Energy Storage: Perspectives

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Management of Energy Demand Through Energy Storage

Solar, wind, wave

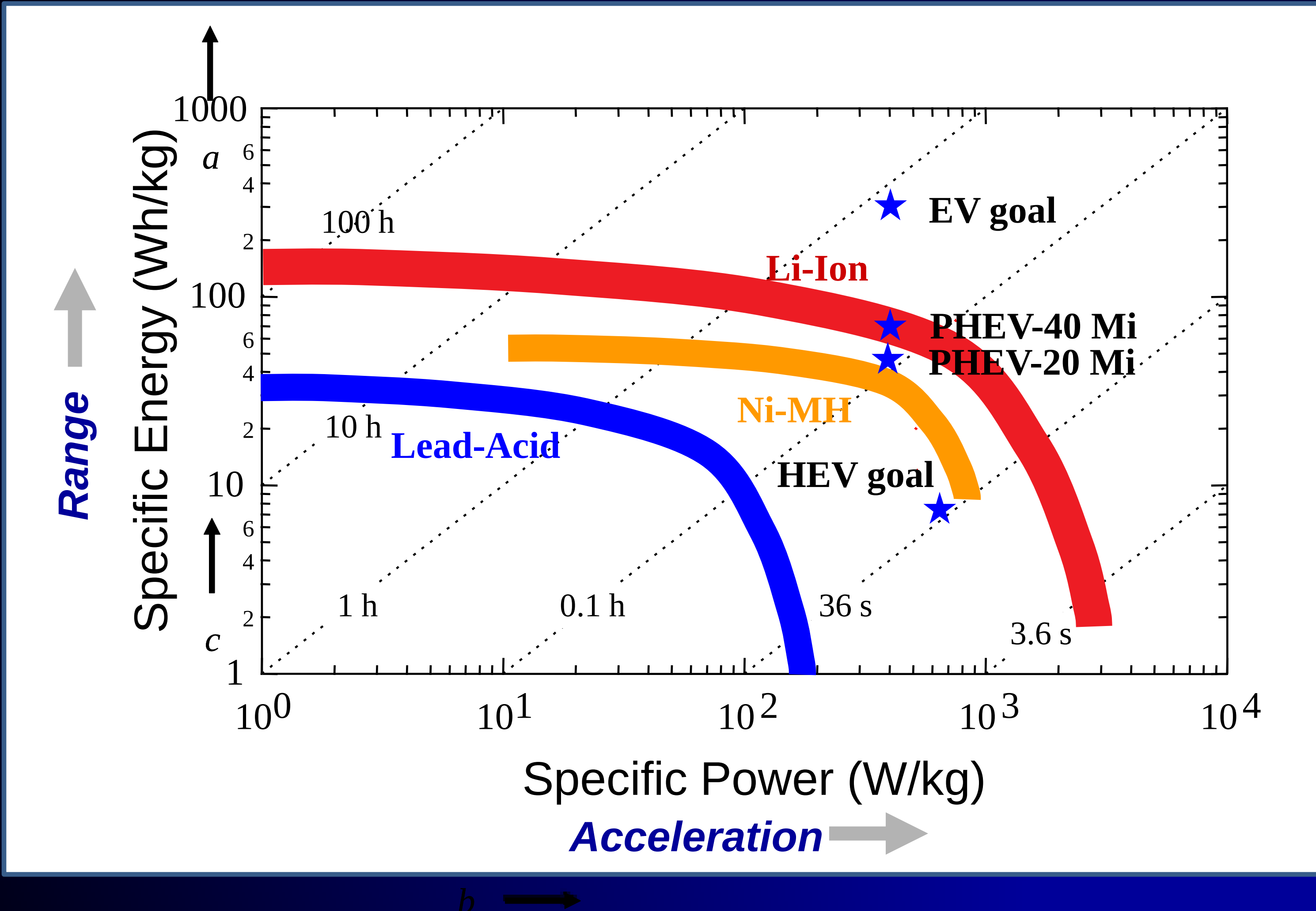
Intermittency of supply

Electrification of transport

Reduction in CO_2 emissions

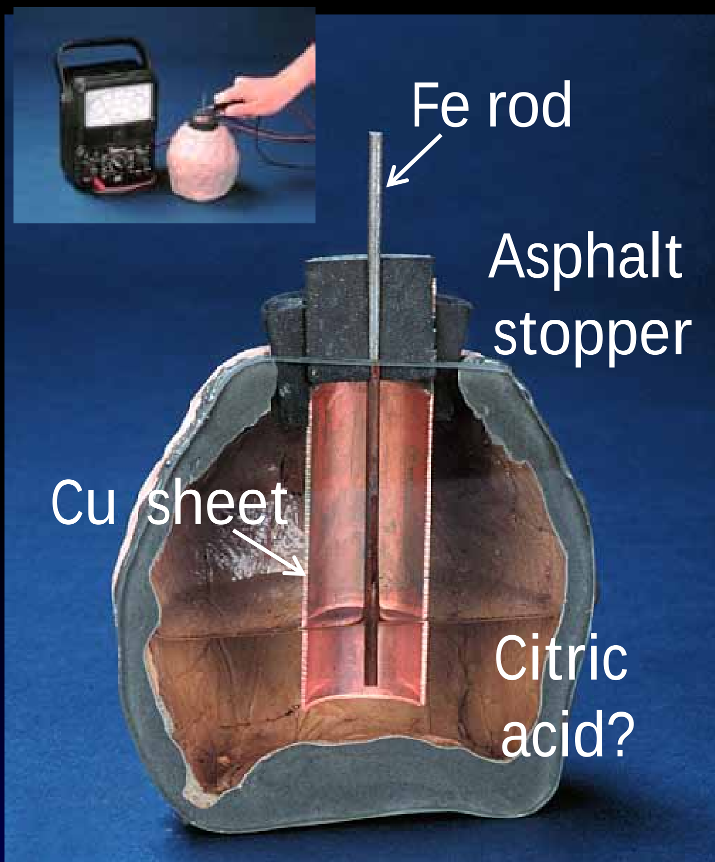
Conservation of petrol

Comparison of Battery Systems for Automotive Transport



Source: Amended from Product Data Sheets

Ancient Electrochemistry: 250 BCE – CE 250



The ancient battery in the Baghdad Museum

There are also copper vases plated with silver in the Baghdad Museum, excavated from Sumerian sites in southern Iraq, dating back to at least 2500 BCE.

When the vases were lightly tapped, a blue patina or film separated from the surface, which is characteristic of silver electroplated onto copper base.

It would appear **that the Parthians inherited their batteries from one of the earliest known civilizations**

è General concept of energy from chemicals

è $DG = - n F E$

Electrochemical Conversions

1. Chemicals to other chemicals through electrochemistry (the ancient electrochemistry)

Electroplating

2. Chemical energy to electrical energy and work

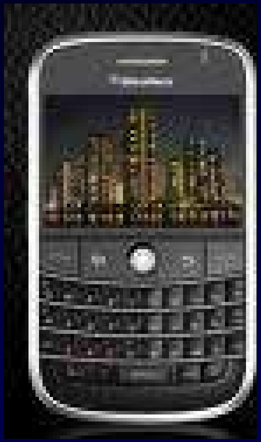
Normal battery discharging

3. Electrical energy to chemical energy

Battery recharging;
The electrochemical storage problem that challenges PHEV's & renewable energy technology

Small Scale to Large Scale

Portable High-Energy Demand Devices



New demands for batteries

larger scale

$LiCoO_2$ — 1987 — Q = 130 mAh/g

$LiCoO_2$ implemented — 1991

$LiFePO_4$ — 1997

Li[Ni,Co, Mn]O_2, $LiFePO_4$ implemented — 2007 — Q = 180 mAh/g

$$Q = \frac{n \cdot F}{M_w \cdot 3.6} (mAh/g)$$

smaller scale

Medical applications

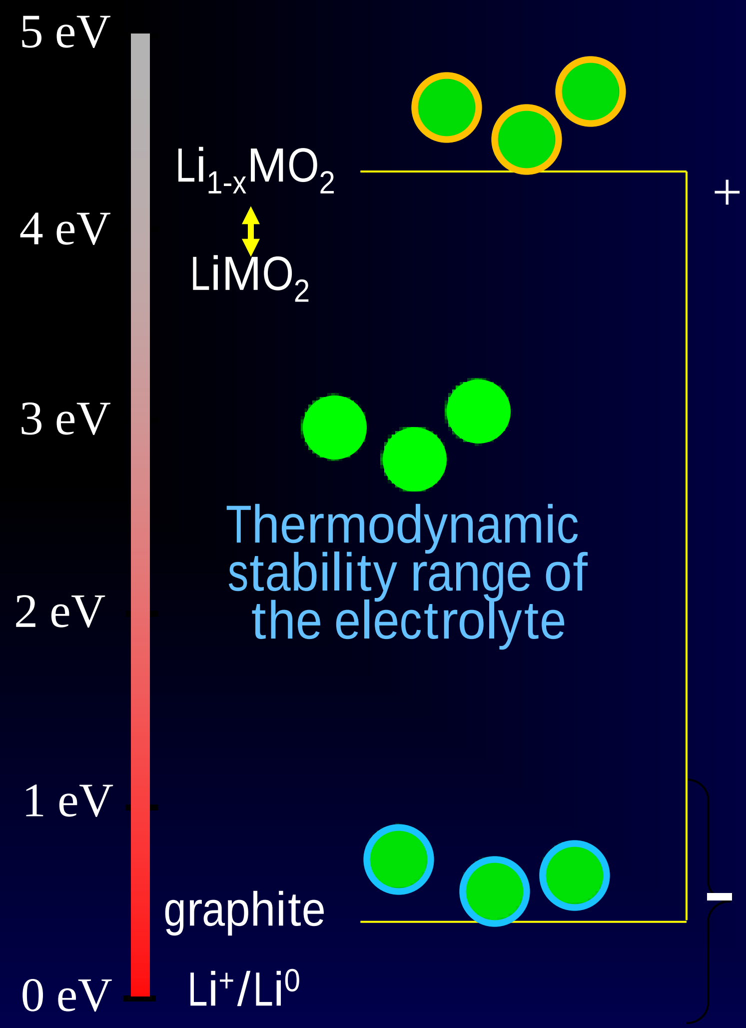
implantable battery

Stability Window Determines Choice of Electrode Materials

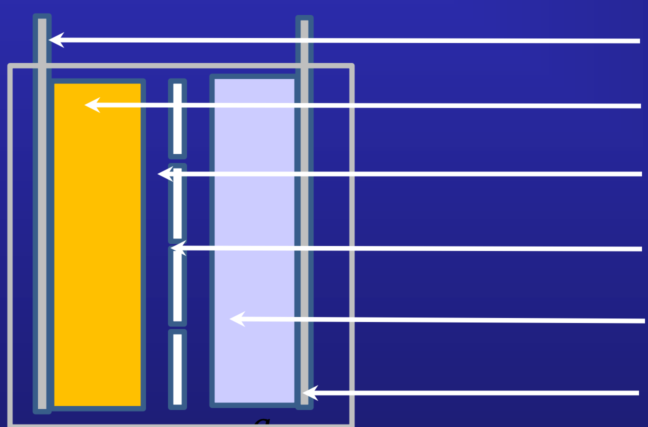
Electrolyte instability to oxidation

Surface area ↑
Surface reactivity ↑

Electrolyte instability to reduction



“Polyanion” Positive Electrode Materials



Li-ion Battery

Stable, Safe Low Cost Storage

GEN 2: Lithium transition metal phosphates. fluorophosphates, sulfates, silicates

