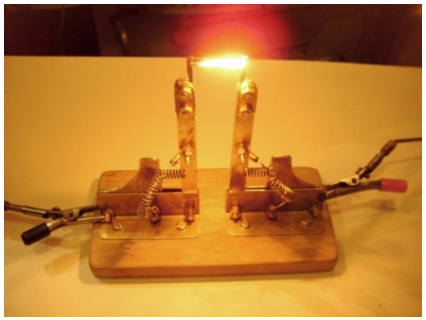
1839 (Michael Faraday) The first solid state electrolyte, **PbF_2** at high temperature

1884 (Warburg) Demonstrated **Na^+** conduction in glass

1888 (Warburg & Tegetmeier) The first measurement of transference number

~ 1900 (Walther Nernst) Discovery of " Nernst glower" – a ceramic rod was heated to incandescence → SOFC (solid oxide fuel cell), oxygen gas sensor





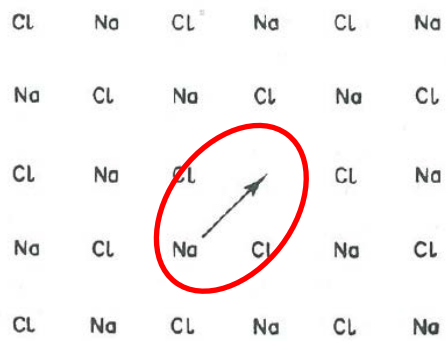
1914 (Tubandt & Lorenz) High Ag+ conductivity of **AgI** at 150°C (Ag/AgI/Ag)

1966 (Kummer & Webber @ Ford Motor) Developed **Na/S** battery by using **Na^+** conductor "**sodium beta alumina (β-Al_2O_3)**".

1973 (P. V. Wright) 1978 (M. B. Armand, J. M. Chabagno, M. Duclot) First polymer electrolyte

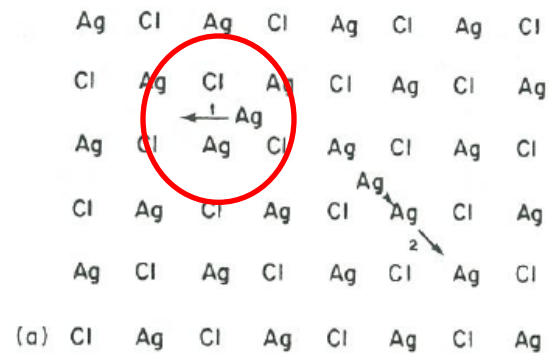
Conduction Mechanisms

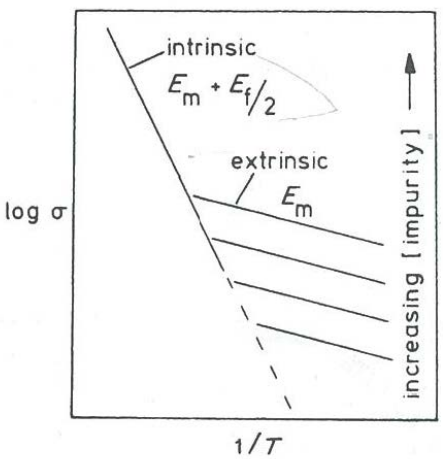
Vacancy conduction



Schottky defect
(a cation & anion vacancy pair)

Interstitial conduction



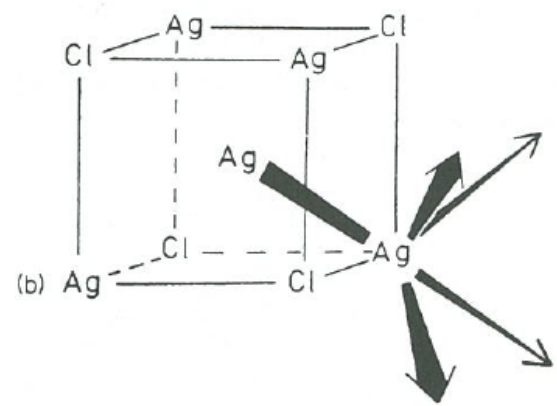


T↑ → defect↑ → conductivity↑

∴shows Arrhenius relationship

$$\sigma T = A\exp\left(-\frac{E_a}{RT}\right)$$

Derived from Random walk theory



Frenkel defect

Basic Theory – the concept of material design

- High mobile ion concentration
- High number of empty/vacant sites for ions hoping
- Small activation energy for conduction
- High number of conduction channel
- High polarizability of framwork ions
- In general, Amorphous > Crystalline

Solid Electrolyte

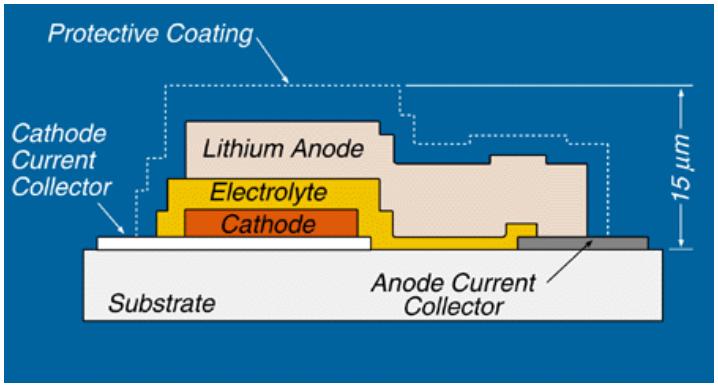
Dry polymer electrolyte – Low ionic conductivity (10^{-5}-10^{-4} S/cm @ **RT**)

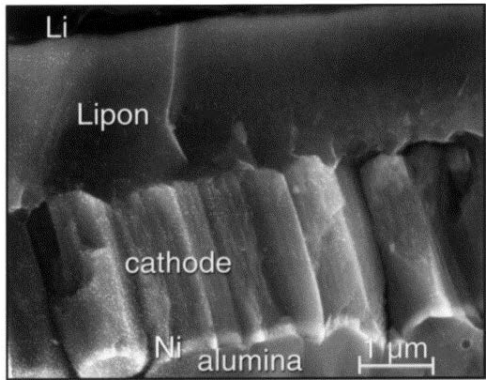
Gel polymer electrolyte – still flammable, poor mechanical property, reasonable conductivity (~10^{-3} S/cm)

Inorganic or ceramic solid electrolyte

Conventional **thin-film micro-battery**

JPS **2000**, *135*, 33

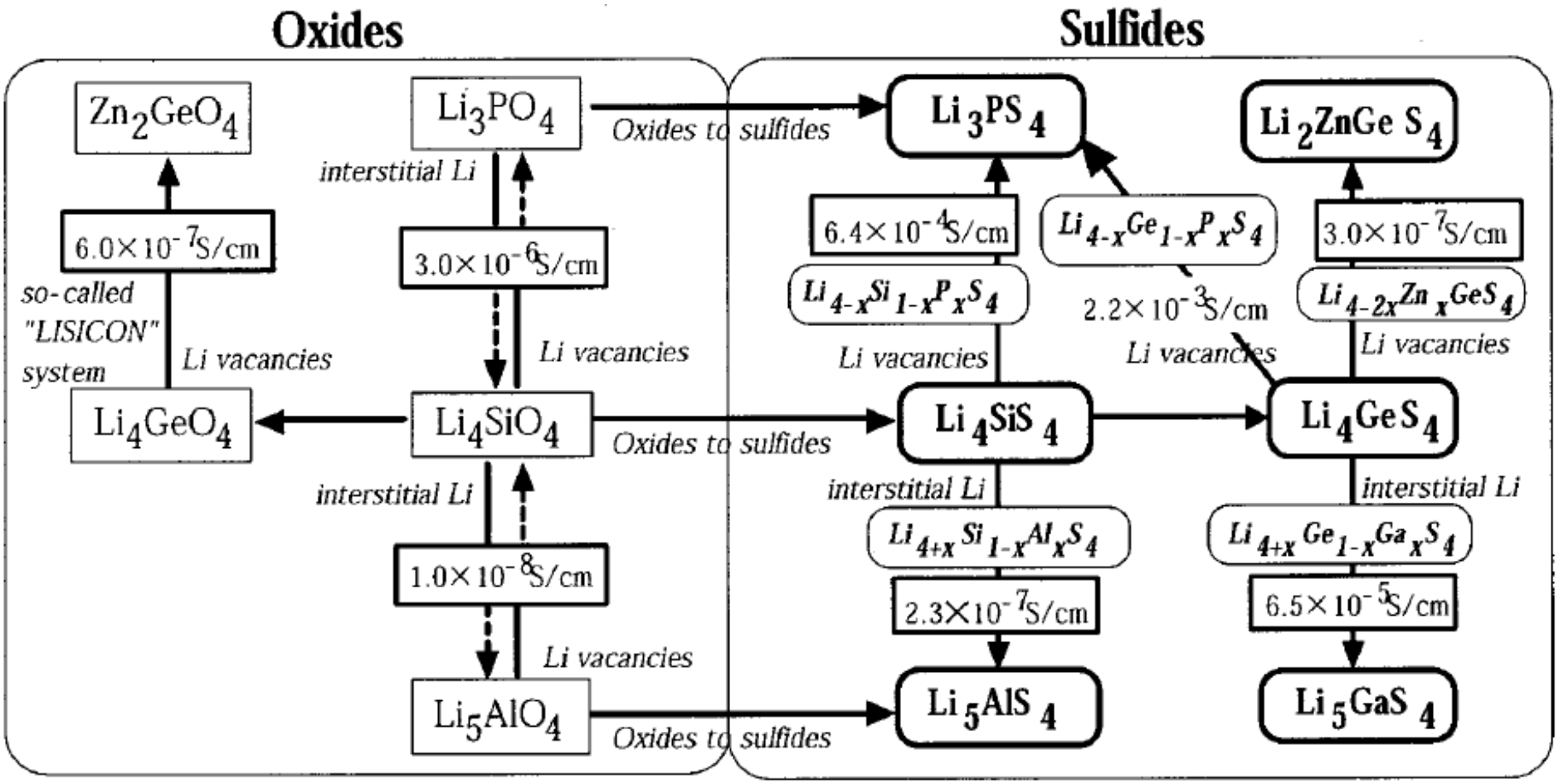




LIPON (lithium phosphorous oxynitride) (~10^{-6} S cm^{-1})

Low cell capacity limits applications (only for special devices)

LISICON



JES **2001**, *148*, A742.

