Advanced Energy Storage Systems: Lithium Ion & Beyond

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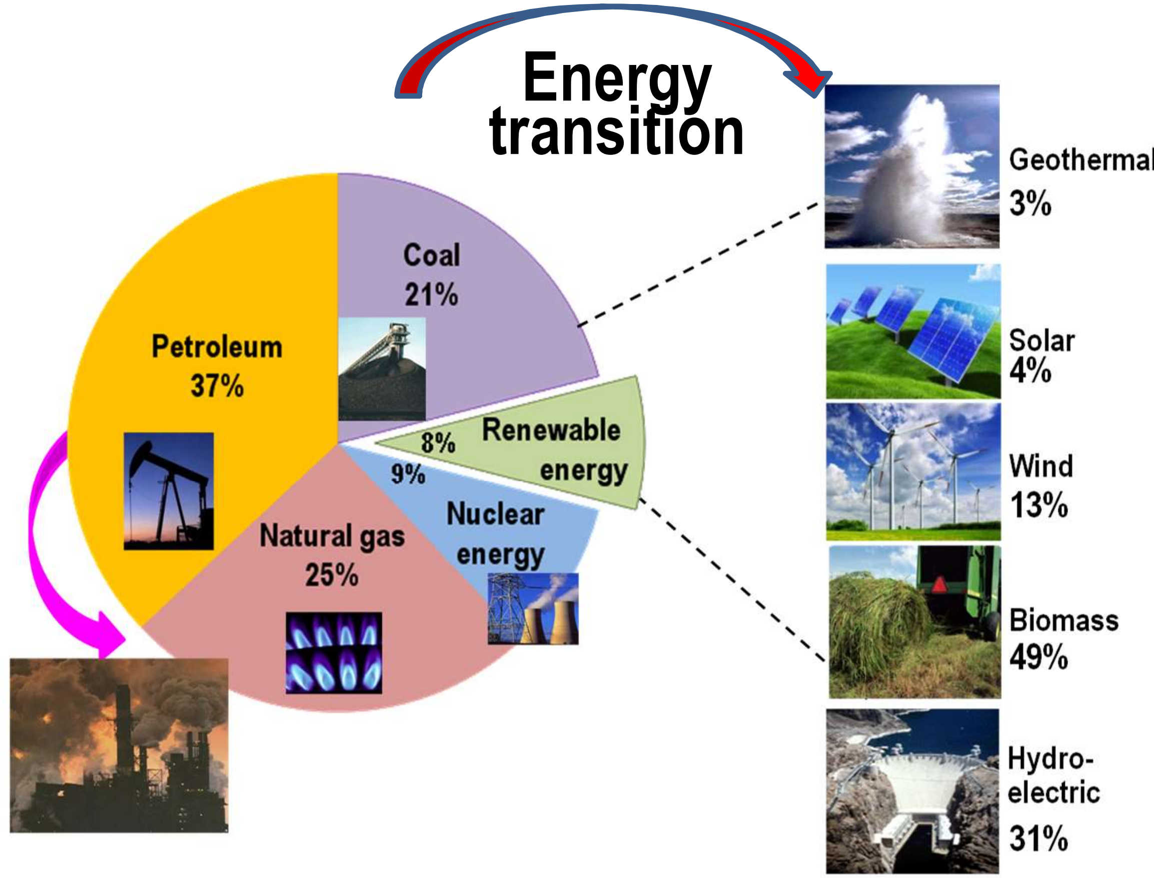
Today's energy overview

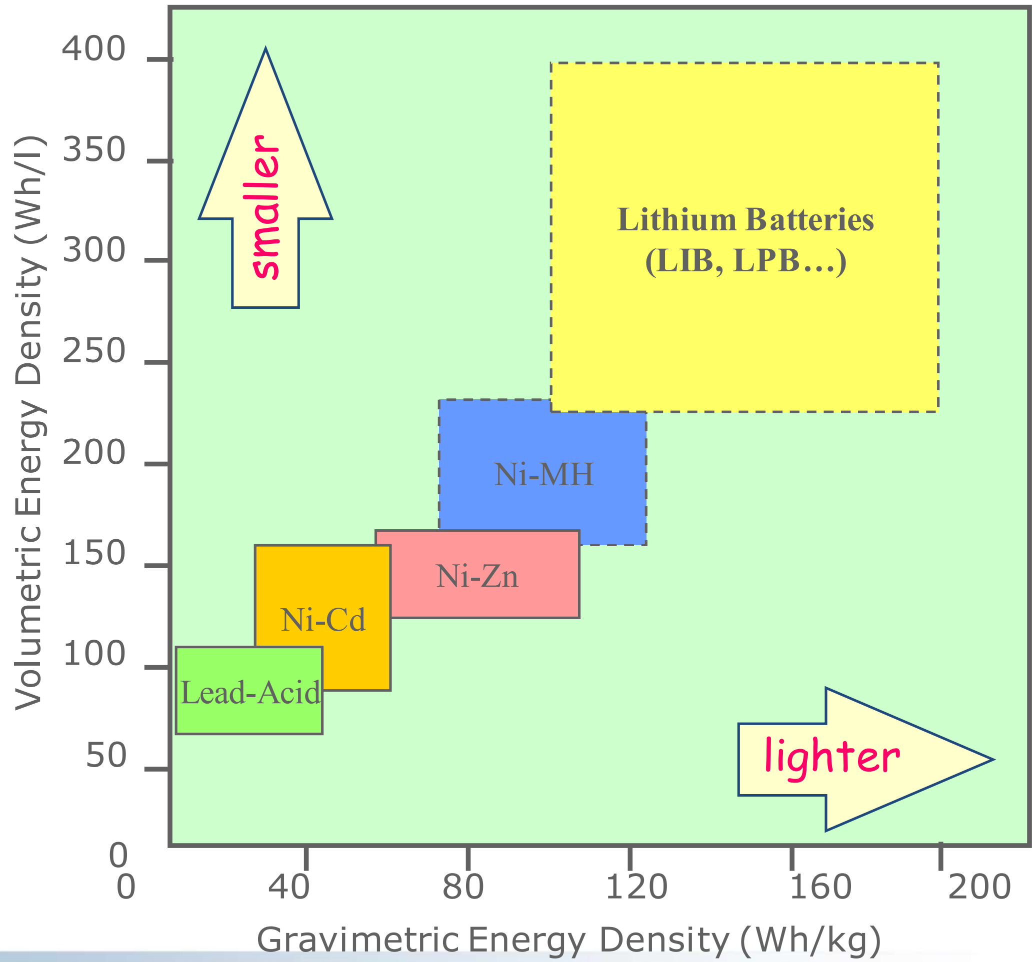
(14 TW) → (28 TW)