Triphylite: $LiFePO_4$

Resource unlimited

Low cost, high safety

Common mineral

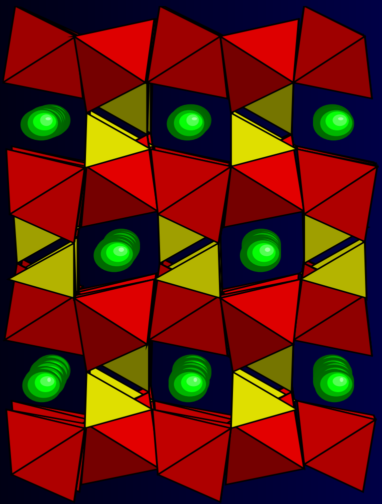
Electrochemistry

FeO_6

PO_4

LiO_6

FeO_6



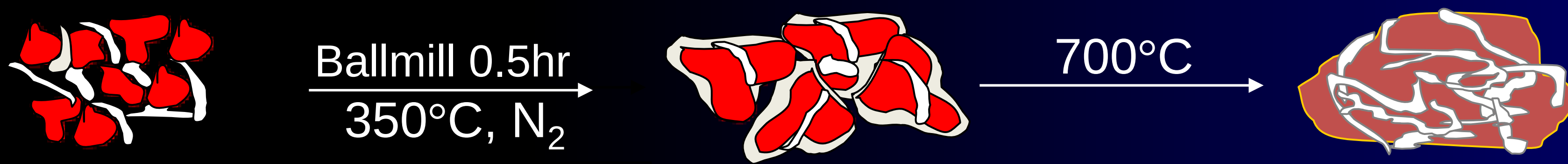
$LiFePO_4$ Fe^{2+}	3.5 V *vs Li+/Li* ⟷	$FePO_4$ Fe^{3+}

J.B. Goodenough et al, *J. Electrochem. Soc*. 144, 1609 (1997)

Ø energy storage systems currently available to global markets in the 100 MW-Hr range, designed for renewable energy project developers

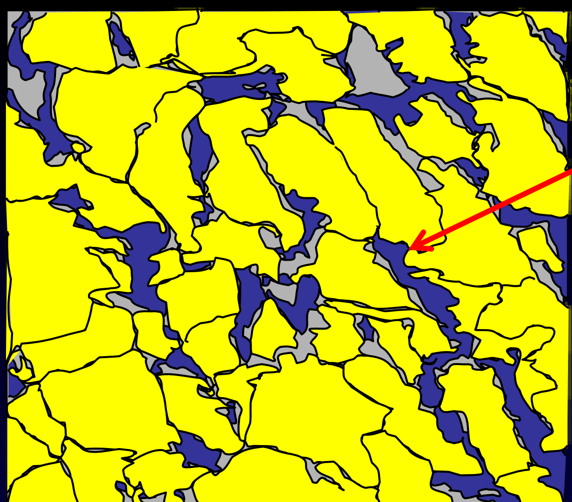
Nano-network Conductivity in $LiFePO_4$

$LiFePO_4$ crystallites are simultaneously growth limited, encapsulated in conductive matrix



Armand et al., JPS 2000; Nazar et al., ECS 2001

è Key: synthesize nano-$LiFePO_4$ at high T (defect free!) using (thin) coating to inhibit growth



TEM image (colored) of $LiFePO_4$ nanocrystallites

metallic FeP + carbon + $Fe_{75}P_{20}C_{15}$ - a metallic glass

s of FeP = 10^3 S/cm

Nazar et al., *Nature Materials* 2004;
JECS, 2006

Carbothermal reduction

Creation of an electronic conducting surface phase via controlled off-stoichiometry

$Li_{0.90}FePO_4$ @ 600°C è $LiFePO_4$ + $Fe_2P_2O_7$ @ 750°C è $LiFePO_4$ + FeP + Li_3PO_4

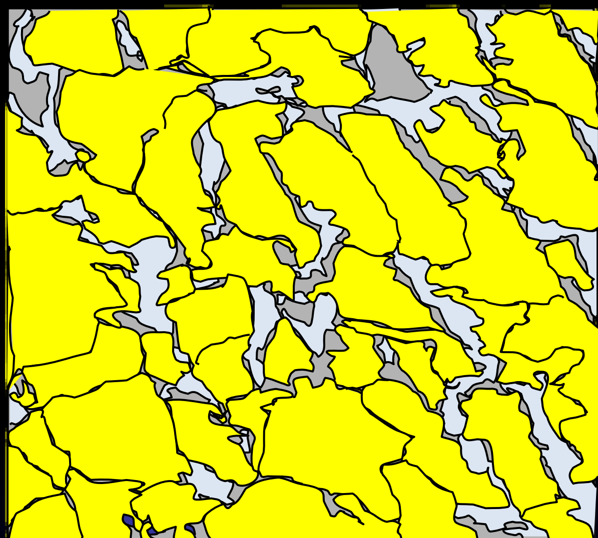
$\not\rightarrow$ Fe_2P + Li_3PO_4

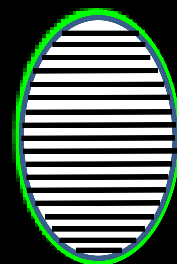
Grain boundary – surface transport of electrons

Amorphous Ion-Conducting Surface on $LiFePO_4$

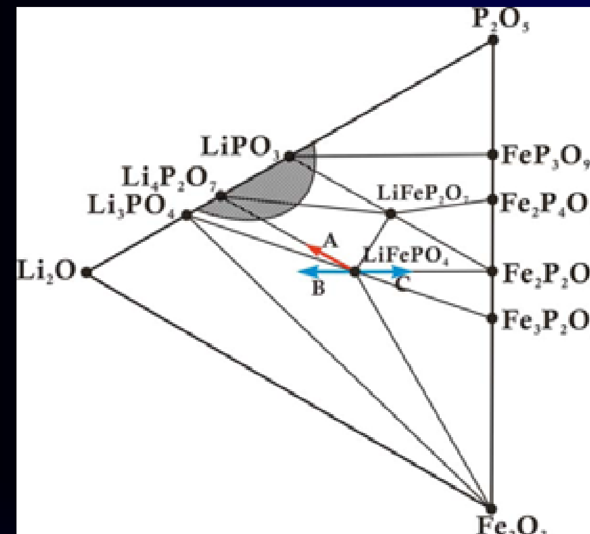
Grain boundary and/or surface transport of ions

- **Example: $LiFePO_4/Li_4P_2O_7$ composite**
  - Enables very rapid discharge rates: 100 mAh/g @ 60C rate





thin LI-ion coating acts to control growth at high T



Concept schematic showing possible glassy $Li_4P_2O_7$ phase in the grain boundaries of $LiFePO_4$ nano-crystallites

G. Ceder et al., Nature 458, 190 (2009)

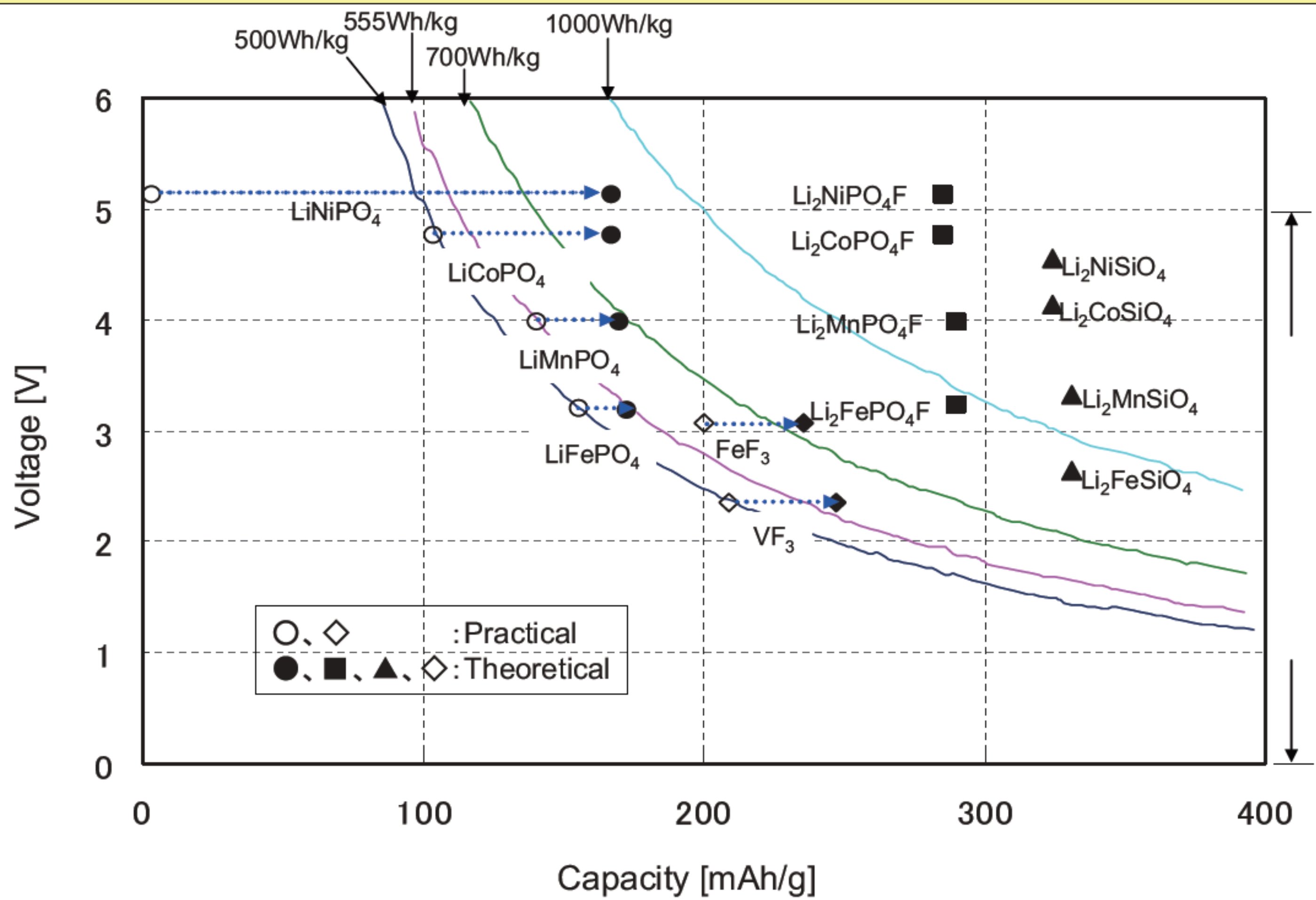
Creation of a fast ion-conducting surface phase through controlled off-stoichiometry