Oxide vs. sulfide: larger, more polarizable framework

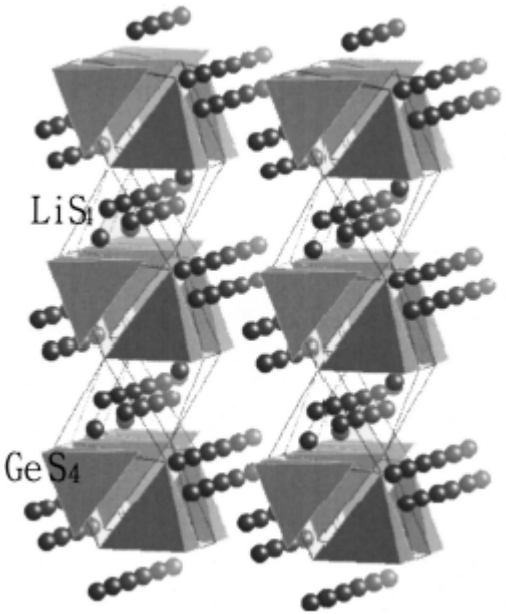
Thio-LISICON – R. Kanno

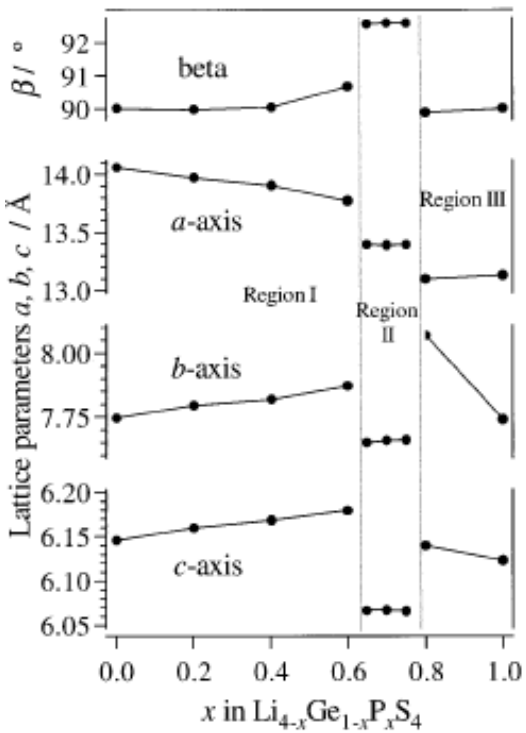
- Large ionic radius & more polarizability
- Amorphous **Li_2S-SiS_2-LiI and Li_2S-SiS_2-Li_3PO_4** (10^{-4}-10^{-3} S/cm)
- Crystalline Rb_4**Cu_{16}**I_7Cl_{13},Rb**Ag_4**I_5 have higher ionic conductivity than any copper and silver conducting glasses. This is not true for crystalline lithium ion conductors.

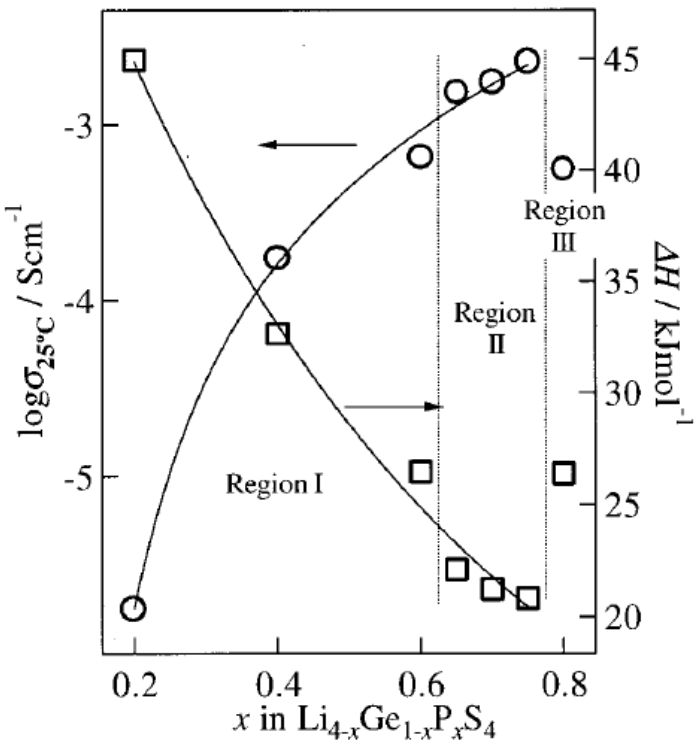
$$Li_4GeS_4 \xrightarrow[Ge^{4+} + Li^+ \rightarrow P^{5+}]{Li^+ \text{ vacancy}} \mathbf{Li_{4-x}Ge_{1-x}P_xS_4}$$

- Ryoji Kano group

Thio-LISICON



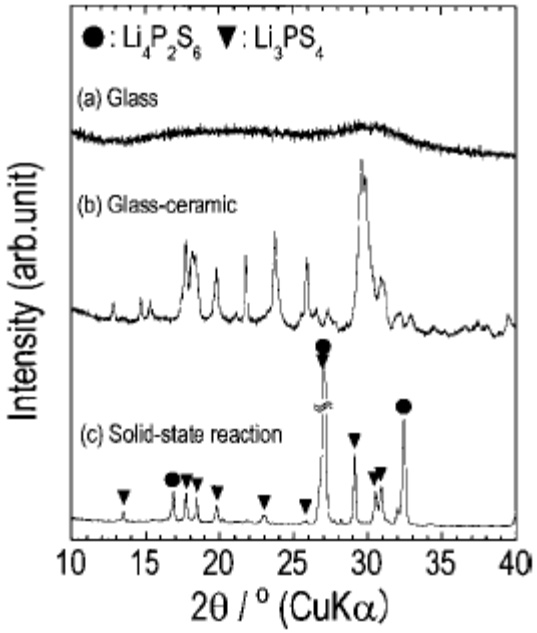


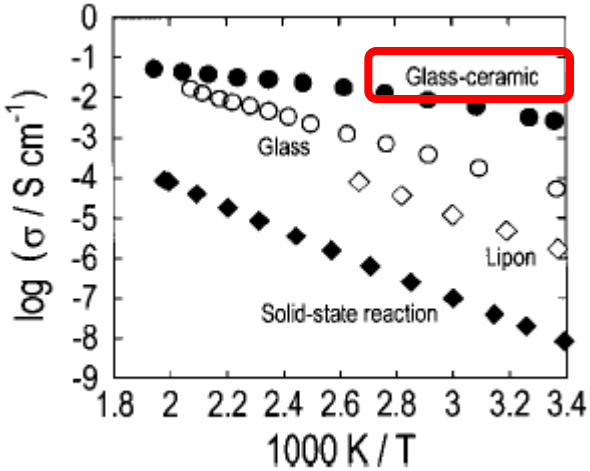


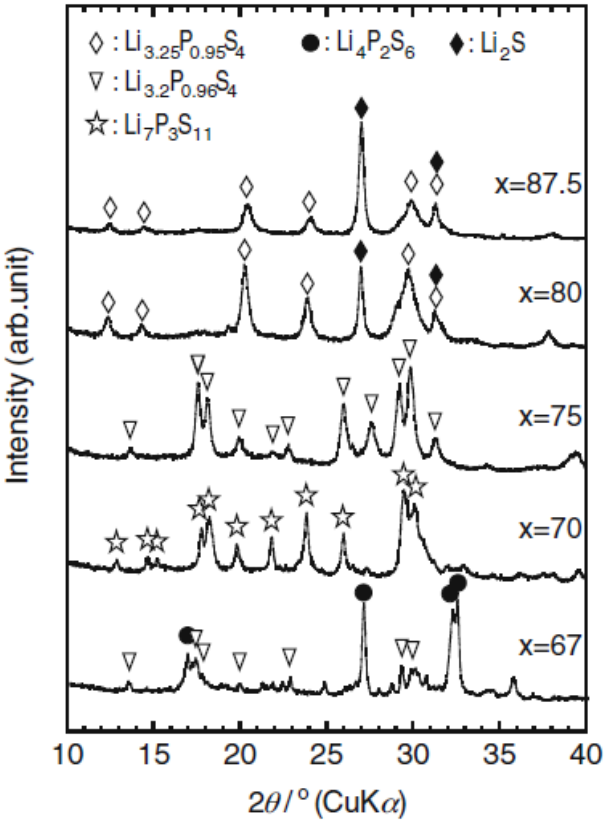
JES **2001**, *148*, A742.

- Partial substitution of $Ge^{4+}$with $P^{5+} \rightarrow Li^{+}$ vacancy

heat treatment temperature (°C)	Precipitated crystal	Conductivity at 25°C (Scm^{-1})	Activation energy for conduction ($kJmol^{-1}$)
None	Glass	5.4×10^{-5}	38
250	$Li_7P_3S_{11}$	2.2×10^{-3}	18
360	$Li_7P_3S_{11}$	3.2×10^{-3}	12
550	$Li_4P_2S_6$, $Li_{3.2}P_{0.96}S_4$	1.1×10^{-6}	50
Solid-state reaction	$Li_4P_2S_6$, Li_3PS_4	1.0×10^{-8}	55