http://americanenergyindependence.com/energychallenge.aspx

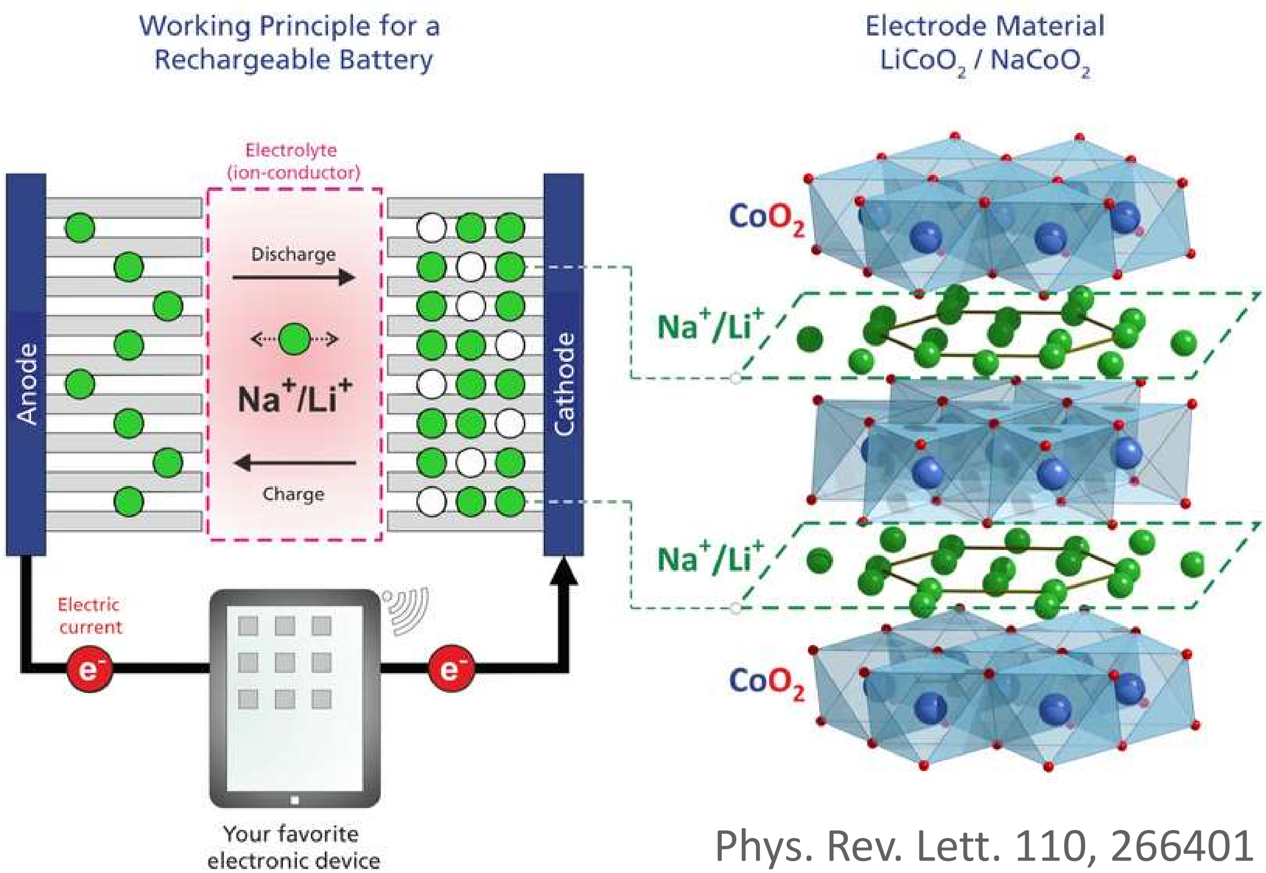


Source: U.S. Energy Information Administration, Monthly Energy Review, Table 10.1 (June 2011), preliminary 2010 data.

Li-ion technology will enable (high energy appications because of its Higher cell voltage & higher energy/power densities



Lithium -ion Battery

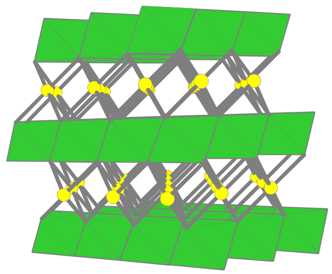


Phys. Rev. Lett. 110, 266401 (2013)

Sodium ion battery undergoes similar electrochemical reaction mechanism with lithium ion battery, and the battery materials are the key for their electrochemical performance

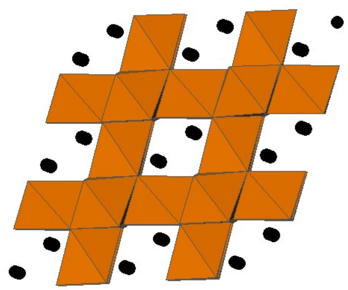
Commercial cathodes for Li-Ion Batteries: 3.5 - 4 V Cathode Materials

ROCKSALT
$LiMO_2$
(**M=Co, Ni, Mn**)
Amine patent



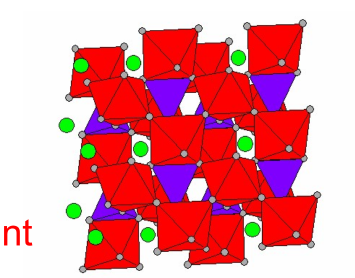
- **Capacity limited** to ~0.5 Li per M atom (i.e., **~180 mAh/g; 4.2V system**)
- 2-D layers for Li^+ transport
- High power and very high energy