$LiFe_{0.9}P_{0.95}O_{4-d}$ @ 600°C è $LiFePO_4 + Li_4P_2O_7 + \ldots$

The Search for New Positive Electrode Materials

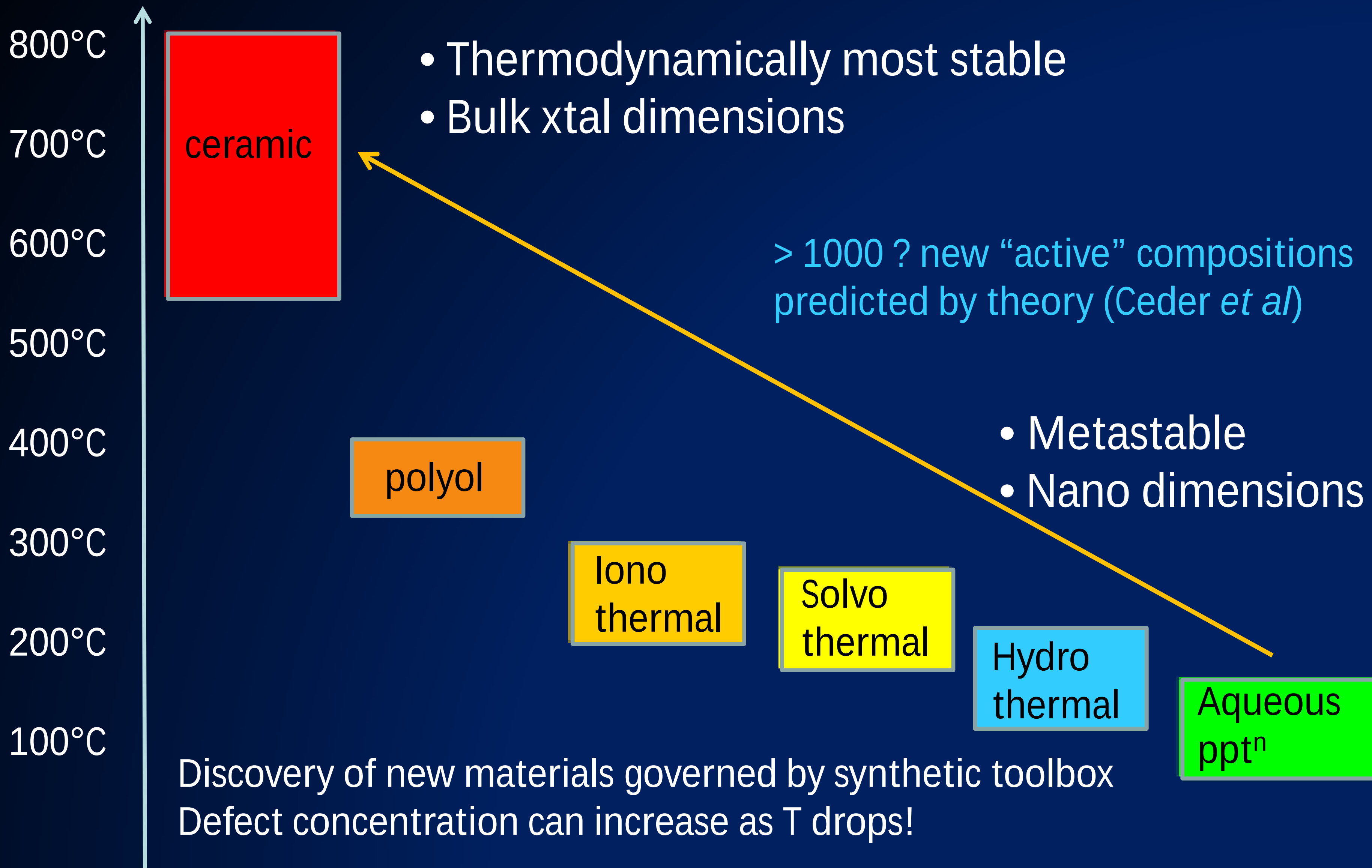
Development map for polyanion-type positive electrode materials

Li phosphates, silicates and borates are promising as thermally stable positive electrode materials

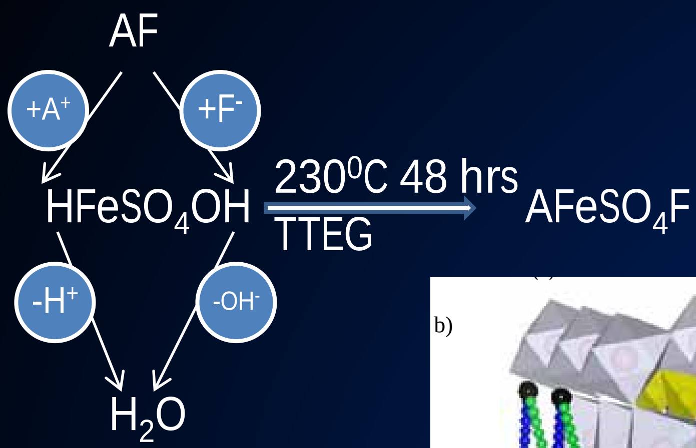


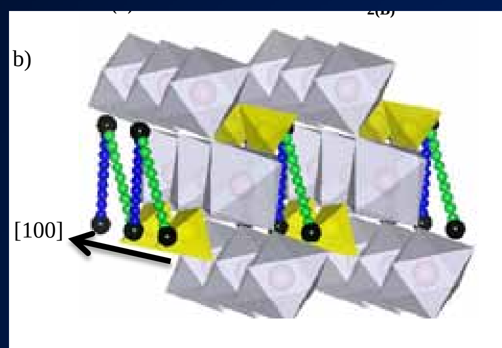
Source: http://www.iem.titech.ac.jp/ishikawa/IWMD-SS_2009.pdf

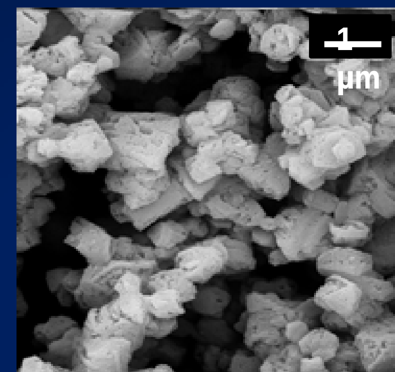
Discovery of New Materials: If Mother Nature Can't Make It...



Solvothermal Synthesis of Fluorosulphates: $LiFeSO_4F$





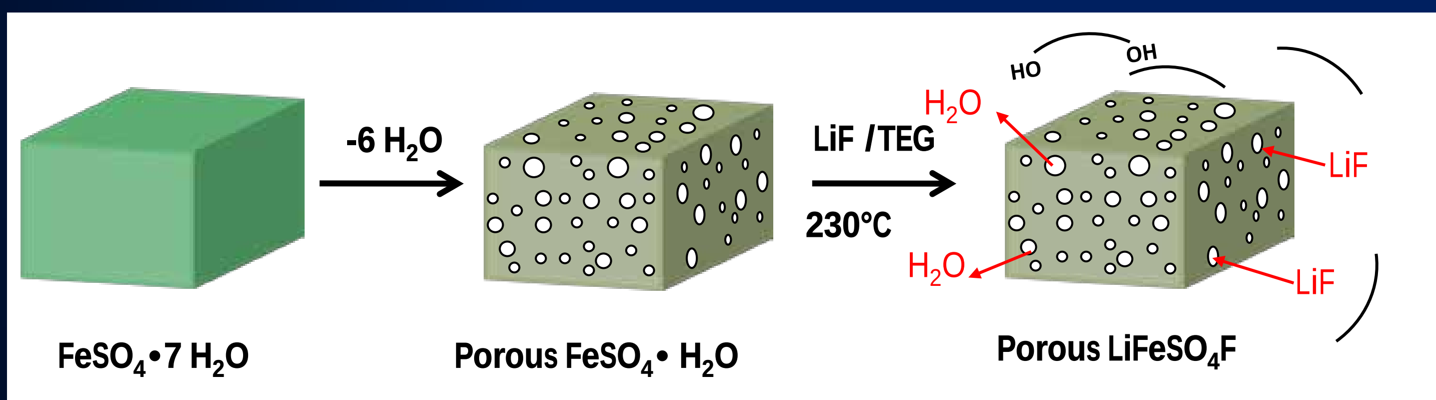


90% of theoretical capacity at 3.6V

è 510 Wh/kg

è Ea = 0.35 eV

$LiFePO_4$: 0.67eV



R. Tripathi L. Nazar et al., *Angew Chemie* 2010

R. Tripathi, MS.Islam and LF. Nazar, *Chem. Mater*, 2011

Na-ion Cells: Coupling to Renewable Energy

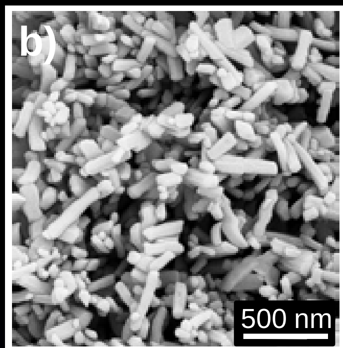
- Sodium is abundant and less costly than lithium precursors

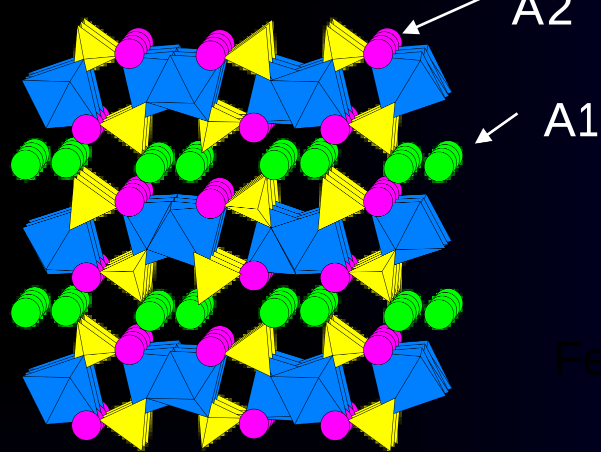
- Demand for Li will rise with auto manufacturers plans for Li batteries in hybrid and electric cars

- Mitsubishi claims that demand will exhaust current Li sources by 2015

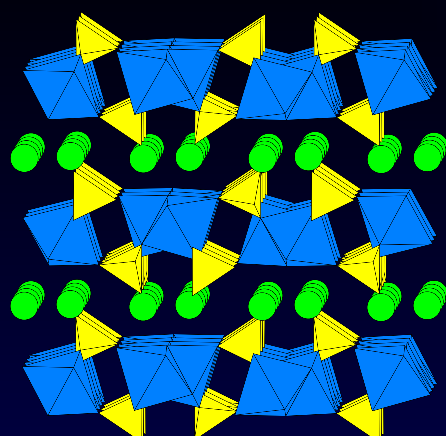
- Much debate over the accessibility of the world's lithium reserves
  - remote locations
  - political factors (New Li sources: Uyuni, Bolivia; Afghanistan?)