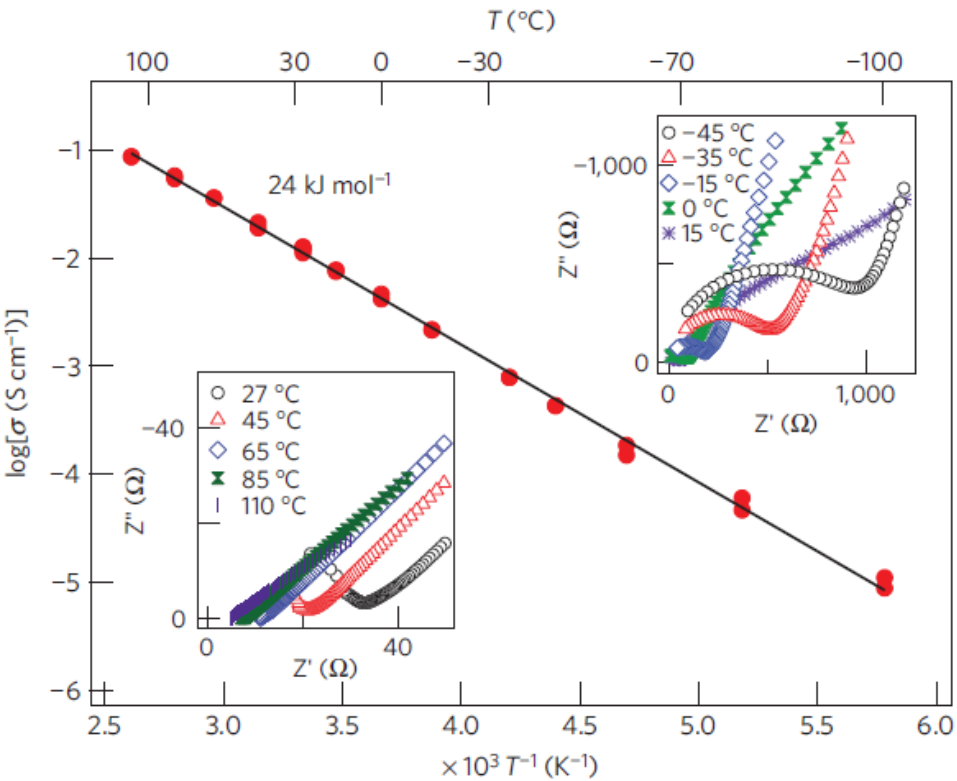


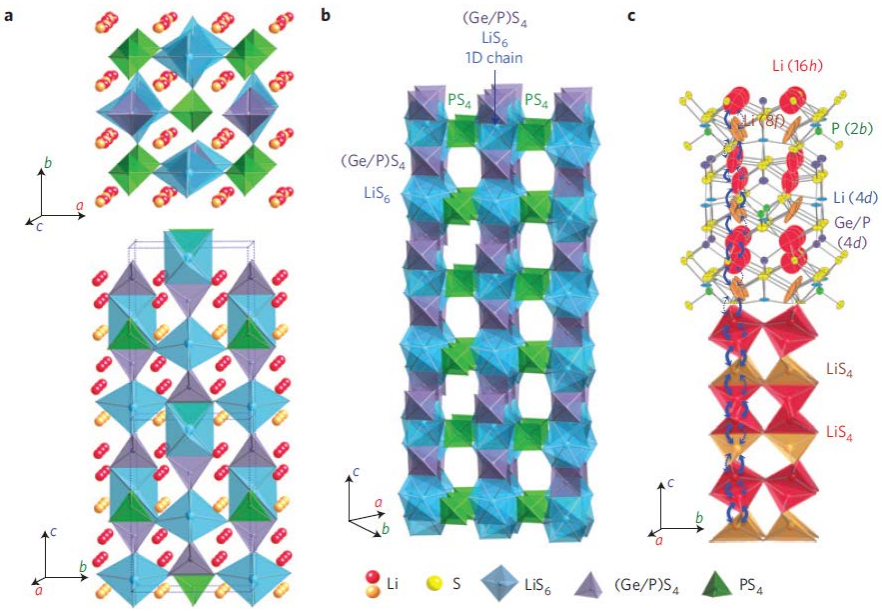
- **Glass-ceramic** shows higher ionic conductivity

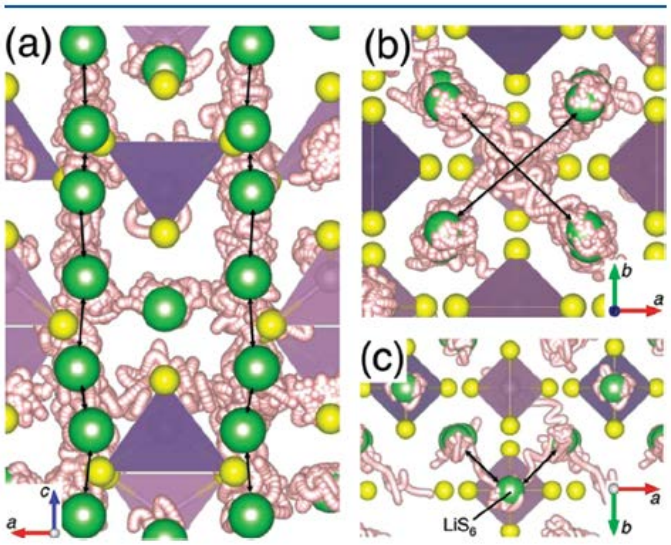
J. Solid State Electrochem. **2010**, *14*, 1761.
Adv. Mater. **2005**, *17*, 918

$Li_{10}GeP_2S_{12}$ – R. Kanno

- **12 mS/cm** @ 27°C







Agree with the computation results by G. Ceder group (9 mS/cm). Proposed 3D channel rather than 1D.

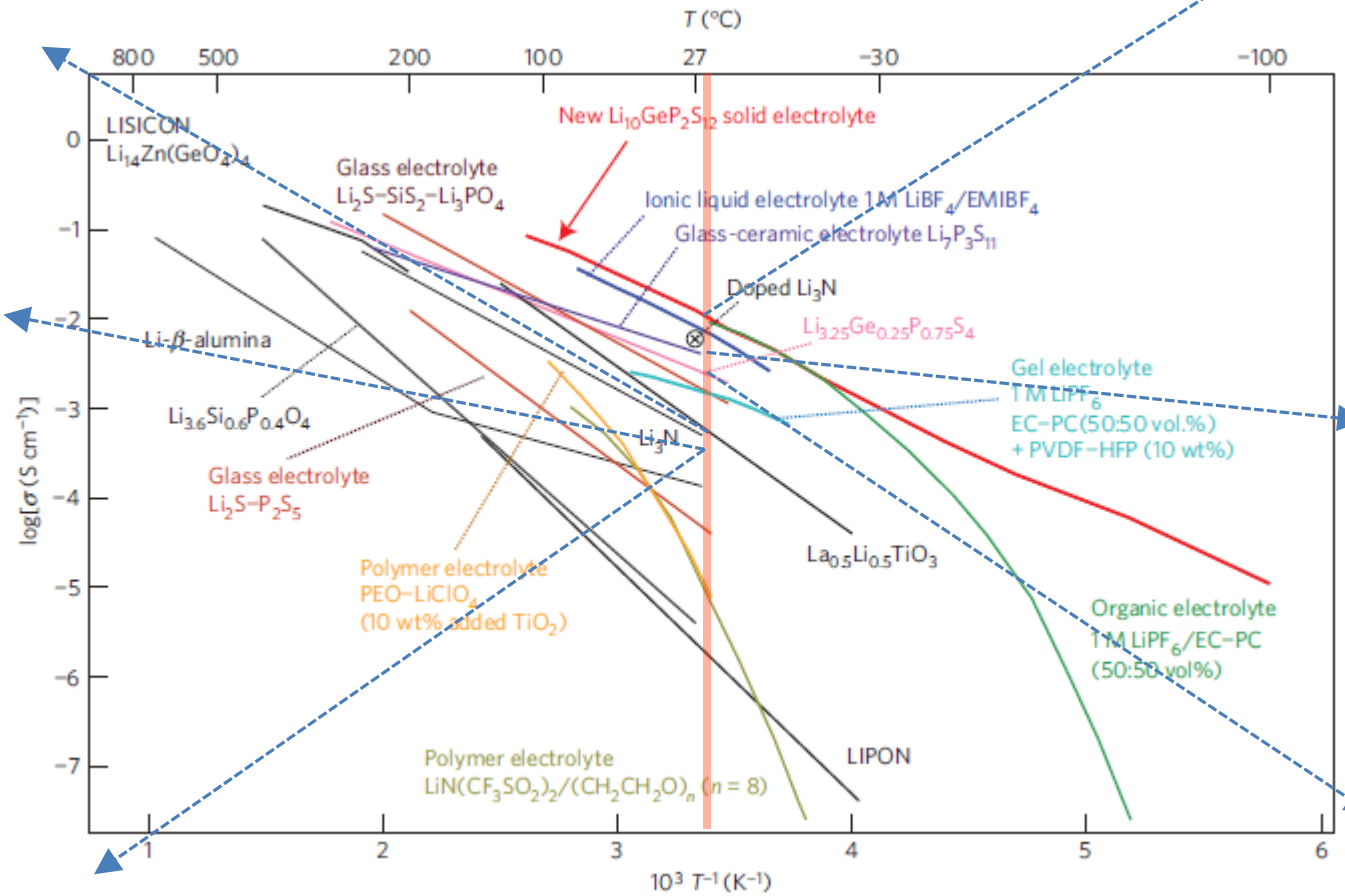
Nat. Mater. **2011**, *10*, 682.
Chem. Mater. doi: 10.1021/cm203303y

Inorganic Solid Electrolytes

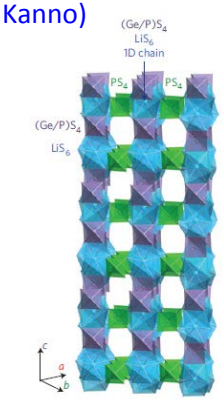
LLT
($La_{0.5}Li_{0.5}TiO_3$)
perovskite

LLZ
($Li_7La_3Zr_2O_{12}$)
garnet

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



$Li_{10}GeP_2S_{12}$
(R. Kanno)



$70Li_2S$-$30P_2S_5$
($Li_7P_3S_{11}$)
(M. Tatsumisago & A. Hayashi)

Thio-LISICON
($Li_{3.25}Ge_{0.25}P_{0.75}S_4$)
(R. Kanno)

Nat. Mater. **2011**, *10*, 682.