SPINEL
LiM_2O_4
(**M=Mn**)
Thackeray Patent



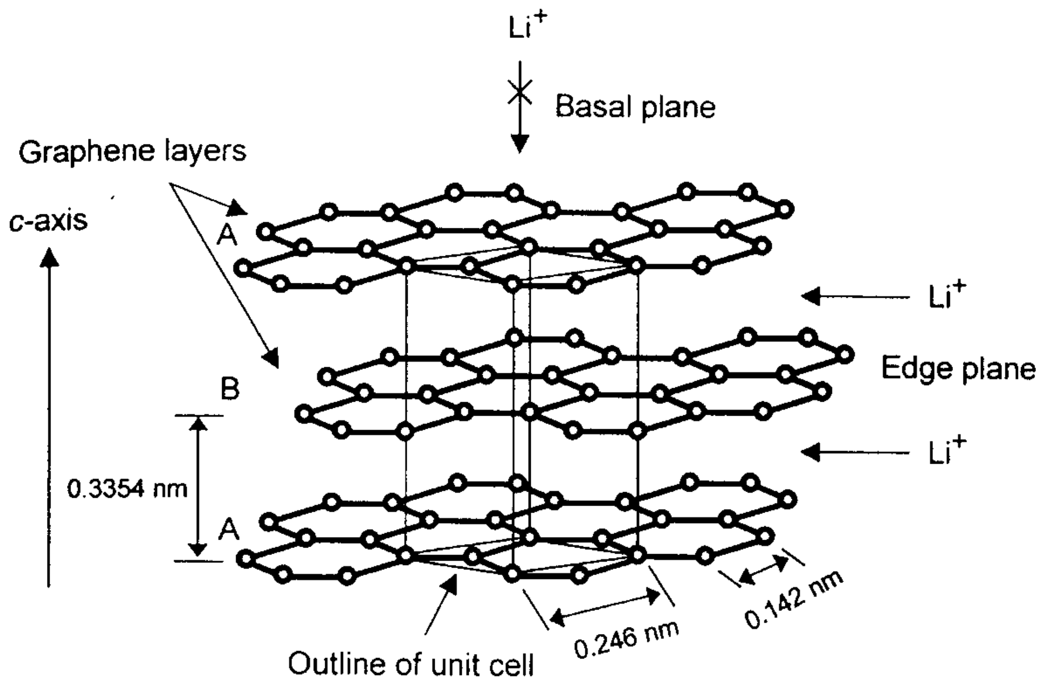
- **Capacity limited** to <0.5 Li per Mn atom (i.e., **~110 mAh/g; 4 V system**)
- 3-D channels for Li^+ transport
- Mn dissolution affects cell performance
- **High power electrode**

OLIVINE
$LiMPO_4$
(**M=Fe, Mn**)
Goodenouph patent



- **Capacity limited** to 1 Li per Fe atom (i.e., **~150 mAh/g; 3.5 V system**)
- 1-D channels for Li^+ transport
- Excellent structural stability

Graphite has been the dominant anode for lithium ion batteries



Scheme of the structure of graphite. The unit hexagonal cell ($P6_3/mmc$) is evidenced with the related ABAB packaging and the interplanar distance c/2=0.3354nm

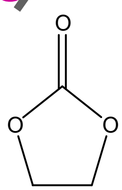
Graphite has a layered structure formed by graphene planes where the carbon atoms are organized via σ bonds in hexagonal cells. The graphene planes are connected each other by weak Van der Waals bonds, following a displaced, alternated ABAB sequence and separated by a distance of about 3.35Å. This separation space is sufficiently large to allow ionic insertion, e.g. lithium ion insertion, in order to form ***Graphite Interlacalated Compounds*** (**GICs**).

Electrolyte used in Lithium Ion Batteries

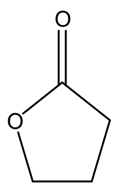
mixture of solvent(s) and salt

solvent

dielectric constant $\varepsilon \nearrow$

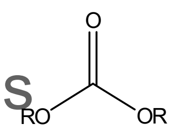


- cyclic carbonates
- cyclic esters

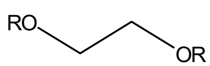


+

viscosity $\eta \searrow$

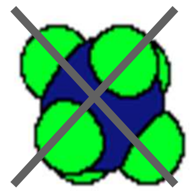


- linear carbonates
- ethers

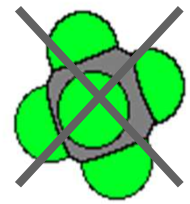


salt

ClO_4^-



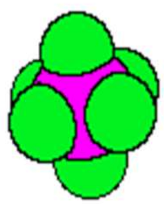
SbF_6^-



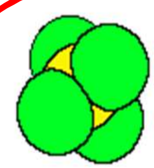
AsF_6^-

Explosive !

Toxic !



PF_6^-



BF_4^-

lower conductivity

Most organic Solvents decompose above 4.3V

AK1

Electrochemical performance of commercial Lithium ion batteries

Cathode	Specific Capacity (mAh g^{-1})	Average Voltage (vs Li/Li^+)	Specific Energy density (Wh kg^{-1})	Volume Energy density (Wh L^{-1})
$LiCoO_2$	160	3.9	624	3157
$LiMn_2O_4$	120	4.05	486	2041
$LiFePO_4$	160	3.4	544	1958
NMC333	165	3.8	627	2978
NMC622	180	3.8	684	3351
NMC811	195	3.8	741	3630
NCA	200	3.75	750	3675