Beyond Li-ion Batteries: Na_2FePO_4F





metastable
< 650°C)
hydrothermal
solvothermal



Two – dimensional ion transport

$Na_2Fe^{II}PO_4F$

Vol = 852Å^3

Reduction

Oxidation

3.7% vol change

$NaFe^{III}PO_4F$

Low strain material on redox

Ellis, Nazar et al., *Nature Mater*., 2007

New family of Na-ion conductors

Future Energy Storage Materials Challenges

F nanocrystallites è nanostructures

F control and design grain boundaries
– inter-particle, inter-electrode & inter-battery

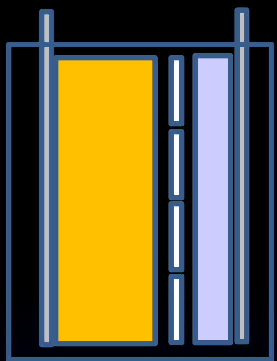
F interface organic, polymer & inorganic materials science
– materials with tailored properties

F electrochemical reactivity of bulk solids - REsearch

Going Beyond the Limits of Intercalation Chemistry: Energy Density (Full Cells)

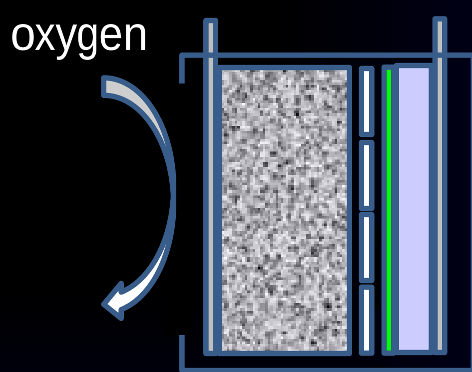
A Comparison of Batteries and Fuel Cells

$S_2 + 4\ Li^+/e^- \leftrightarrow 2Li_2S$



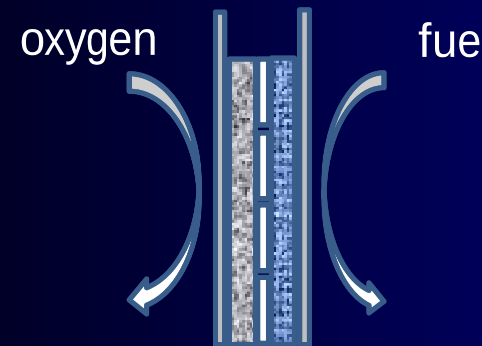
Li-S Battery
product: Li_2S
stored in carbon cathode

$O_2 + 2\ Li^+/e^- \leftrightarrow Li_2O_2$



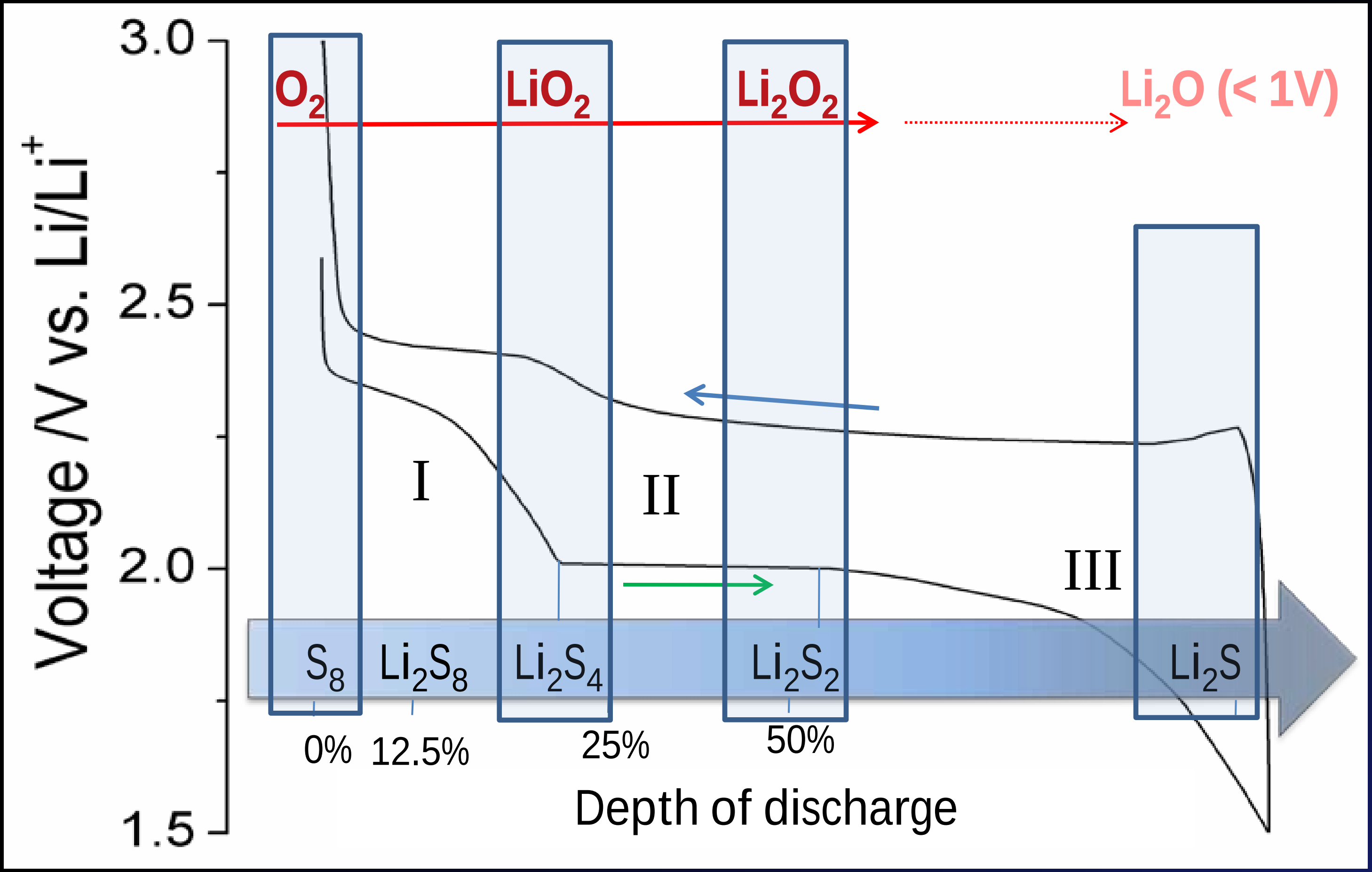
Li-Air Battery
product: Li_2O_2
stored in carbon cathode

$O_2 + 4\ H^+/e^- \leftrightarrow 2H_2O$



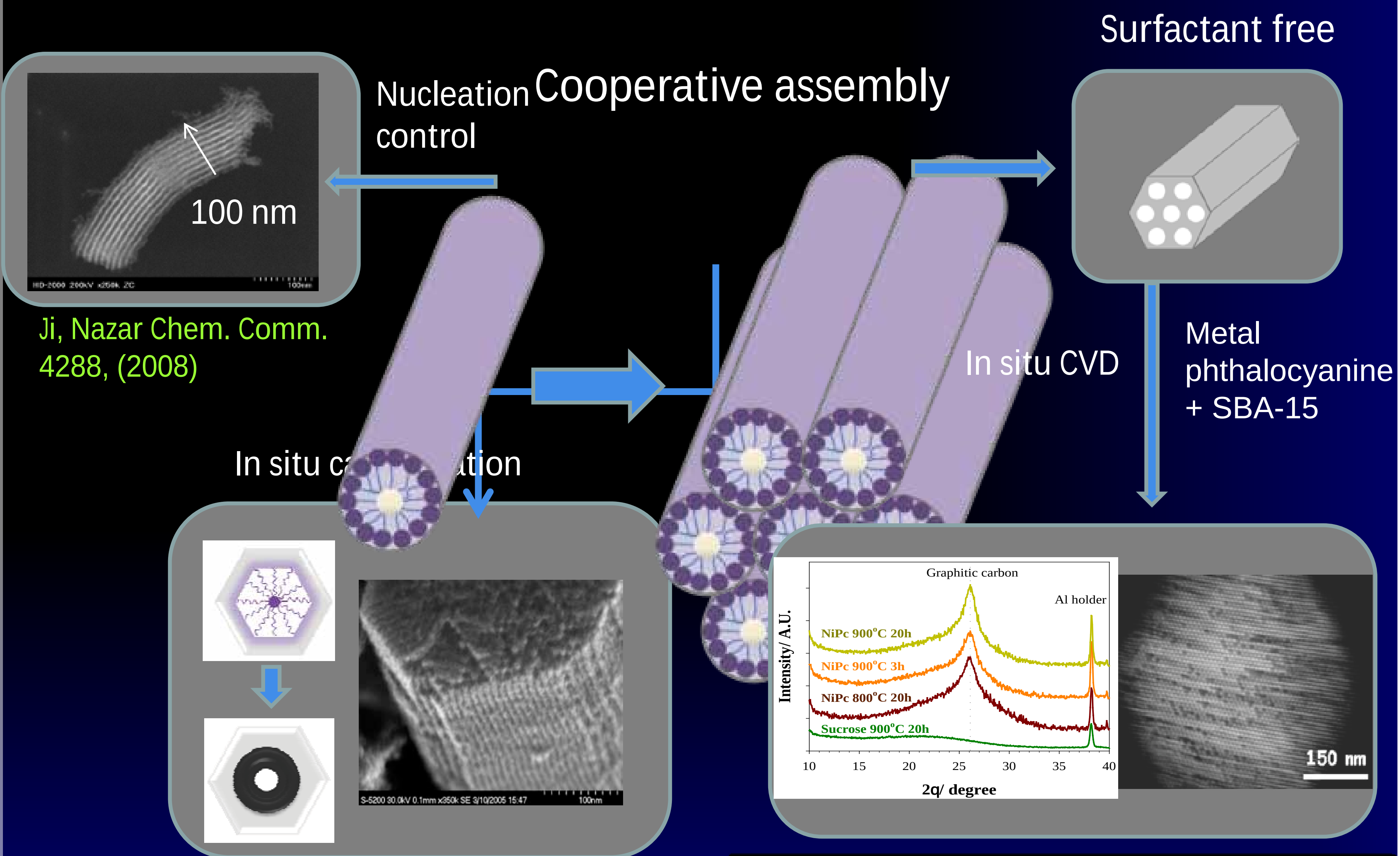
Fuel Cell
Product: H_2O
eliminated

Electrochemistry of the Sulphur *vs* Oxygen Electrode



O_2 reaction mechanism: K. Abraham, J. Phys. Chem C 2009

Tailoring Mesoporous Carbon Hosts



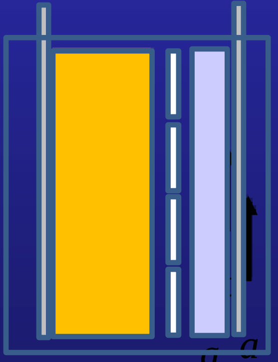
Ji, Nazar Chem. Comm. 4288, (2008)

Ji, Nazar et al, *Chem. Mater* 19, 374 (2007)

Lee, Nazar et al., Angew Chemie, 48, 5661, (2009)