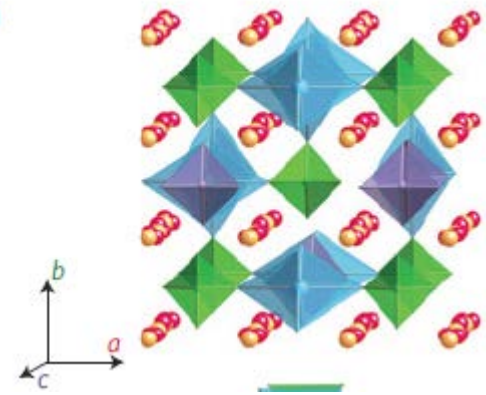
nature materials

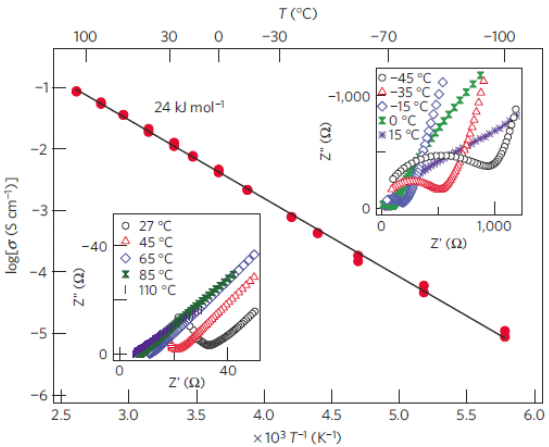
LETTERS

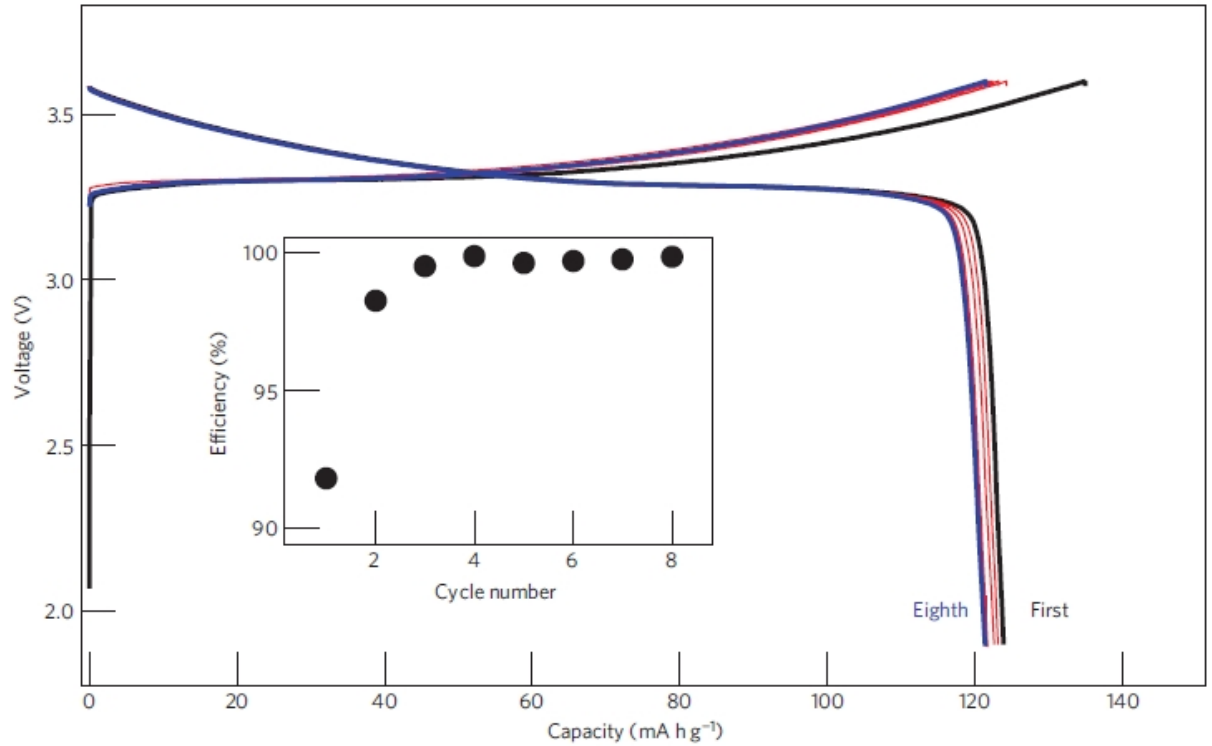
PUBLISHED ONLINE: 31 JULY 2011 | DOI: 10.1038/NMAT3066

A lithium superionic conductor

Noriaki Kamaya[1], Kenji Homma[1], Yuichiro Yamakawa[1], Masaaki Hirayama[1], Ryoji Kanno[1]*, Masao Yonemura[2], Takashi Kamiyama[2], Yuki Kato[3], Shigenori Hama[3], Koji Kawamoto[3] and Akio Mitsui[4]



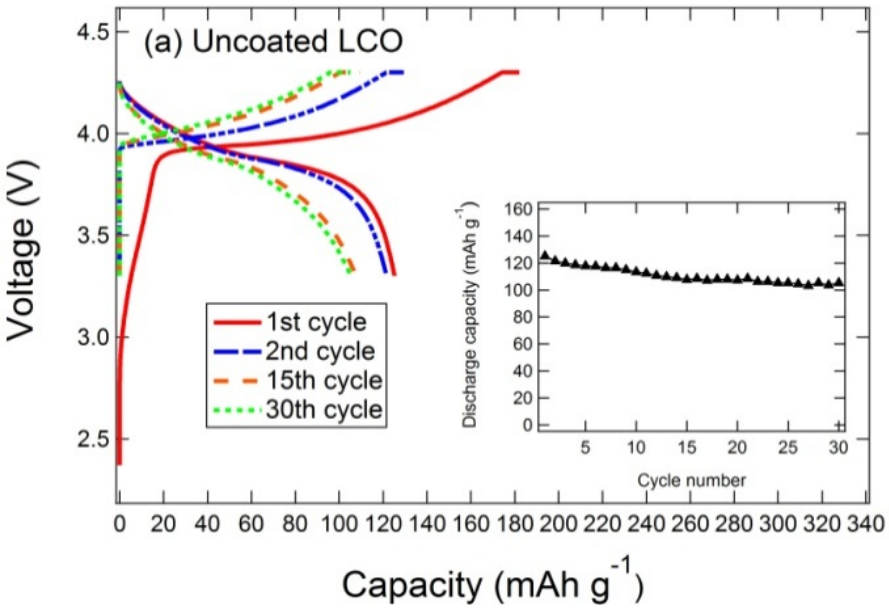


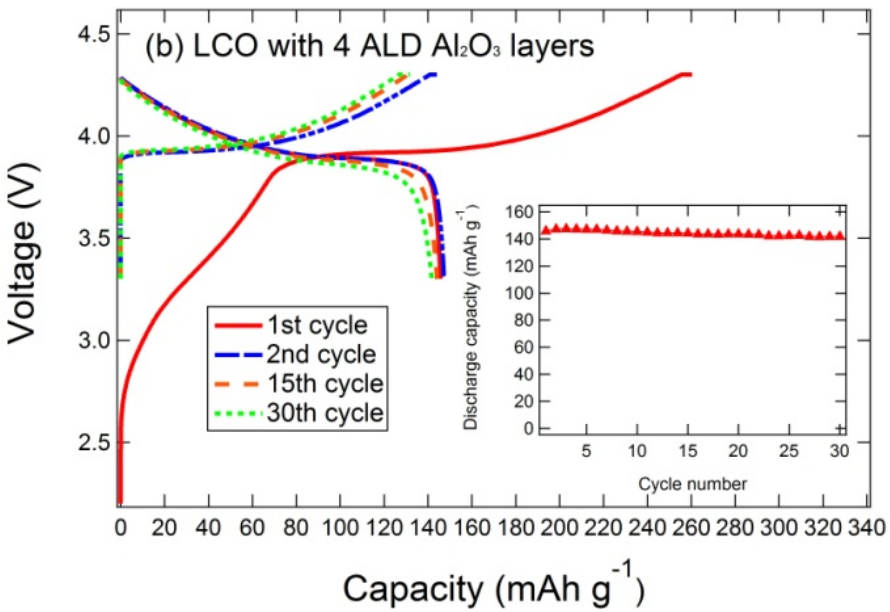


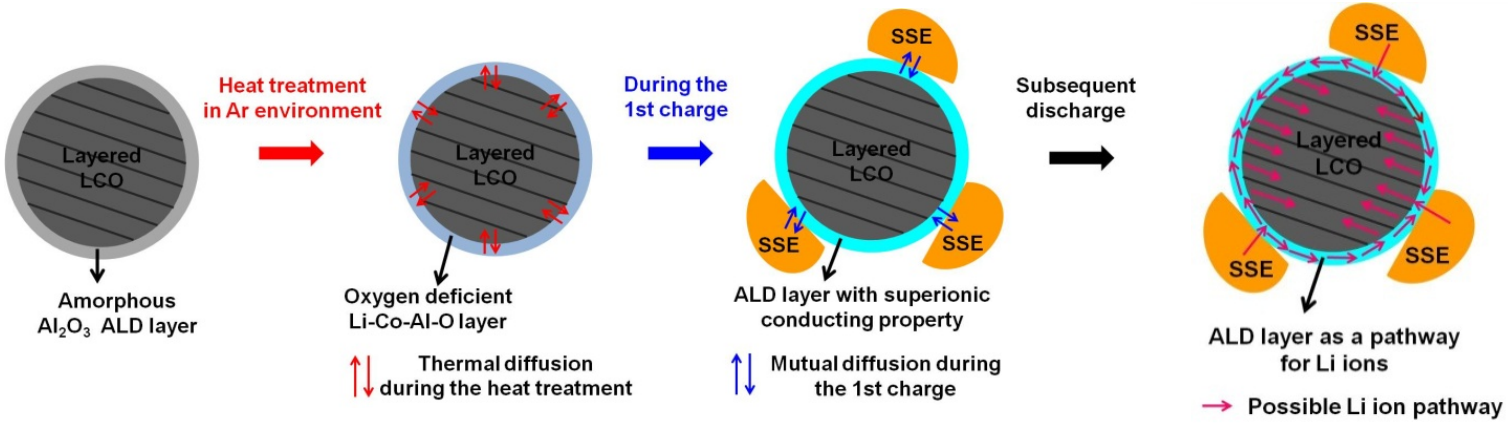
Schematic description of typical solid state lithium battery