Slide 8

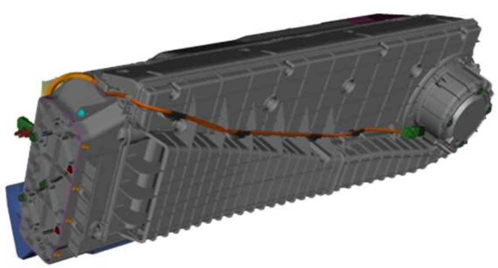
AK1 mercial

Amine, Khalil, 5/11/2020

Needs to increase energy to lower cost

EV Battery

- 23kWh
- 500lbs
- 125 liters



1st Gen

EV Battery

- 23kWh
- 250lbs
- 75 liters

Future

Urgent Need to Develop next generation high energy lithium battery technology

Anodes

300% Increase

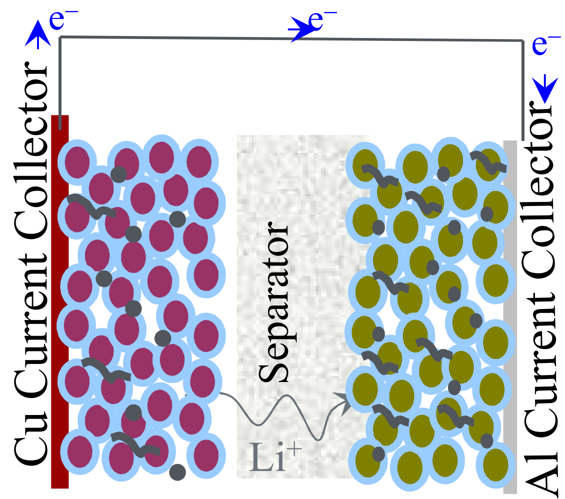
Today's Technology

350mAh/g based on graphite

Next Generation

1,000⁺ mAh/g

Intermetallic Composites



Electrolytes

0.3 V Increase

Today's Tech

<4.3V vs <4.0V (2012)

Next Generation

4.6-5.0 volts

Cathodes

80% Increase

Today's Technology

170mAh/g
vs 120 (2012)

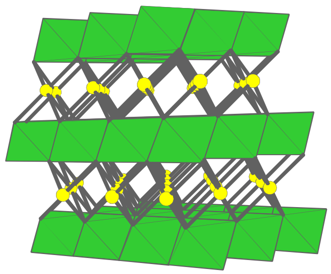
Next Generation

250~300 mAh/g

High Voltage Layered Oxides (Ni & Mn rich)

$LiMO_2$ layered oxide can offer high energy at high Voltage

ROCKSALT
$LiMO_2$
(**M=Co, Ni, Mn**)



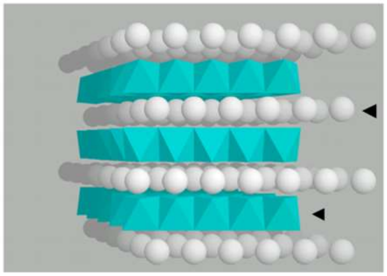
- **Capacity limited** to ~0.5 Li per M atom (i.e., **~140 mAh/g at 4.1V**)
- 2-D layers for Li^+ transport
- Co^{4+} and Ni^{4+} unstable/highly oxidizing
- Structures destabilized at low Li content

$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$: NCA
$LiMn_{1/3}Co_{1/3}Mn_{1/3}O_2$: NMC

1. ***Capacity of 250mAh/g can be obtained if material is charged to 4.6V***

2. ***Electrolyte will decompose at high voltage and battery will fade quickly***

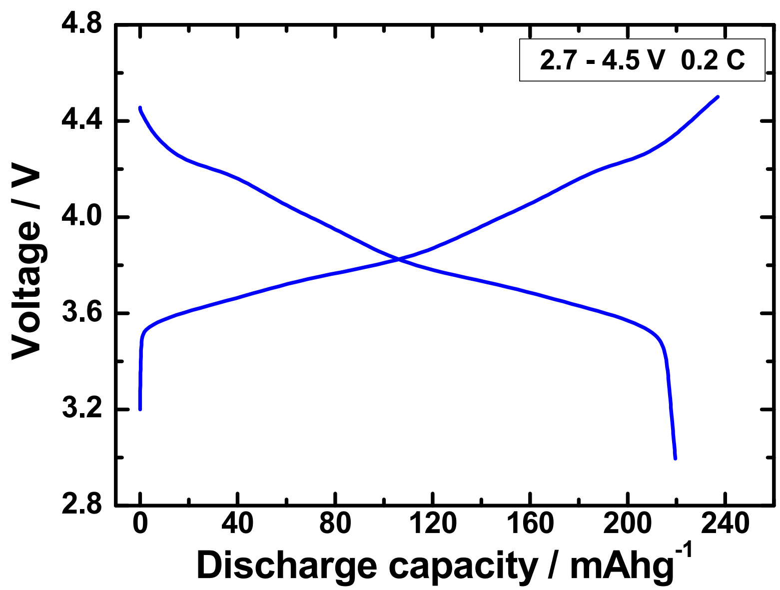
Increase capacity of conventional cathodes by operating at high voltages (250wh/kg)