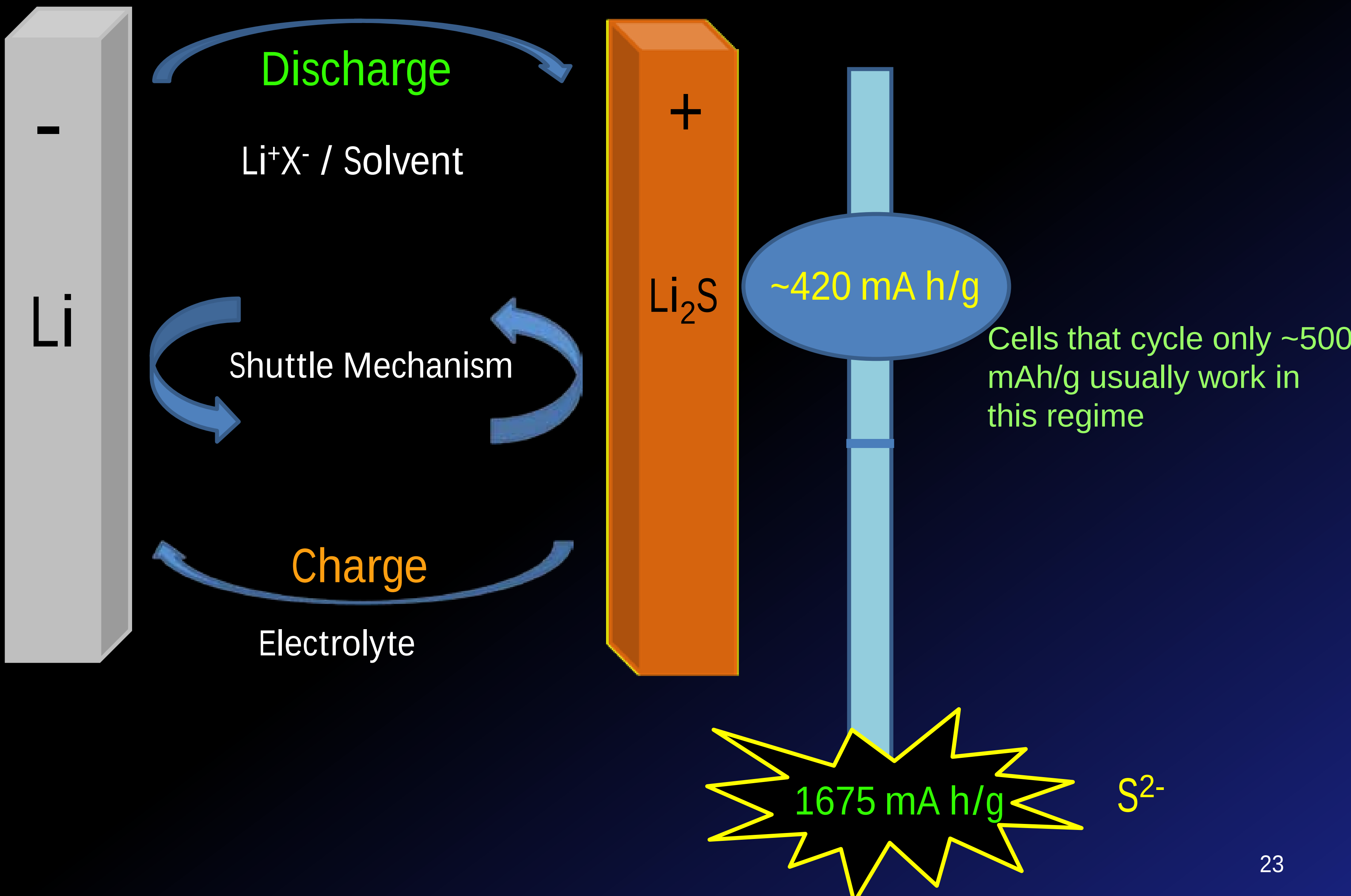
Li-S Energy Storage

$S_2 + 4\ Li^+/e^- \leftrightarrow 2Li_2S$



Li-S Battery
product: Li_2S
stored in carbon cathode

Li-S Battery: Reaction Scheme



Sulfur Abundance and Cost

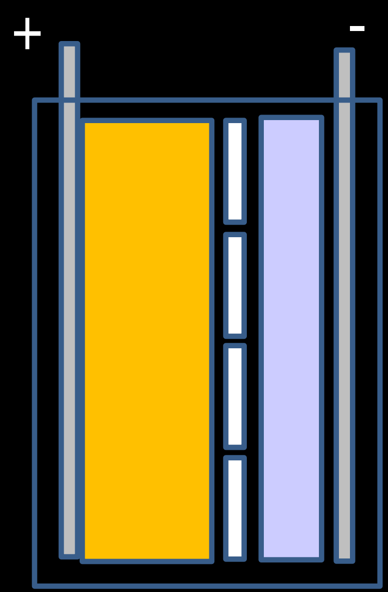
•Resources of elemental sulfur (volcanic deposits, sulfur associated with natural gas, petroleum, tar sands, and metal sulfides:

- about 5 billion tons.

http://minerals.usgs.gov

Li-S Diametric Approaches: Contain or Let Free

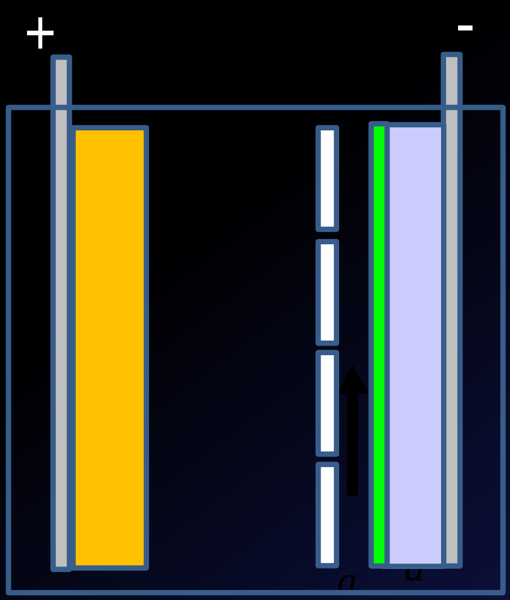
Contained Cathode



Insoluble product: Li_2S
stored in carbon cathode

High volumetric capacity
Lower power

Catholyte



Soluble product: Li_2S_n
stored in electrolyte

Low volumetric capacity (150 Wh/l)
Higher power

All of our studies are conducted with unprotected
Li negative: worst case scenario

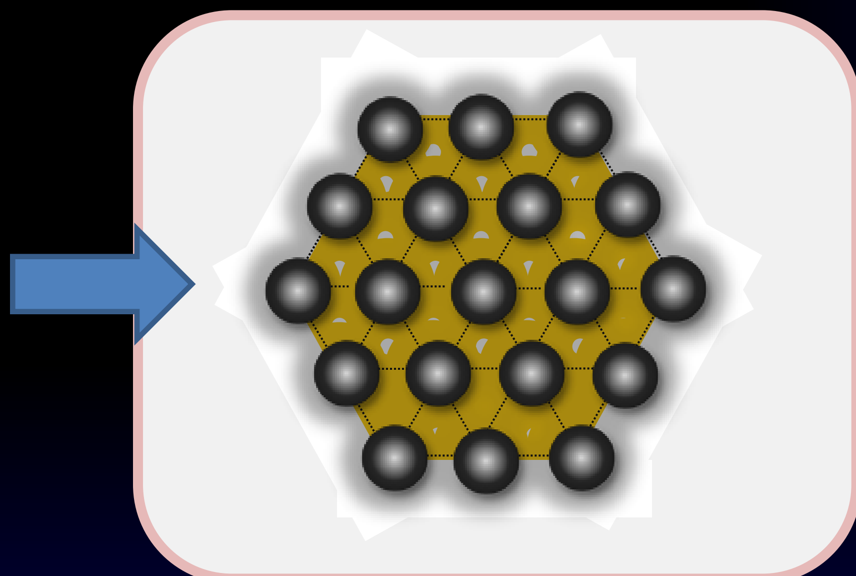
Conductivity Ensured

Electrical Conductivity: CMK-3: 0.25 S/cm
CMK-3/S: 0.21 S/cm

Ionic Conductivity:
- Space is precisely tuned to accommodate swelling of S to Li_2S