- High interfacial resistance
- Poor interfacial contact

ALD for Solid State Li Batteries

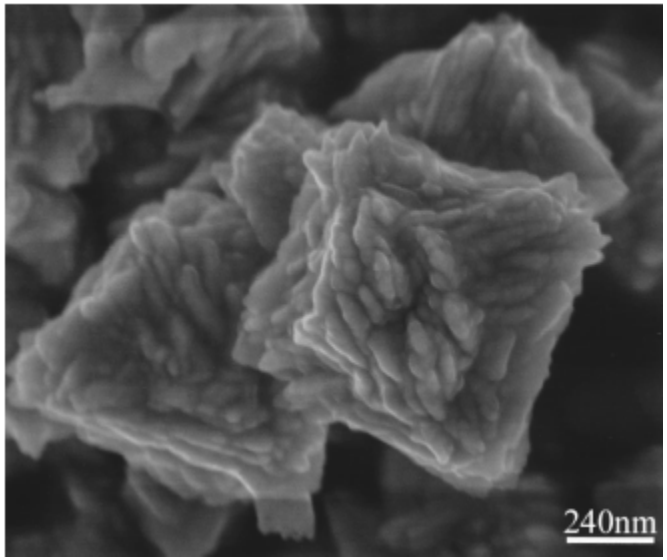


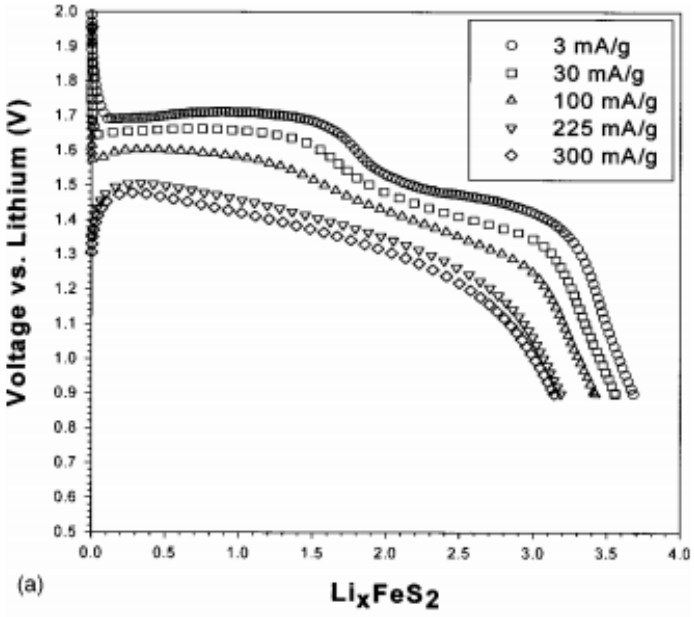




Energizer Primary Lithium Cells

www.energizer.com, 6 February 2012





Yang Shao-Horn et al., *Journal of the Electrochemical Society,* 2002

Overall Reaction

$FeS_2 + 4Li^+ + 4e^- \leftrightarrow 2Li_2S + Fe^0$

894 mAh g^{-1}

vs.

$Li_{1/2}CoO_2 + ½Li^+ + ½e^- \leftrightarrow LiCoO_2$

140 mAh g^{-1}

A four electron reaction, but it's only a one time use battery!

Why is the FeS_2 four electron redox reaction so troublesome?

- Dissolution of soluble polysulfides, S_n^{2-}

- Agglomeration of elemental iron nanoparticles, Fe^0

Initial Discharge

(1) $FeS_2 + 2Li^+ + 2e^- \leftrightarrow Li_2FeS_2$

(2) $Li_2FeS_2 + 2Li^+ + 2e^- \leftrightarrow 2Li_2S + Fe^0$

Subsequent Charge and Discharges

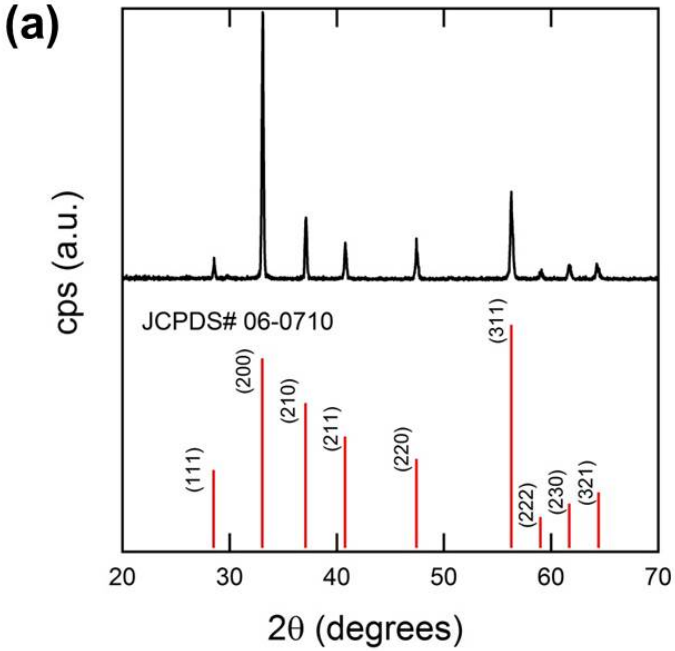
(3) $Fe^0 + Li_2S \leftrightarrow Li_2FeS_2 + 2Li^+ + 2e^-$

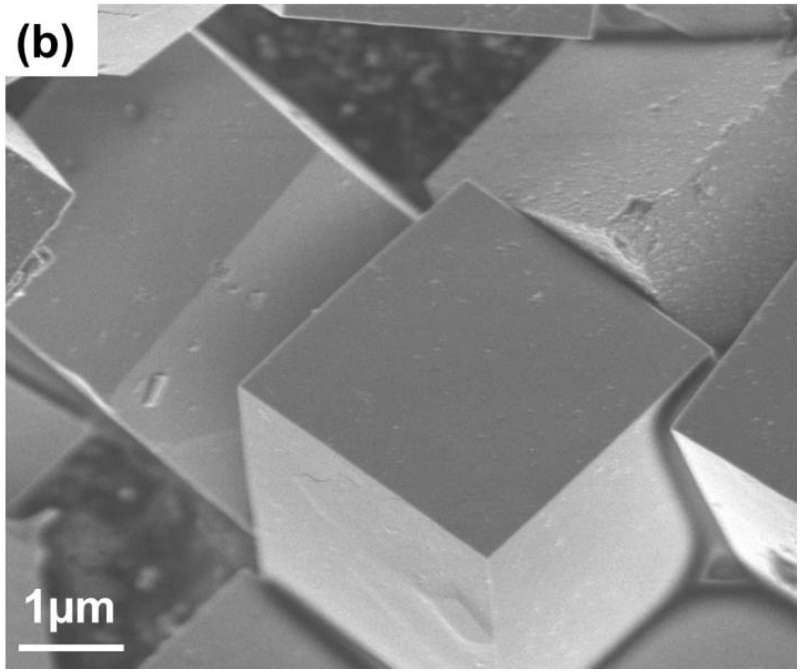
(4) $Li_2FeS_2 \leftrightarrow Li_{2-x}FeS_2 + xLi^+ + xe^-$ $(0.5 < x < 0.8)$

(5) $Li_{2-x}FeS\text{-}_2 \leftrightarrow FeS_y + (2-y)S + (2-x)Li^+ + (2-x)e^-$

A model system:
Solvothermally synthesized FeS_2

- We study this ideal system in order to gain a better understanding of the FeS_2 redox chemistry. (*Solid state enabled four electron storage.* Submitted to AEM; under review)