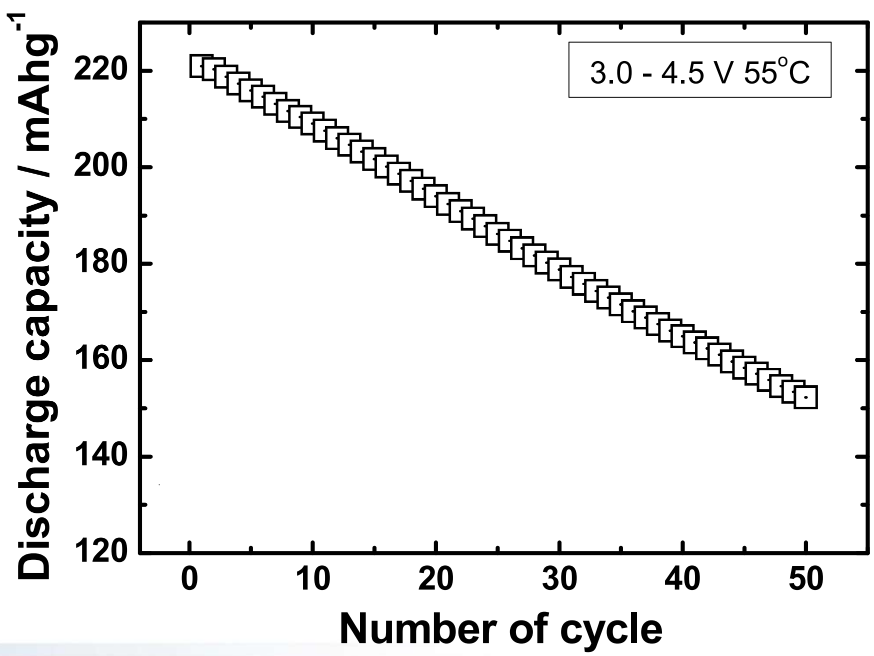


NCA provide 140 mAh/g at cut off voltage of 4.1V

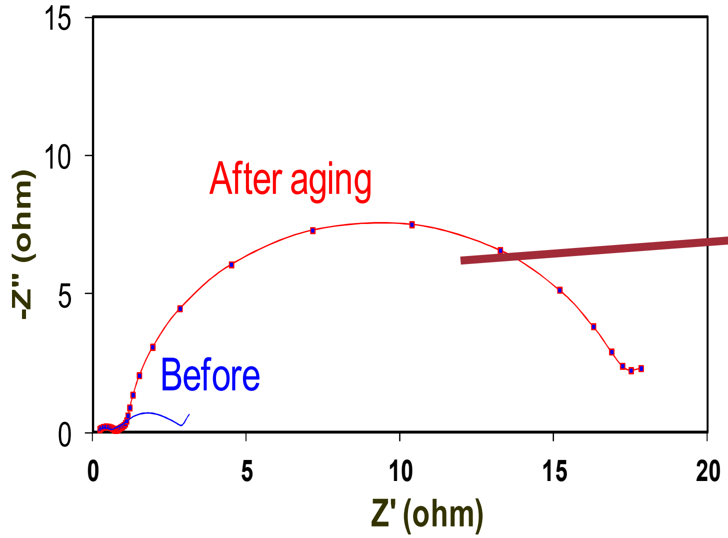
At 4.5V, NCA provide 220mAh/g capacity but poor cycle life

$LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$ (NCA)

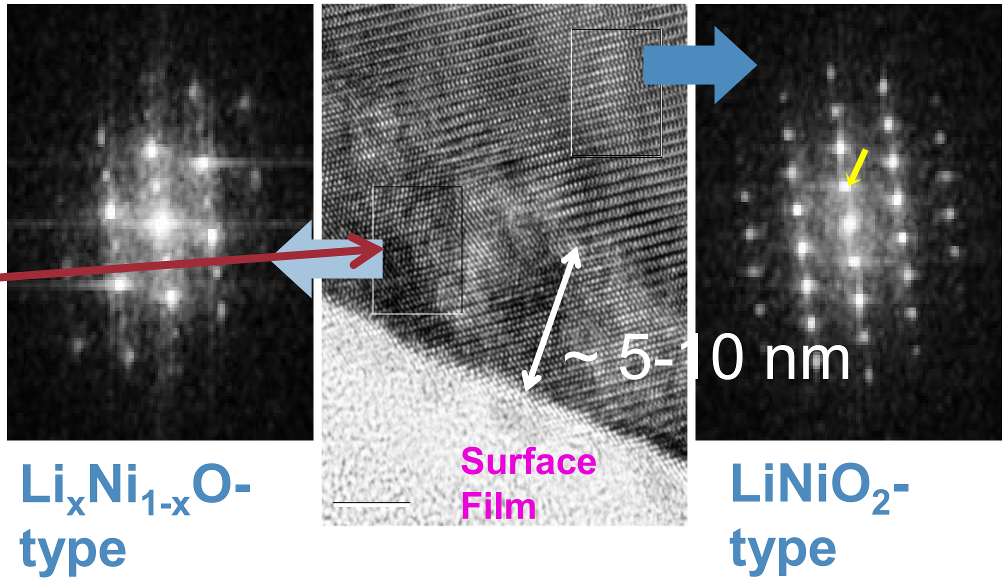




Surface reactions is the cause of power and capacity fade in NCA at high voltages



AC impedance of aged NCA/Graphite cell (55°C) using reference electrode



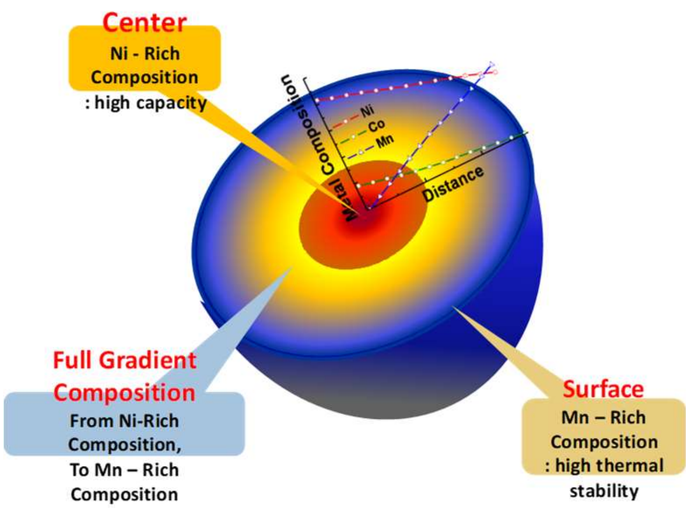
HRTEM of aged NCA electrode

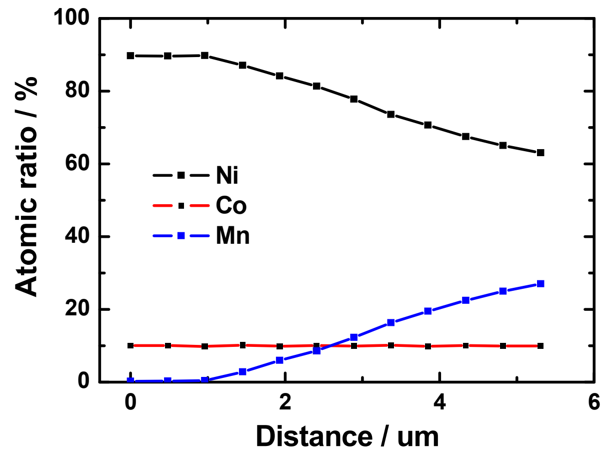
$$LiNi_{0.85}Co_{0.15}O_2 \text{ ------} Ni_{0.8}Co_{0.15}O_2 + Li^+ + 1e^-$$