Molten S within pores
(incomplete Filling)
Solidificaton

C/S – 70 wt%



Li_2S formation

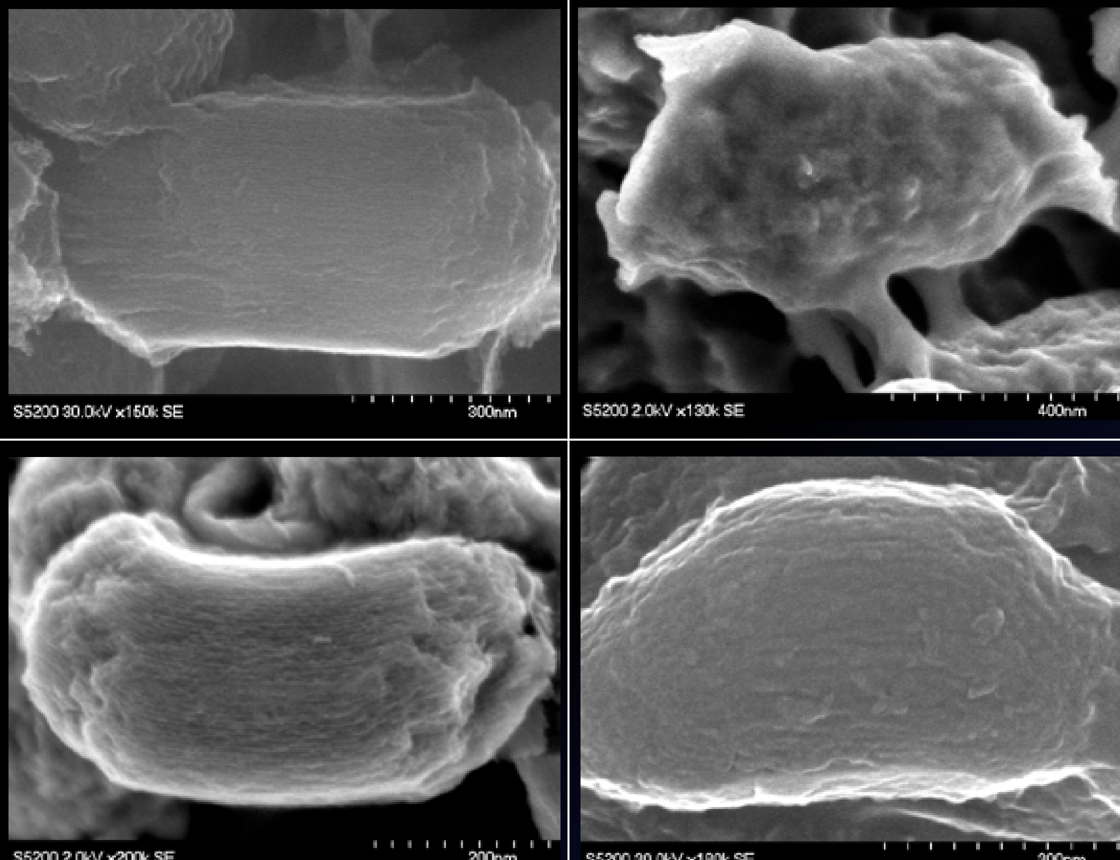
Mesoporous carbon

Role of the Polymer Surface Modifier

Before cycling | **30th charge**

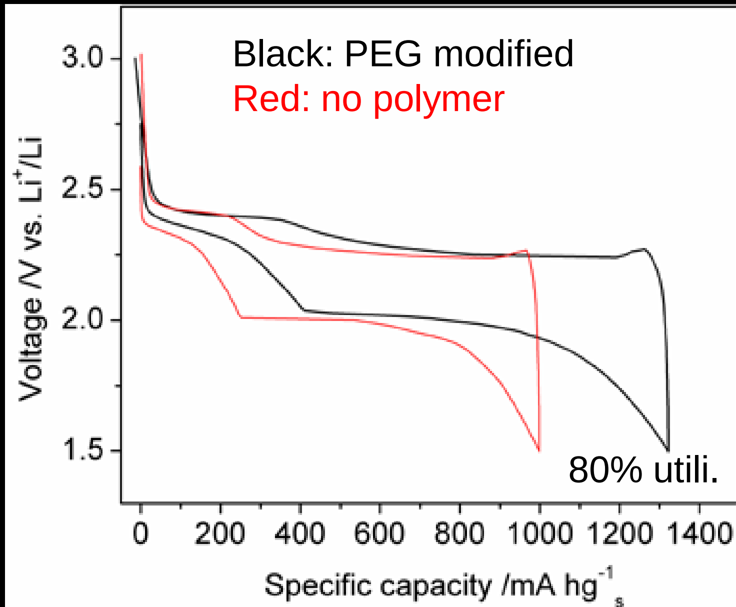
CMK-3/S

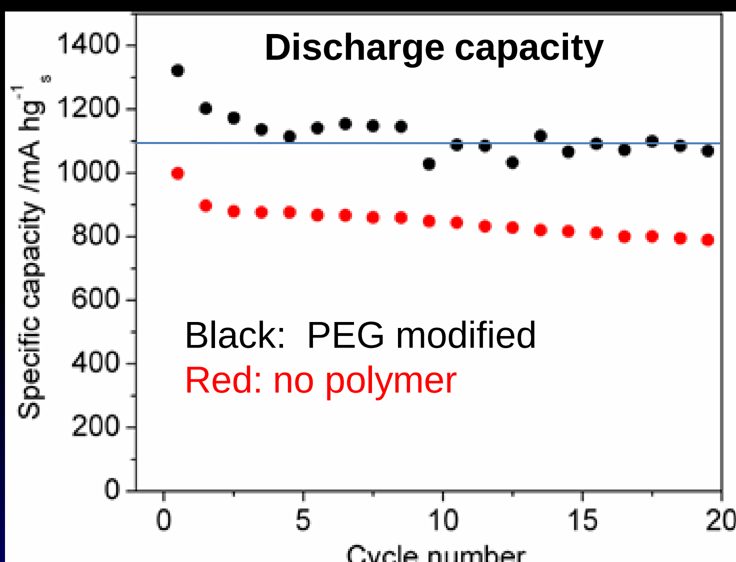
PEG-CMK-3/S



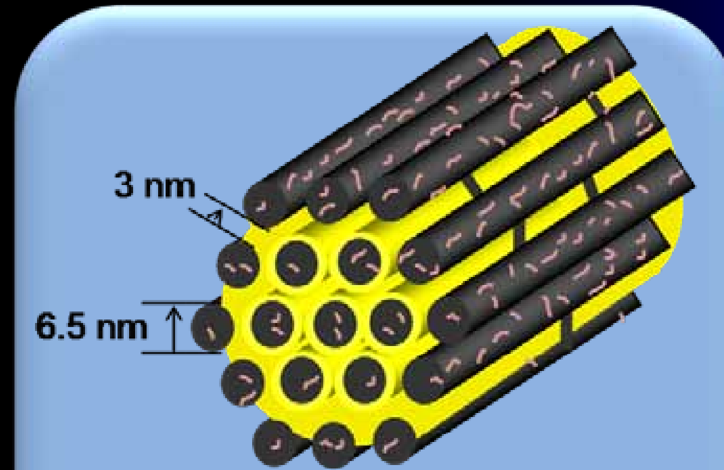
- Polymer inhibits precipitation on the external surface of mesoporous carbon.

CMK-3/S/Hydrophilic Polymer Surface Modifier





PEG = polyethylene glycol (Mw = 4600)



Surface-bound PEG provides hydrophilic gradient to partition polysulfide ions

For 1000 mAh/g capacity:

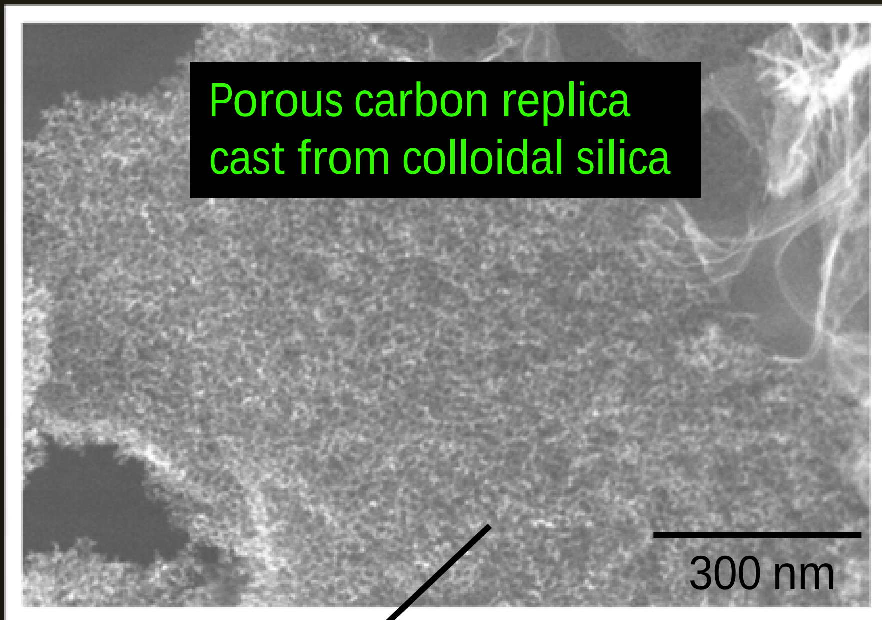
è 1400 Wh/kg based on total mass of cathode (S + carbon + binder)

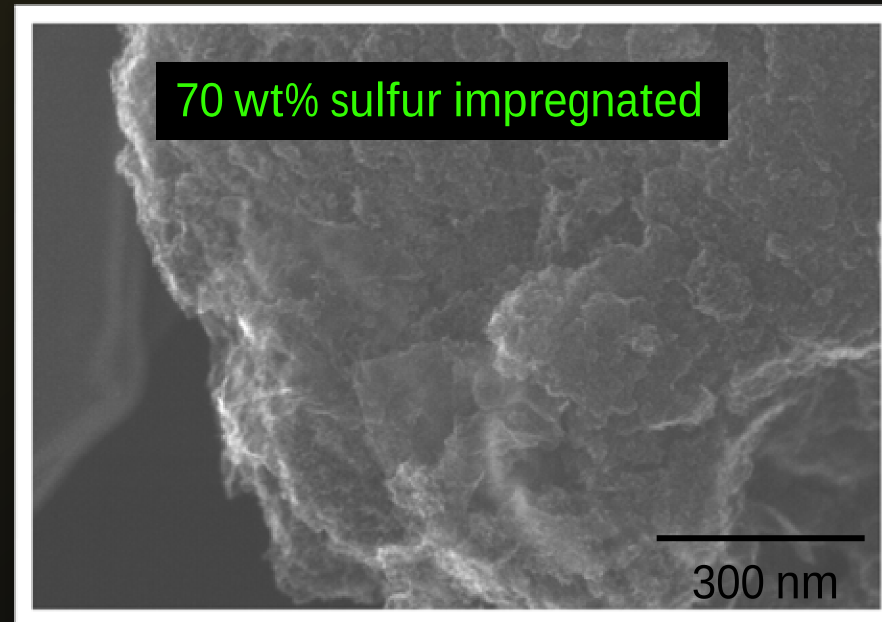
è 2330 Wh/l volumetric for cathode

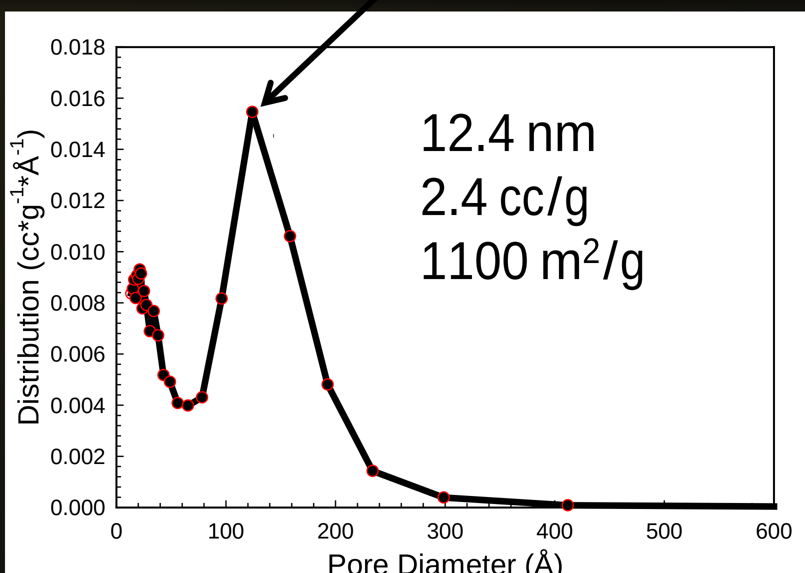
è 600 – 800 Wh/kg for a full cell

D. Ji, K T Lee, L.F. Nazar , *Nature Mater.*, 8, 500 (2009)

Large Pore Carbons: SCM







2.4 cc/g specific pore volume > 2.1 (CMK-3)

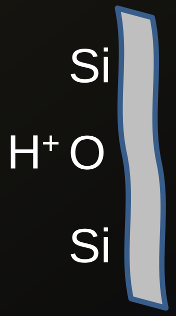
Theoretical fill for sulfur is 85 wt%

Ji et al. *Nature Comm.*, in press, (2011)

Reservoir Concept

ü Assume ADsorption:

~ 20 -30 % of the dissolved polysulfides can be contained.

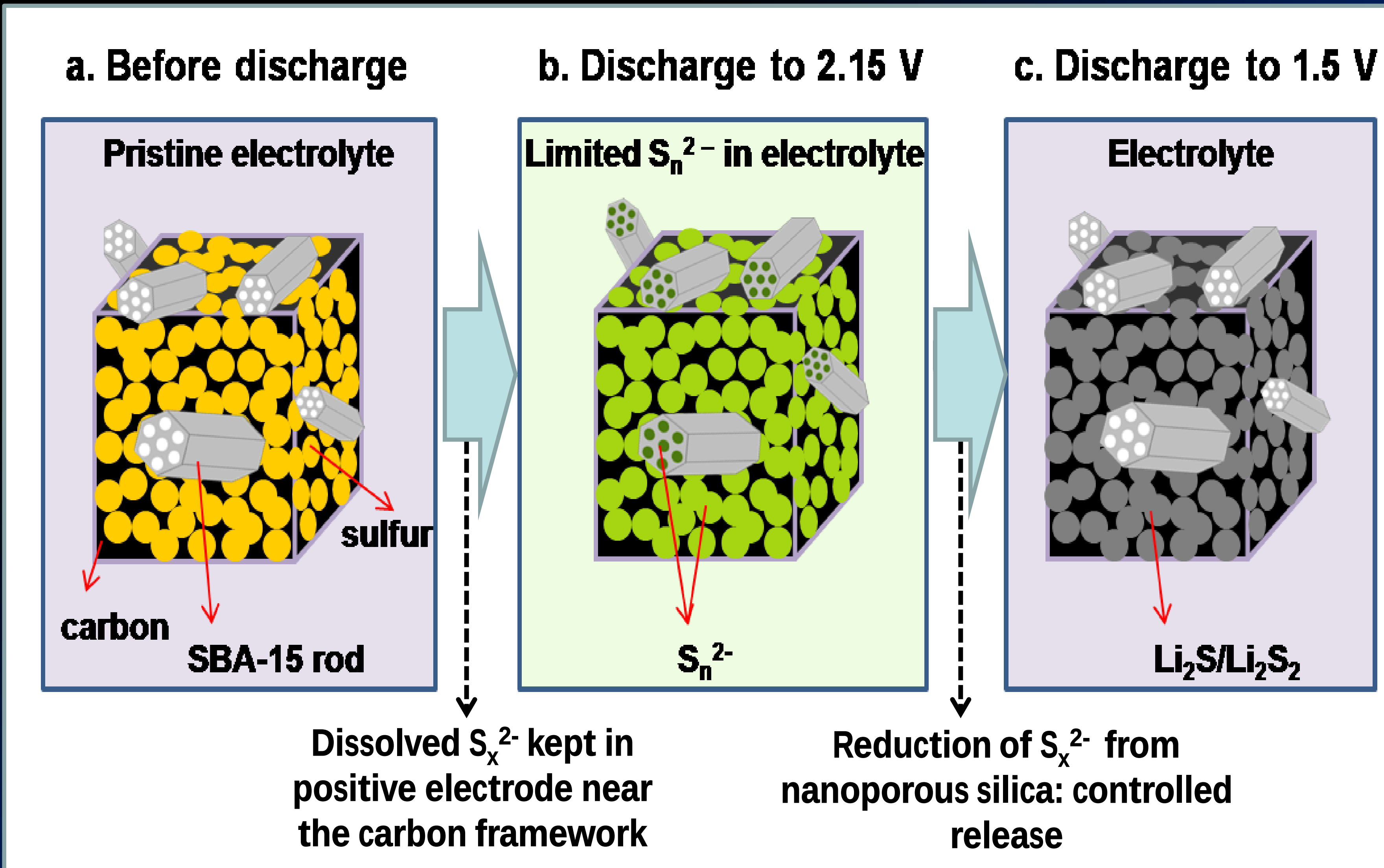


ü Assume ABsorption:

~ 96% of the dissolved polysulfides can be contained.