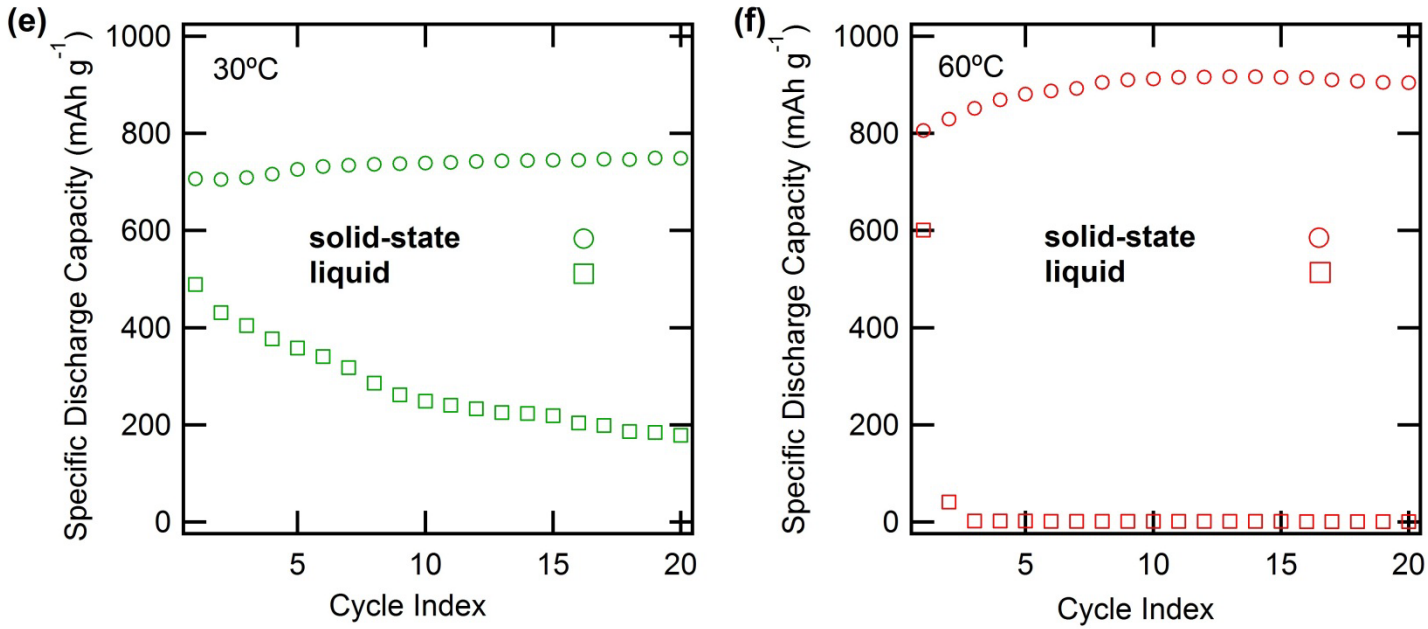




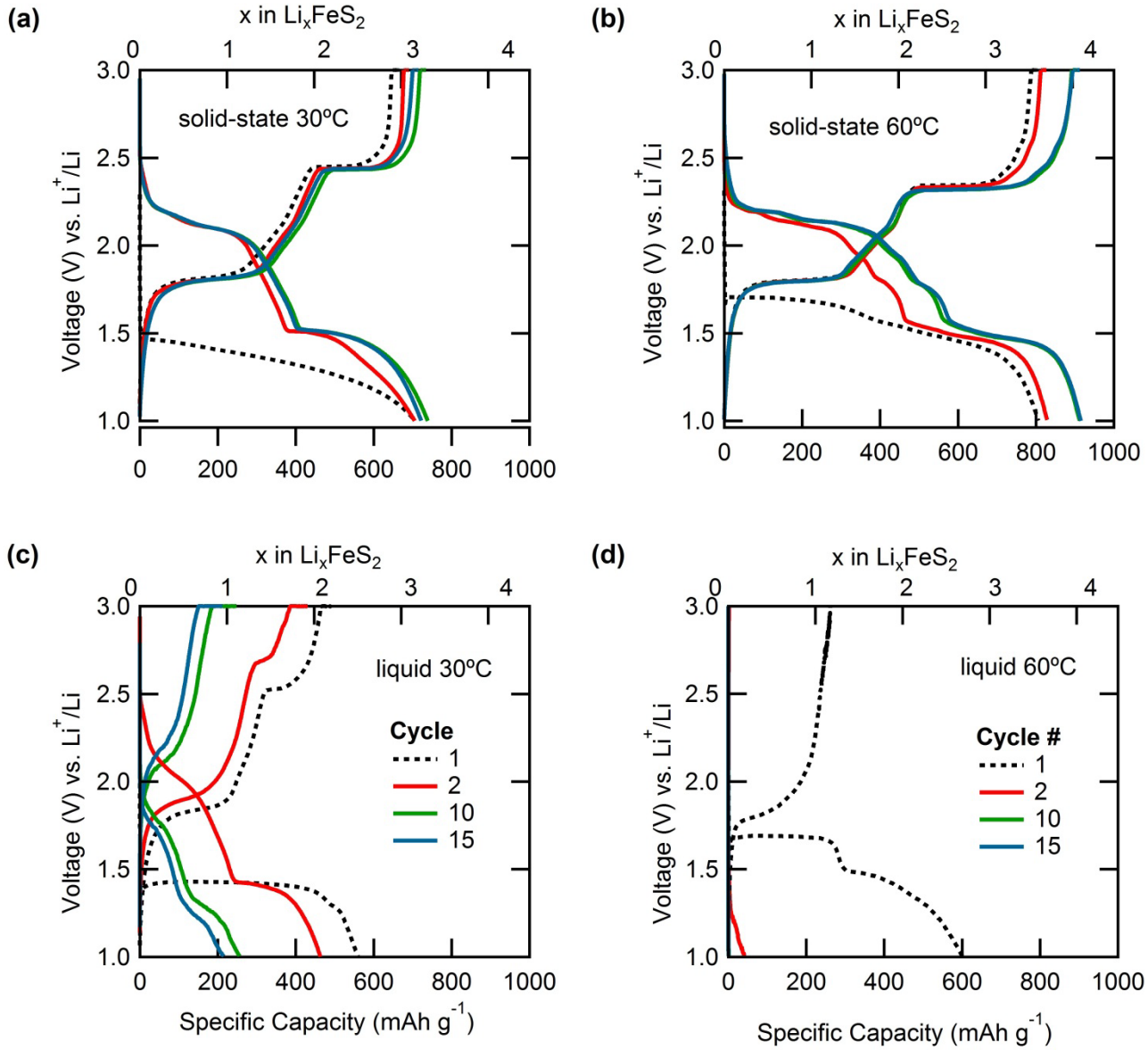
A rechargeable FeS_2/Li battery

- First demonstration of a reversible FeS_2/Li battery at the moderate temperature of **30-60 C**.

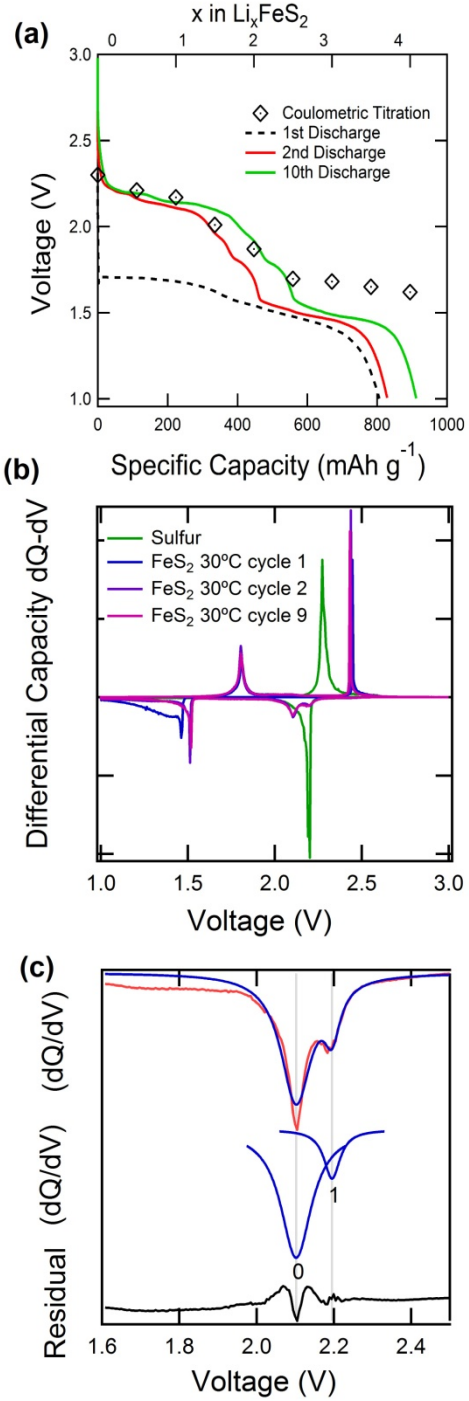
- Previously, the only reversible FeS_2/Li batteries were thermal batteries with a molten salt electrolyte and an operating temperature in excess of **400 C** (Henriksen et al. *Handbook of Batteries,* 2002).