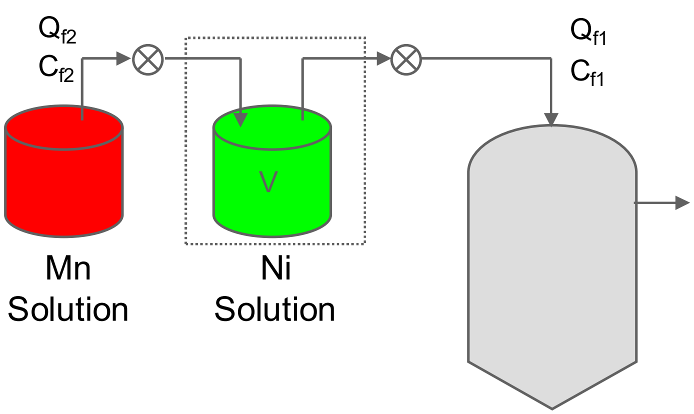
$$\text{-----}\mathbf{Ni_{0.8}Co_{0.15}O + 1/2O_2}$$

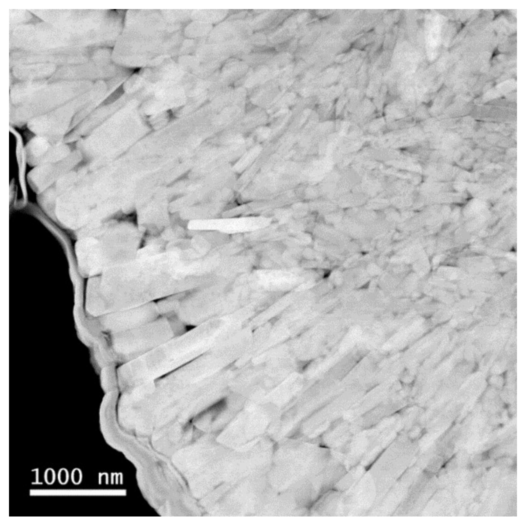
New High energy cathode with full concentration gradient across each particle

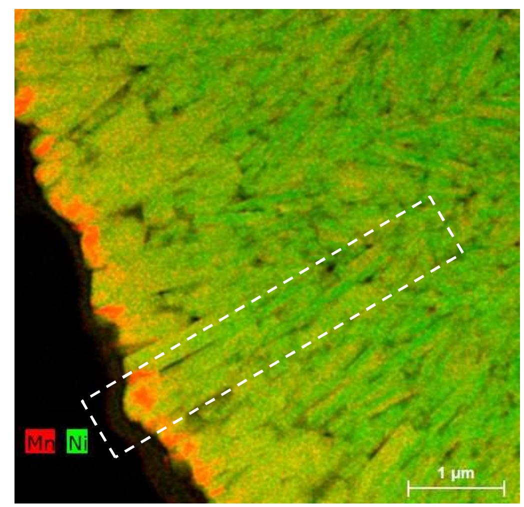
FCG $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$









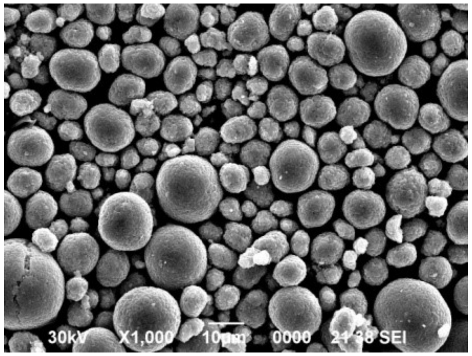


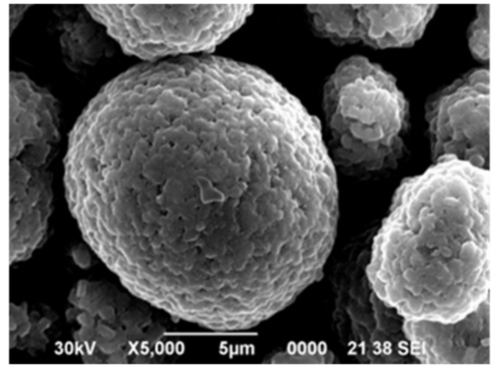
Nature material 11, 942 (2012)

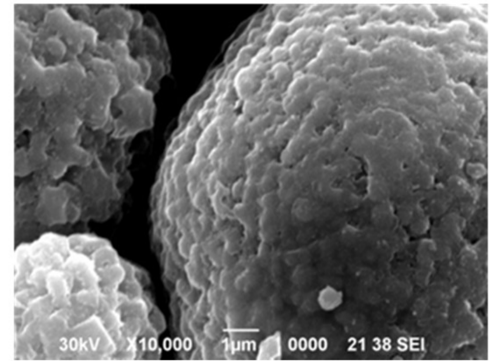
ANL patent: No: 8,591,774 (2013)