Ji et al. *Nature Communications* (2011)

Polysulfide reservoirs: a concept borrowed from drug delivery

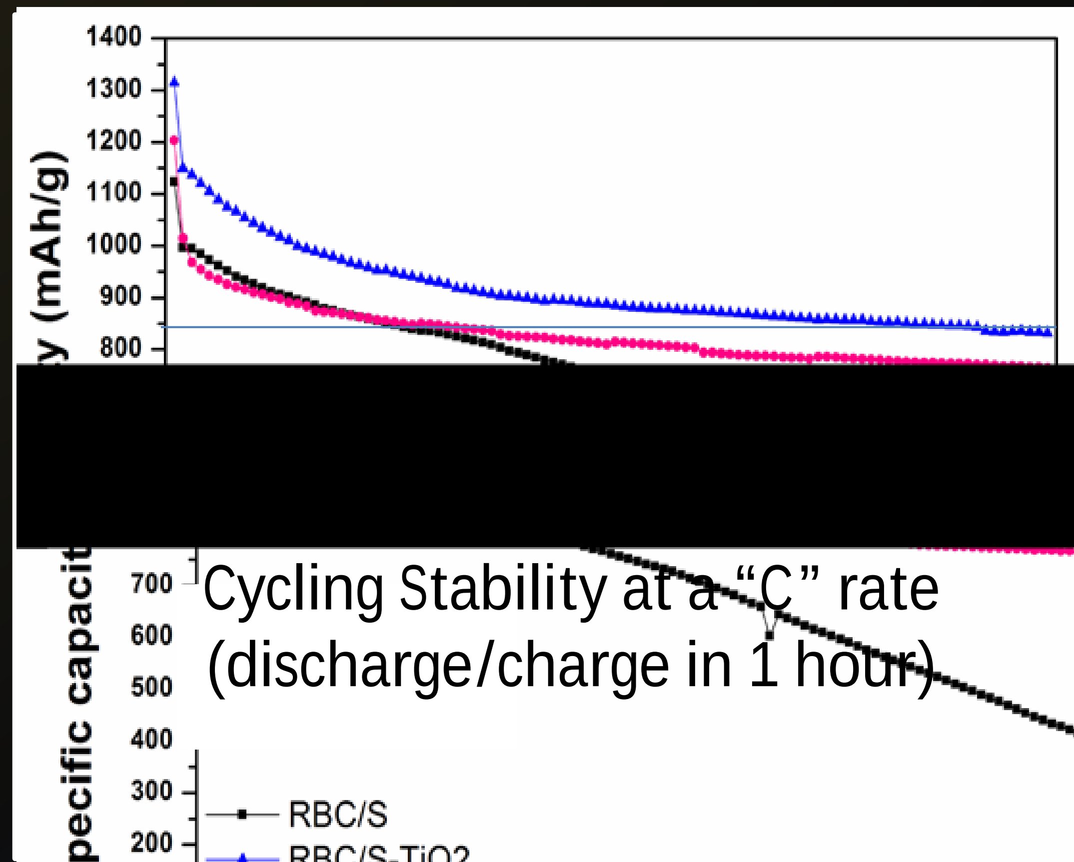


Large Pore Carbons + Reservoir: High Capacity at Faster Rates with Good Retention

ü "C" rate = discharge or charge in one hour

ü Stabilized at 850 mAh/g

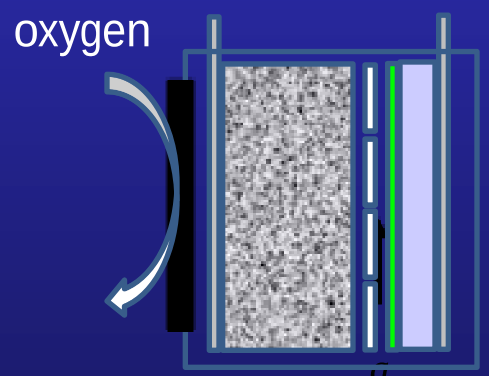
ü 77% retention over 100 cycles



Ji , Nazar et al. *Nature Comm*, 2011
He, Nazar et al., Energy Environ. Sci, 2011
Yim, Nazar et al, Adv. Mater, submitted

Li-O_2 Energy Storage

$$O_2 + 2\,Li^+/e^- \leftrightarrow Li_2O_2$$

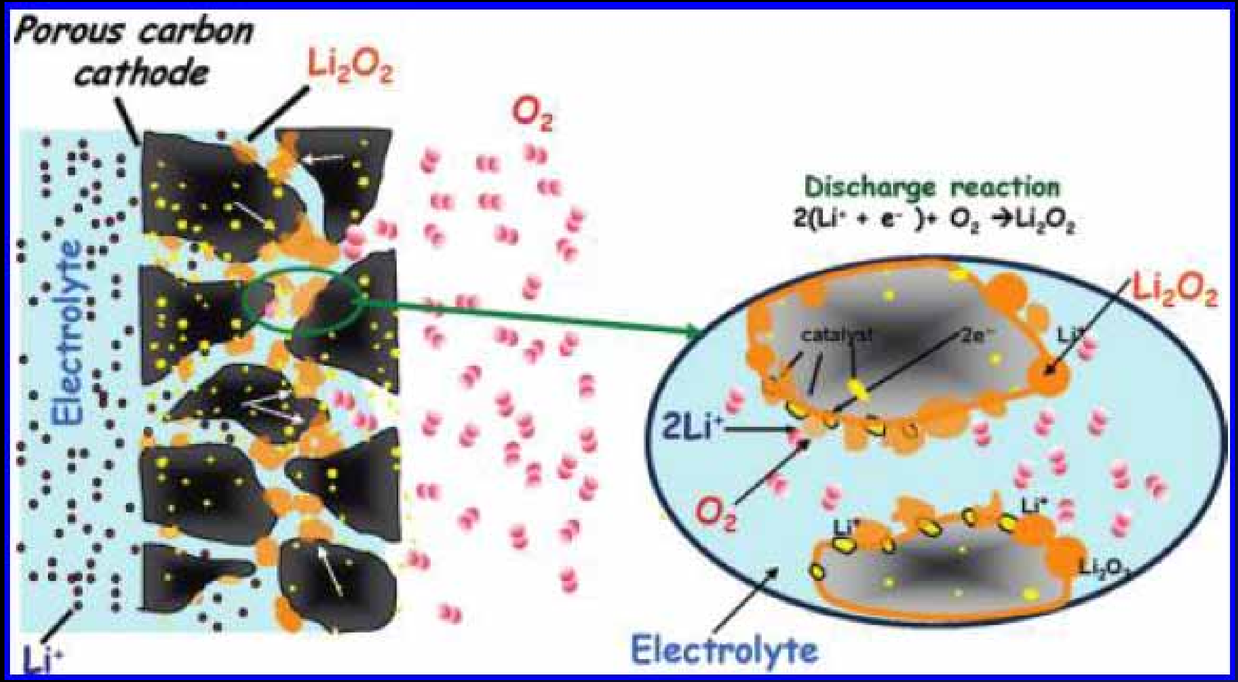


Li-Air Battery
product: Li_2O_2
stored in carbon cathode

b

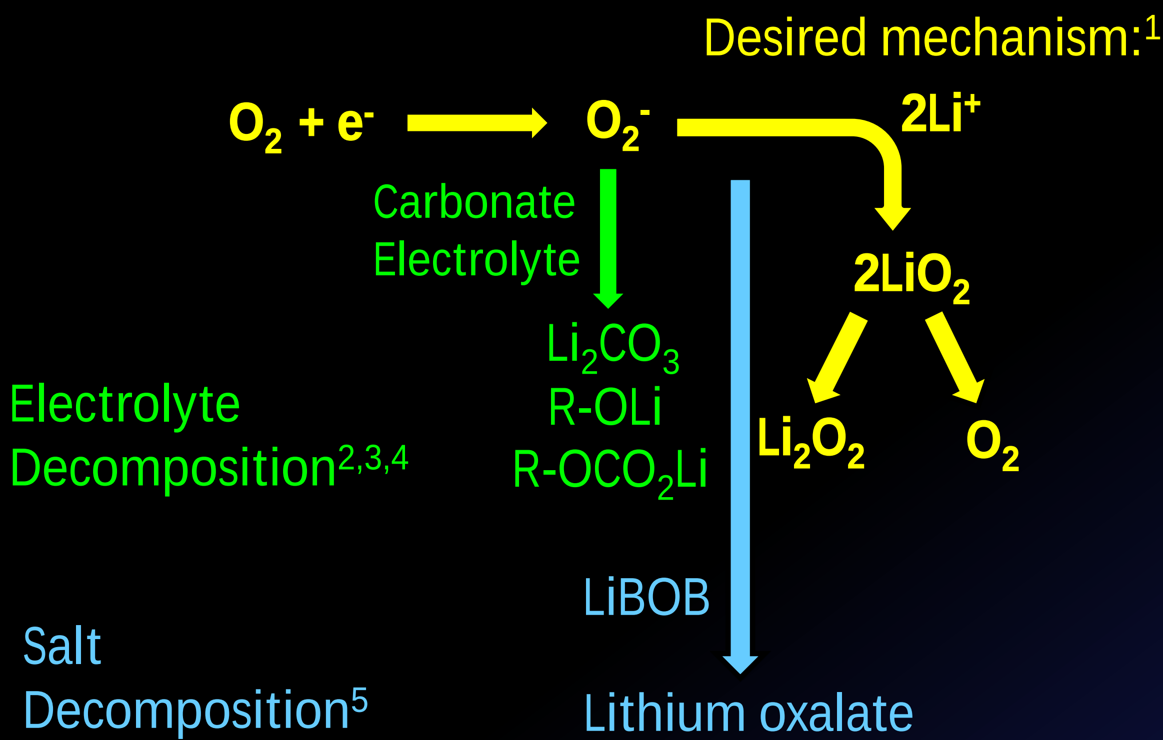
Positive Electrode Challenges

- Air breathing cathode materials
  - Allow all reactants (Li^+, O_2, e^-) to the active catalyst sites
  - Host solid Li_xO_y products while maintaining conductivity
  - Carbon surface area is tantamount



G. Girishkumar, et al., *J. Phys. Chem. Lett*. **2010**, 1, 2193-2203.
G. Q. Zhang, et al., *J. Electrochem. Soc.,* **2010**, 157, A953-A956.