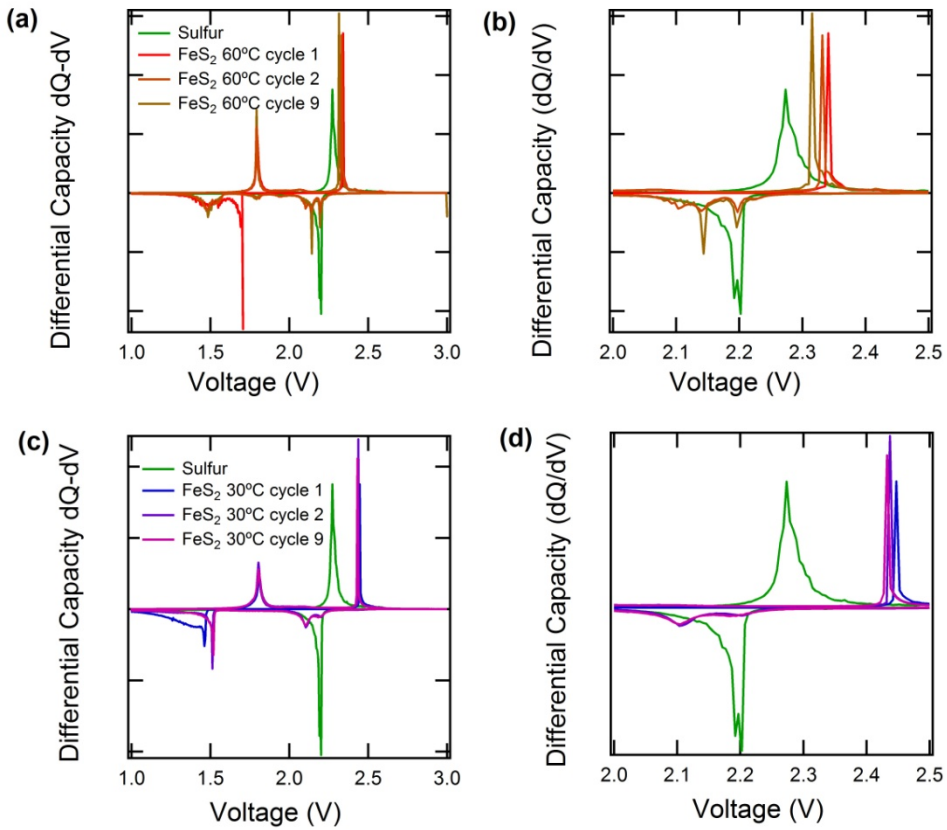


A rechargeable FeS_2/Li battery

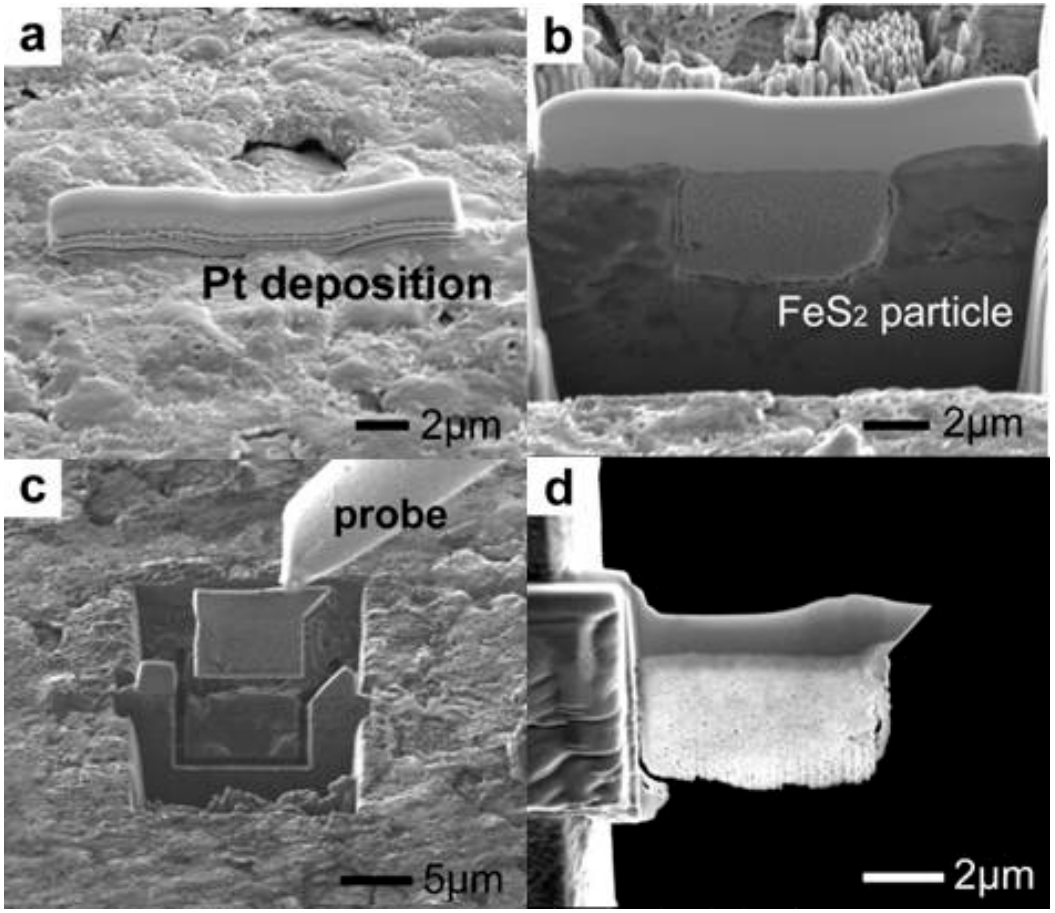


Coulometric Titration and dQ/dv of FeS_2





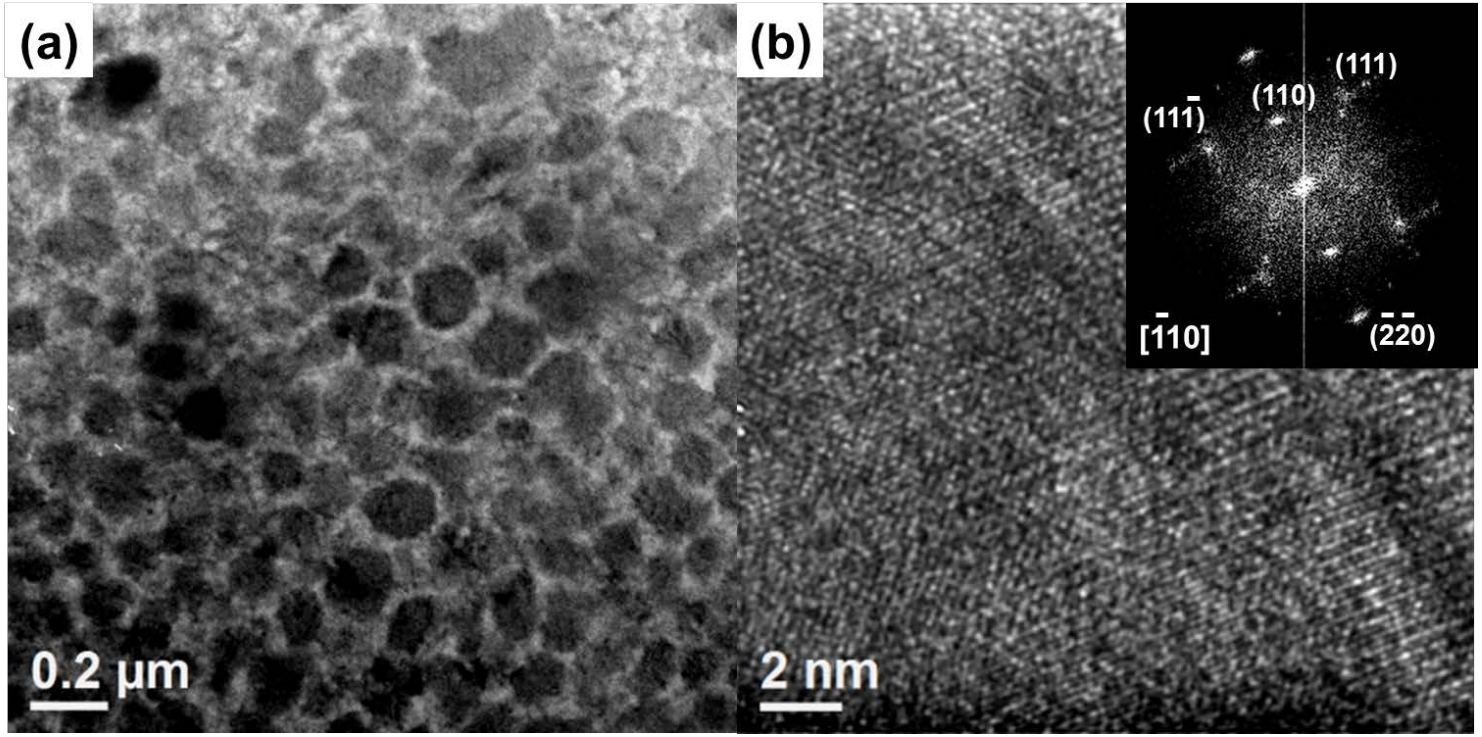
Focus Ion Beam (FIB) sample preparation of charged FeS_2 electrode for TEM analysis



Transmission Emission Microscopy (TEM) Analysis of charged FeS_2 electrode

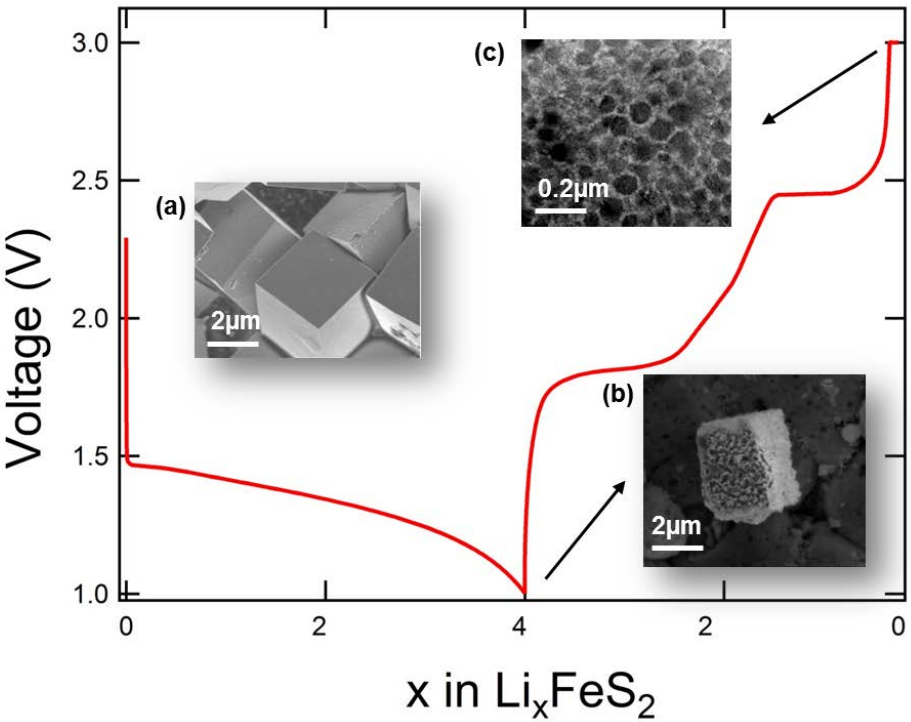
Nanoparticles of orthorhombic FeS_2 explain better reaction kinetics of subsequent cycles. We can now revise eqn. 5 to the following:

(6) $Li_{2-x}FeS\text{-}_2 \leftrightarrow 0.9\text{ortho-}FeS_2 + 0.1FeS_{8/7} + 0.085S + (2\text{-}x)Li^+ + (2\text{-}x)e^-$



How did we revise the FeS_2 redox chemistry at ambient to moderate temperature?

- Coulometric titration
- dQ/dV analysis
- TEM and fast Fourier analysis
- DFT simulation



Initial Discharge

(1) $FeS_2 + 2Li^+ + 2e^- \leftrightarrow Li_2FeS_2$

(2) $Li_2FeS_2 + 2Li^+ + 2e^- \leftrightarrow 2Li_2S + Fe^0$

Subsequent Charge and Discharges

(3) $Fe^0 + Li_2S \leftrightarrow Li_2FeS_2 + 2Li^+ + 2e^-$

(4) $Li_2FeS_2 \leftrightarrow Li_{2-x}FeS_2 + xLi^+ + xe^-$ $(0.5 < x < 0.8)$

(5) ~~$Li_{2-x}FeS\text{-}_2 \leftrightarrow FeS_y + (2-y)S + (2-x)Li^+ + (2-x)e^-$~~

(6) $Li_{2-x}FeS\text{-}_2 \leftrightarrow 0.9\text{ortho-}FeS_2 + 0.1FeS_{8/7} + 0.085S + (2-x)Li^+ + (2-x)e^-$

Advanced Energy Materials (in press)

FeS_2/Li Battery

1. Threefold improvement over the specific energy density of the state of the art $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$/graphite cells High Energy Density (1340 Wh/kg vs. 500 Wh/kg)

2. Excellent cycling stability enabled by solid state electrolyte which **successfully confines electro-active species**

3. FeS_2: inexpensive, environmentally benign and energy dense

Solid Power, Inc.

Doug Campbell, COO
dougcampb@gmail.com
(720) 300-8167

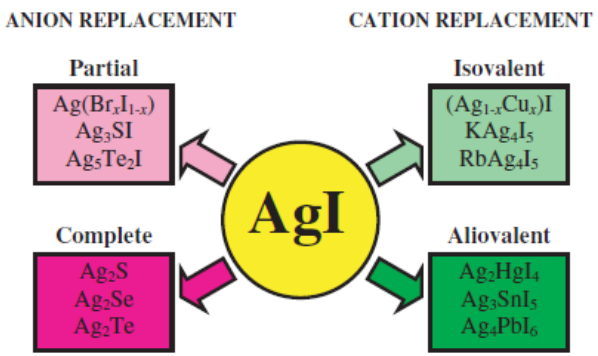
solidpower INC

- Spin-Out of Univ. of Colorado at Boulder
  - Research under Profs. Conrad Stoldt and SeHee Lee
  - 3 year, $1.7M funding from DARPA DSO to establish feasibility
- Need: Ultra-high energy, rechargeable and safe batteries
- Problem: Lithium metal anode can potentially meet this need; however, limited cathode capacity and cell stability have thus far stalled further development
- Solution: Solid Power's solid-state battery configuration has shown feasibility in addressing these issues
- Benefits:
  - High specific energy (600 Wh/kg vs. ~200 Wh/kg SOTA Li-ion)
  - Eliminates most safety concerns associated w/ Li-ion technology
- IP: 3 patents covering cathode and anode chemistry
- IP Rights: Exclusive Option from CU-Boulder Tech-Transfer

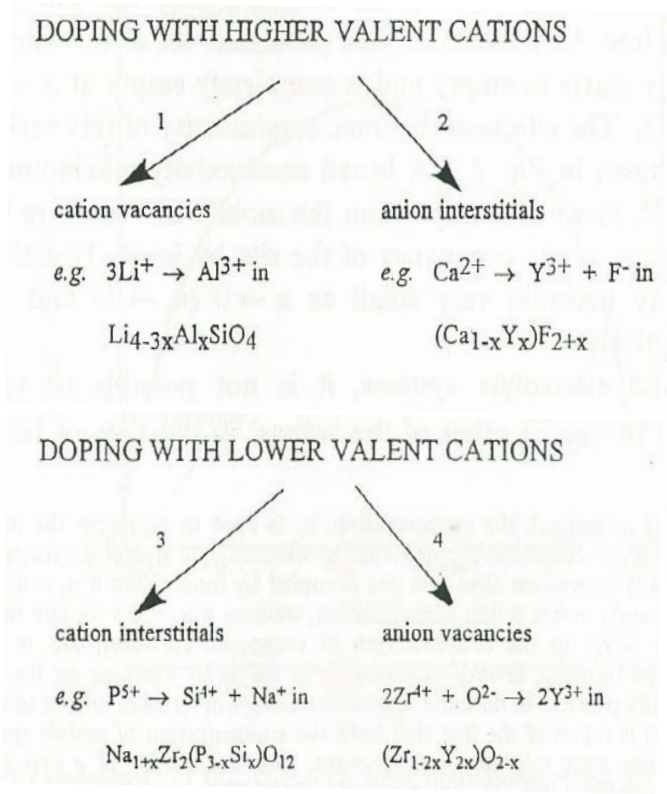
Thank you for your attention!