Comparison of morphology of FCG 6:2:2 and NMC 6:2:2

Caoted NMC (6:2:2)
Densiy: 2.5g/cc

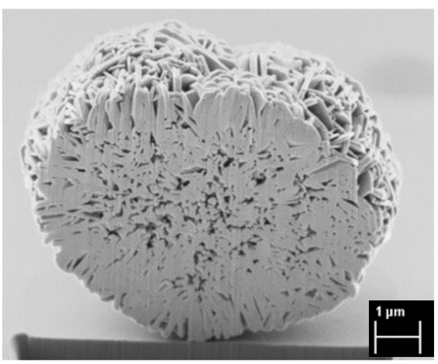


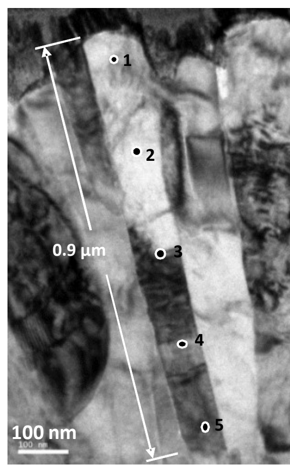




Primary particles are spherical and lithium move trough grain boundaries, extraction of lithium is not high at low voltage

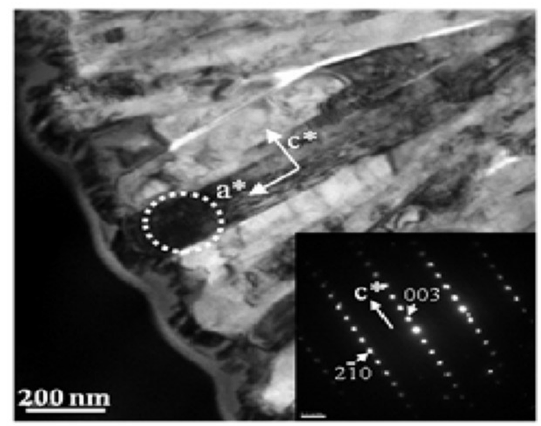
FCG 6:2:2
Density:2.7g/cc





	Co/Ni
1	0.291
2	0.286
3	0.274
4	0.253
5	0.246

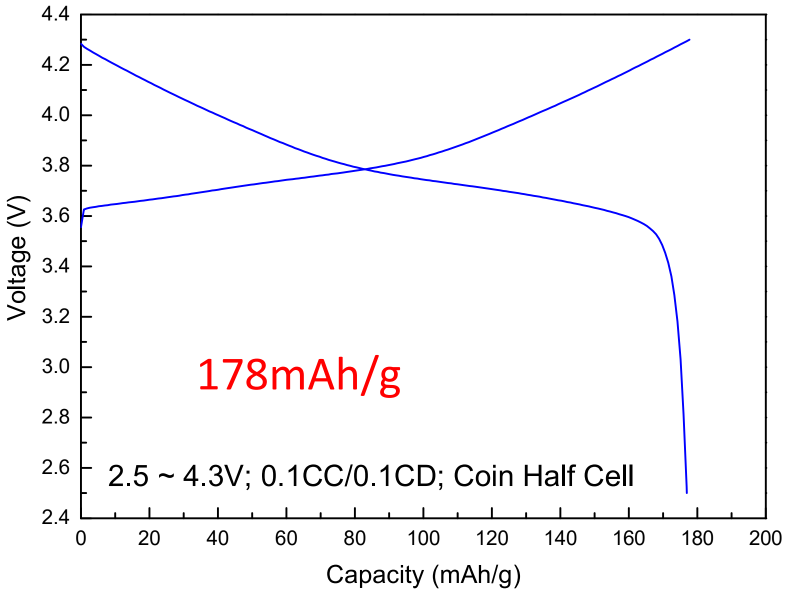
Primary particles are dense rode with gradient composition across the rode



TEM image showing the layered are parallel to the rod indicating high & fast lithium removal at low voltage.

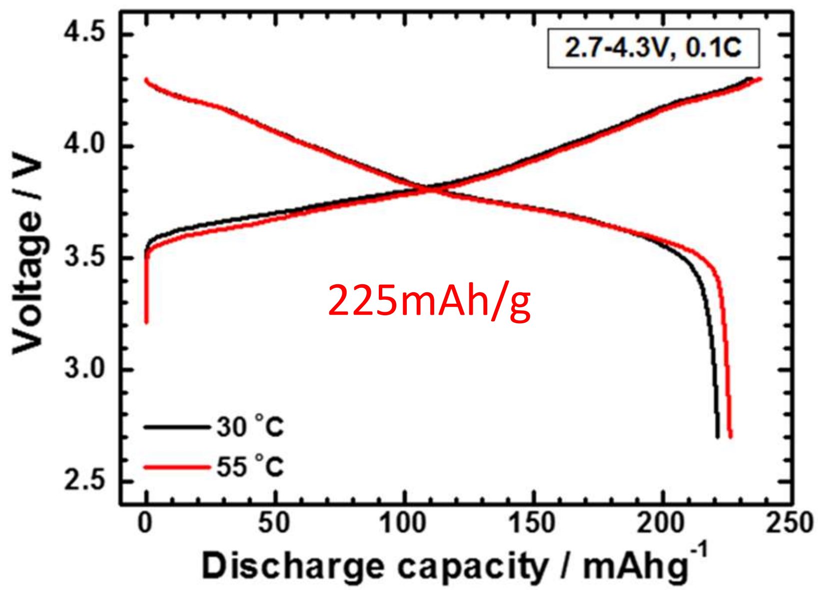
Comparison of first charge & Discharge of NMC 6:2:2 and FCG 6:2:2 Cathode vs Li

Commercial NMC (6:2:2)