The Electrolyte Problem



1. K.M Abraham et.al., *J. Phys Chem C*, **113** (2009) - mechanism
2. Mizuno et. al., *Electrochemistry*, **78** (2010) - proof of electrolyte decomp
3. P.G. Bruce et.al., *J. Am. Chem. Soc 2011 (on line)* – elucidation of electrolyte decomp
4. A. Luntz, W. Wilcke et al., J. PhyS Chem. Lett, 1168 (2011) – det'm of stable solvents
5. S. Oh, T. Yim, and LF. Nazar, ESL, in press (2011) - studies of stable salts

Choice of Electrolyte

LiBOB, $LiBF_4$

Alkyl Carbonates

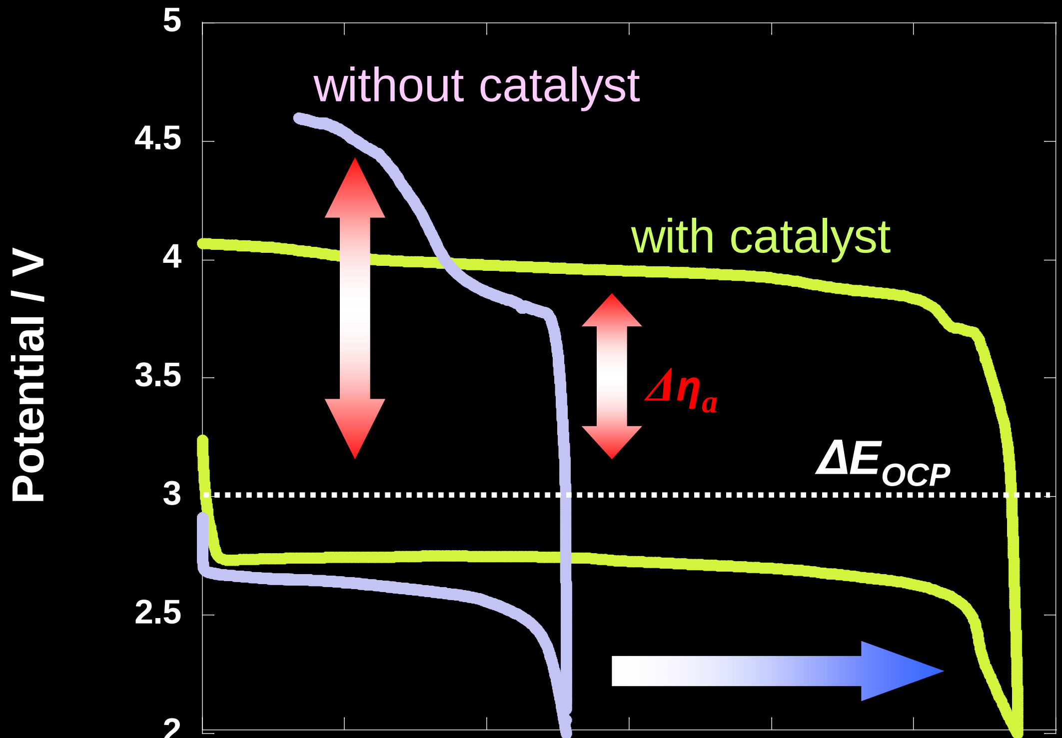
ü DME, TEGDME, DMSO…

ü $LiPF_6$, $LiClO_4$…

- **Many additional challenges facing the Li-Air system must also be overcome :**
  - **understand role of catalyst in ORR and OER involving Li_2O_2**
  - **role of surface defects in controlling Li_2O_2 particle size and morphology**

Required: A bifunctional catalyst

- Increase in discharge capacity?
- Lowering of charge overpotential: Li_2O_2 morphology/size; OER
- Increase in reversible capacity



$O_2 + 2Li \rightarrow 2Li_2O_2$

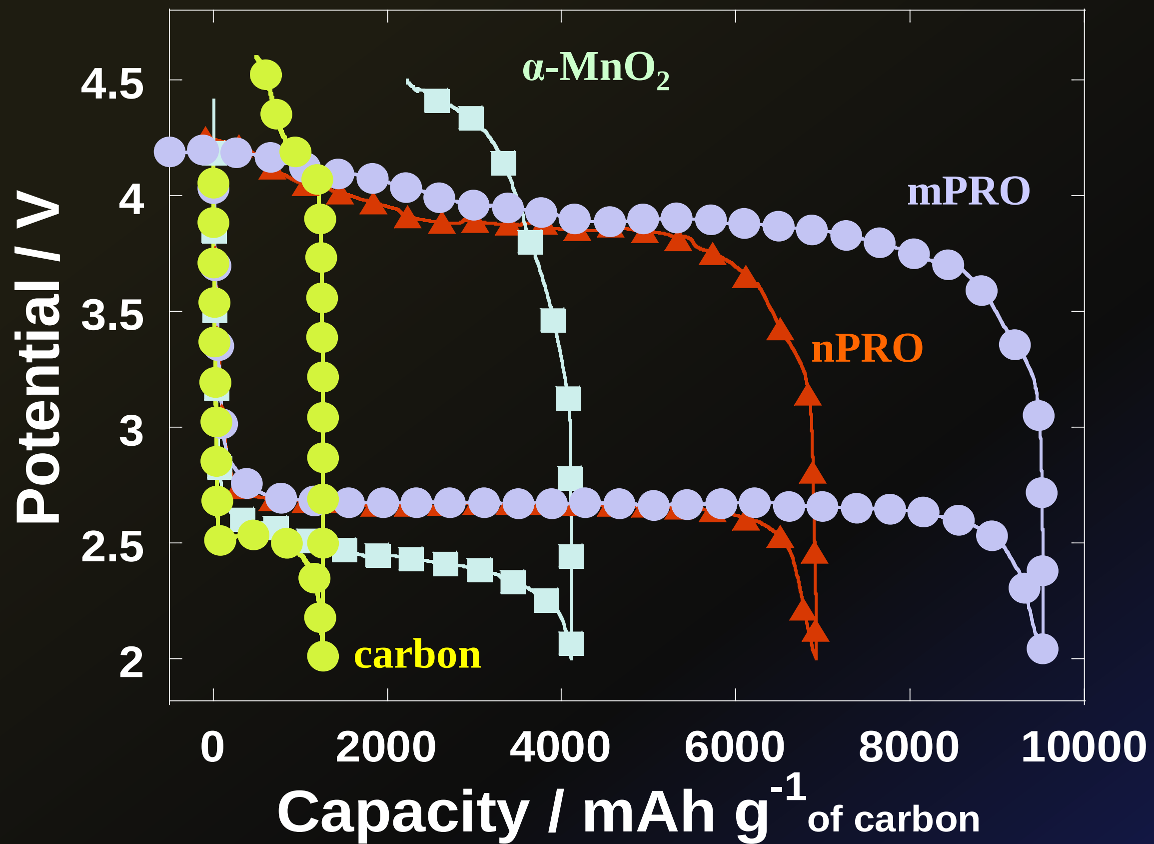
$\Delta_f G^o = -570.954$ kJ/mol

$E^o = 2.96$ V

- a – MnO_2?
  - P. G. Bruce et al., Angew Chemie 2008
- Pt-Au bimetallic nanoparticles?
  - Shao-Horn et al., *J. Am. Chem. Soc.* 2010
- However….
  - PC electrolyte
  - O_2^- decomposes solvent
  - Oxidation of decomposition products (not Li_2O_2)

Mesoporous and nanocrystalline metal oxide catalysts:

Mesoporous metal oxide (mPRO) increases capacity and lowers OER voltage in comparison to nanocrystalline (nPRO) or state-of-the-art catalyst (a-MnO_2). Results are compared with no catalyst (carboon membrane)

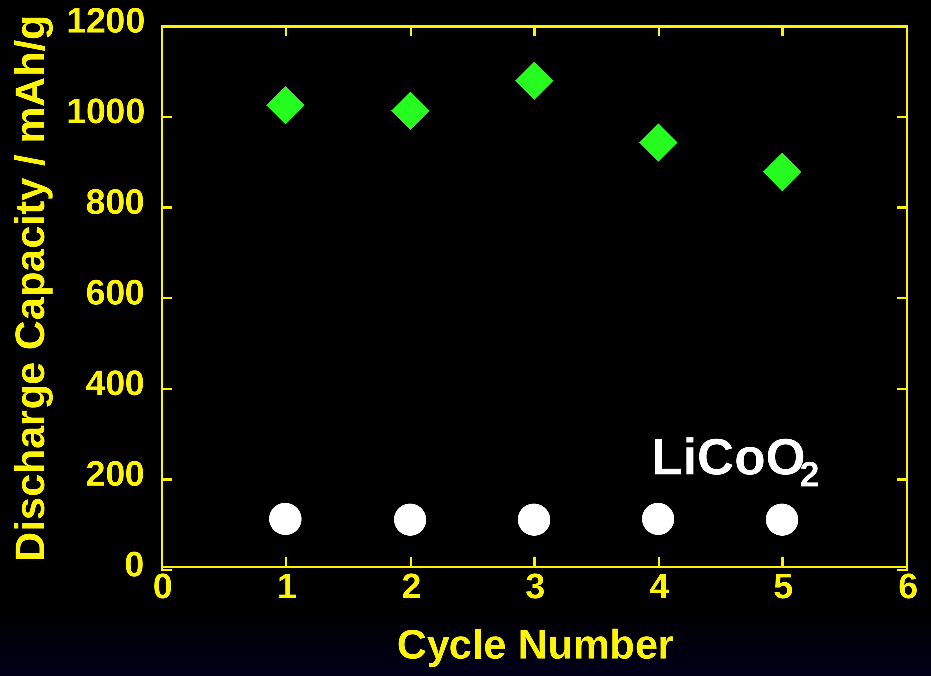


Oh, Nazar et al. , *Nature Materials*, in review

Capacity and Stability of Li-O_2 Battery

Based on data for m-PRO system:

Voltage is higher than Li-S = higher energy density



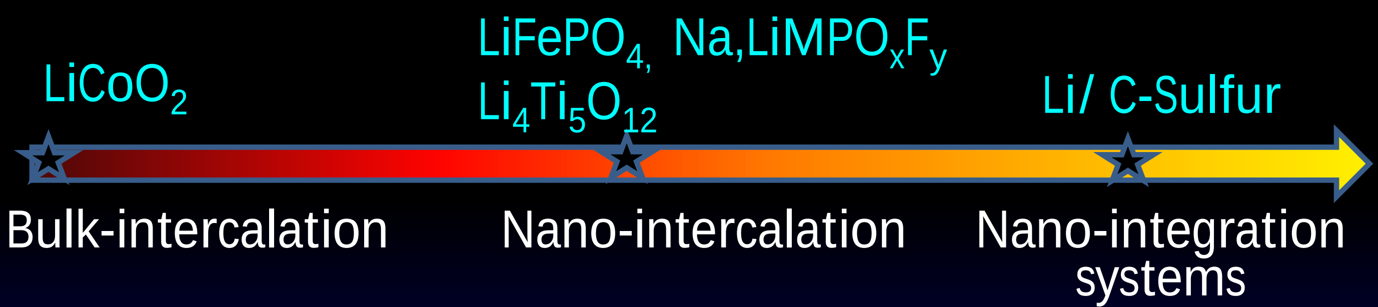
1090 $mAhg^{-1}$ (carbon + catalyst + binder)

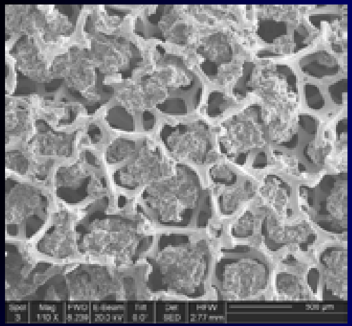
130 $mAhg^{-1}$ (total mass)

Voltage difference between discharge/charge is higher than Li-S = poorer efficiency

Increasing Complexity of Demands – and Materials

		(Wh/kg)	(MJ/kg)	
lead acid		35		0.13
NiCd		45		0.16
NaS		80		0.28
NiMH	90		0.32	
Li ion		150		0.54
LiS		? 600		
Li-O_2		? 1000		
MgS		?		
gasoline		12000		43





Lithium – Air
$Li + O_2 \leftrightarrow Li_2O_2$
Nano-meso-micro

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