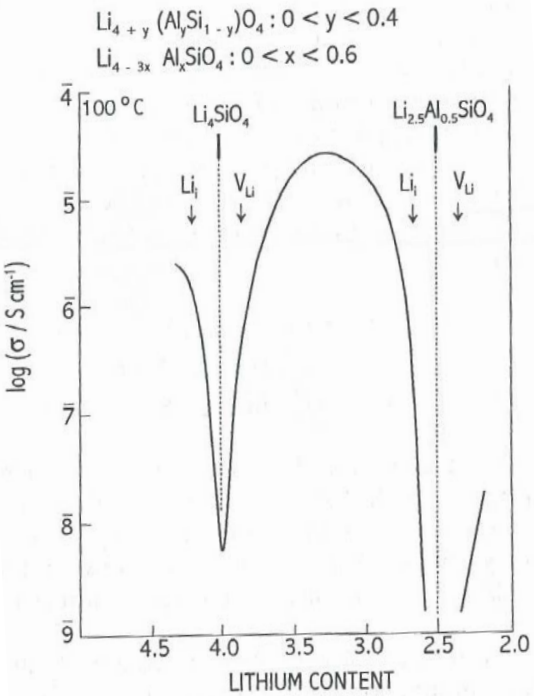
Strategies For Increasing Conductivity

- **Open framework**
  - Sodium beta alumina, NASICON, Li_3N, etc
- **Doping**



Rep. Prog. Phys. **2004**, *67*, 1233.

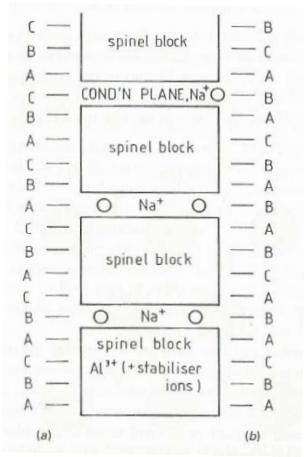


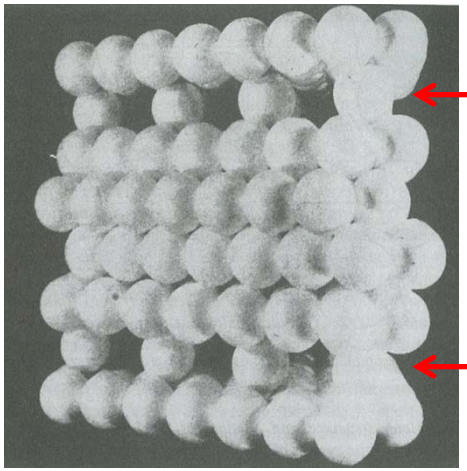


- **Composites**
  - LiI/Al_2O_3: high ionic conductivity along the grainboundary of LiI and Al_2O_3

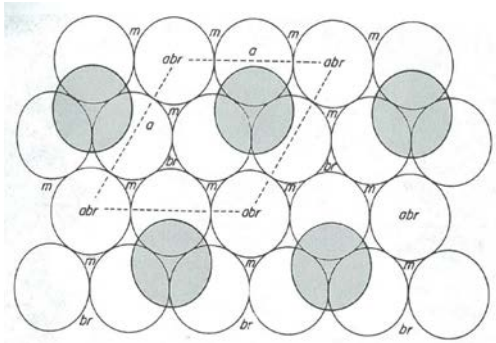
Sodium beta alumina

- **β-alumina**: $M_2O{\cdot}nX_2O_3$ (n = 5-11, M = monovalent cation – **alkali$^+$**, Cu^+, Ag^+, Ga^+, In^+, Tl^+, NH^{4+}, H_3O^+, X = trivalent cation – **Al^{3+}**, Ga^{3+}, Fe^{3+})
- Sodium beta alumina: **$Na_2O{\cdot}Al_2O_3$**





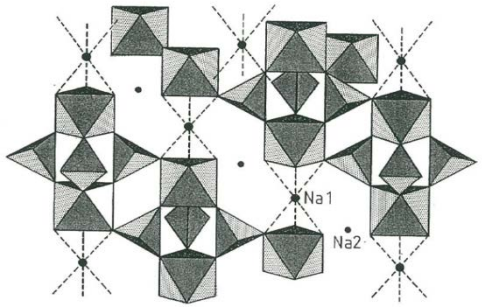
partially occupied layer → fast Na^+ conduction



NASICON: Na superionic conductor

$Na_{1+x}Zr_2(P_{1-x}Si_xO_4)_3$ (0<x <3)

Partially occupied된 Na^+ 이온
3D하게 빠른 이온전달 가능

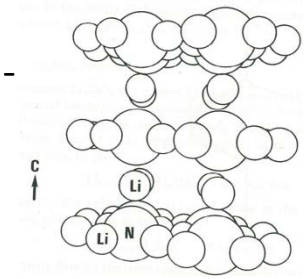


Li_3N

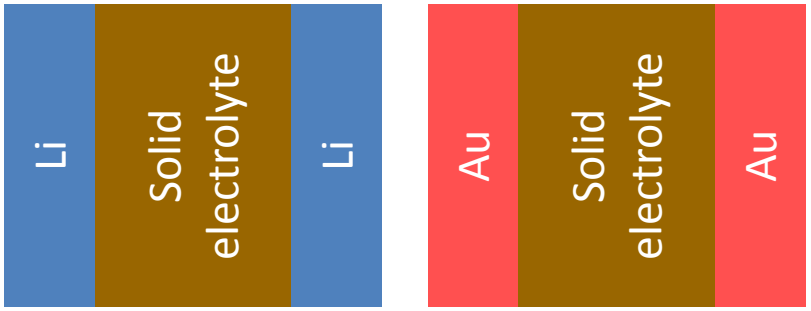
Layered structure

10^{-3} S/cm (in-plane, H-doped)

Low decomposition potential: 0.445 V

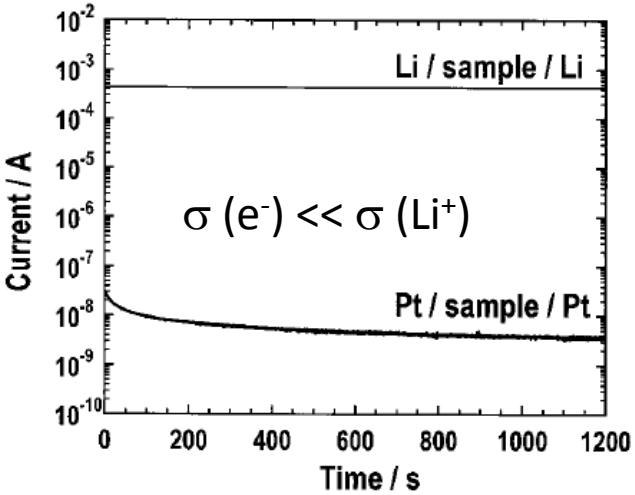


Conductivity Measurement



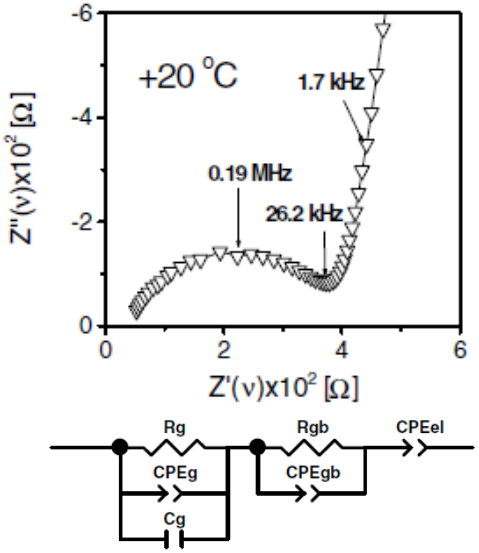
DC	$e^- + Li^+$	e^-
AC	$e^- + Li^+$	$e^- + Li^+$

DC

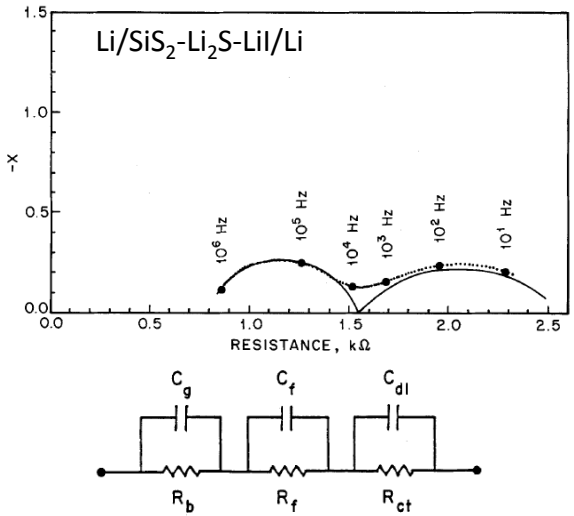


JES. **2001**, *84*, 477.

AC (impedance)

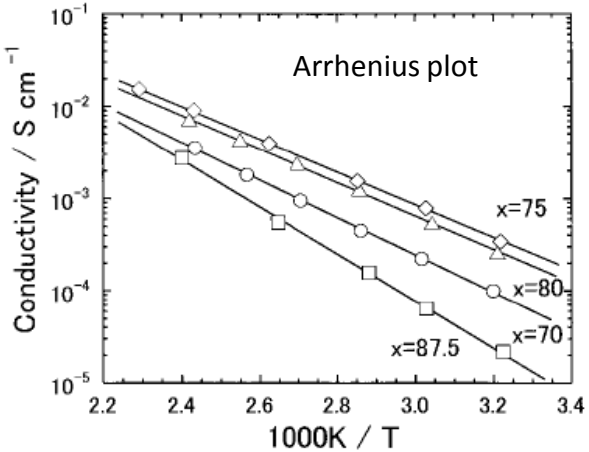


Electrochem. Commun. **2012**, *14*, 25.



JES. **1988**, *135*, 859.

→ 저항 분리 (deconvolution)



JES. **2001**, *84*, 477.

→ slope: 활성화 에너지 (activation energy)