The first charge capacity of caoted NMC 6:2:2 at 4.3V is 178 mAh/g

FCG 6:2:2

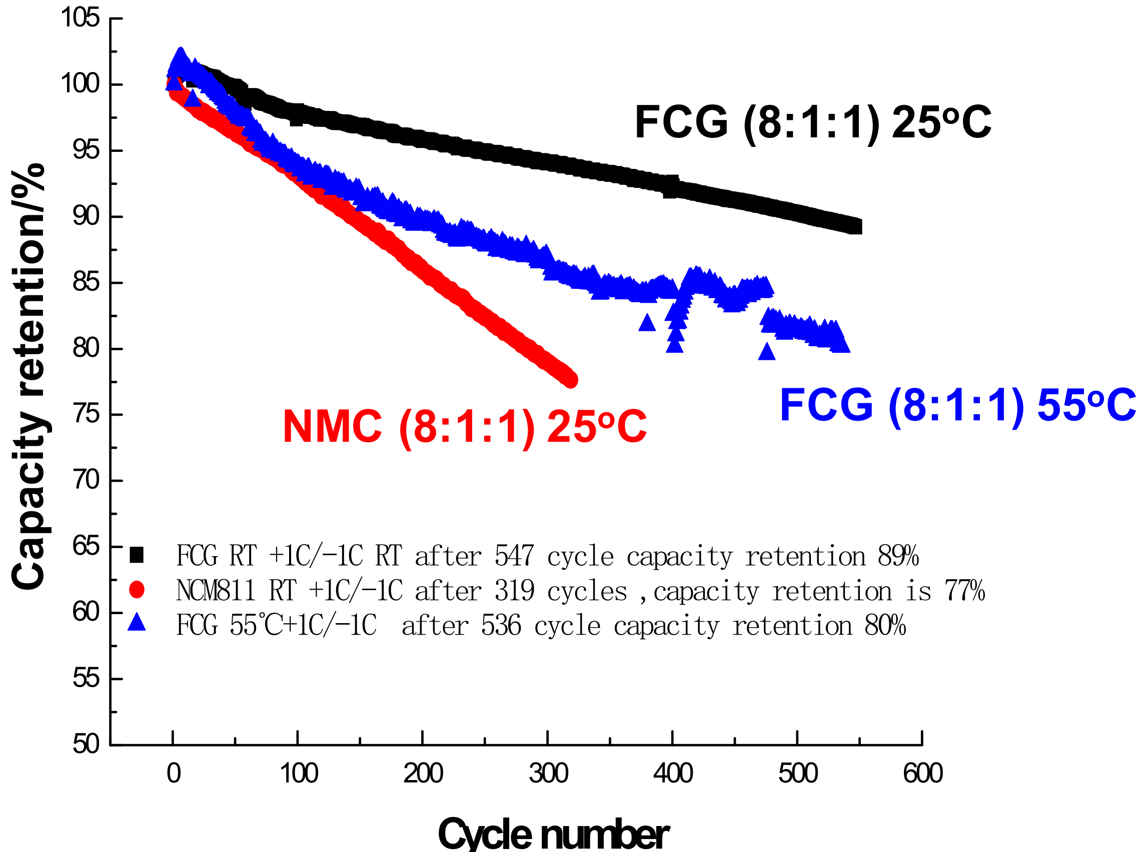


Initial cycling at 30°C and 55°C

Because of the unique morphology (layered parralel to primary particle rodes), the first charge capacity of FCG 6:2:2 at 4.3V is 225mAh/g

Cycling performance of 2Ah cells based on scaled FCG 811 (industrial partner) and NMC 811

Cut off voltage is 4.3V
Electrolyte: 1.2MLiPF6/EC:EMC+1%additive

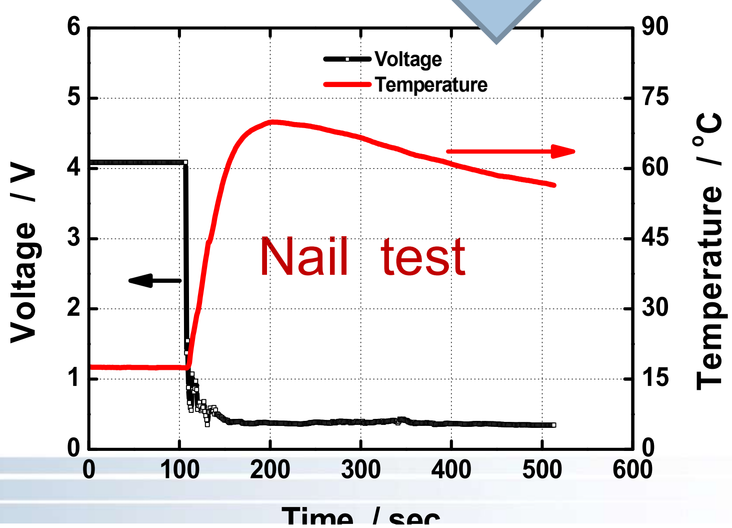


FCG 8:1:1 based cell shows much better cycle life than NMC8:1:1 and outstanding safety.

Nail penetration test; charged to 4.2 V

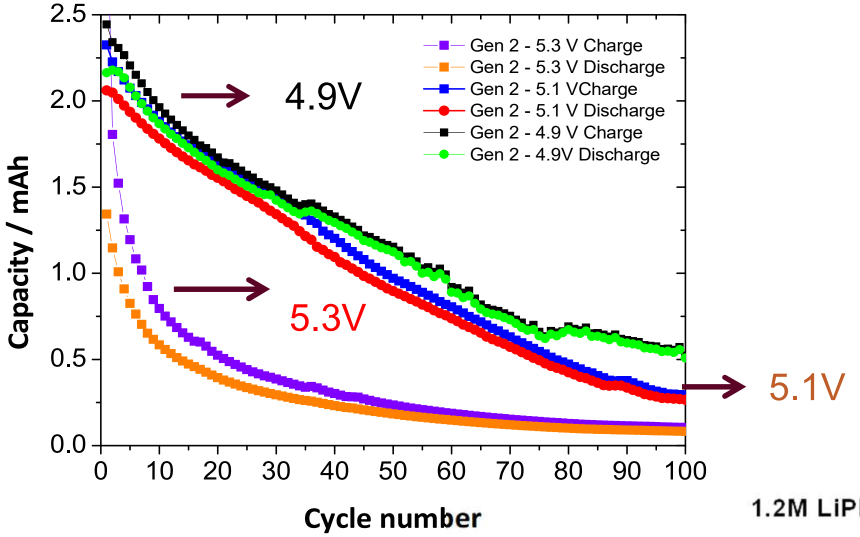
Nail test (Conventional NCA system)

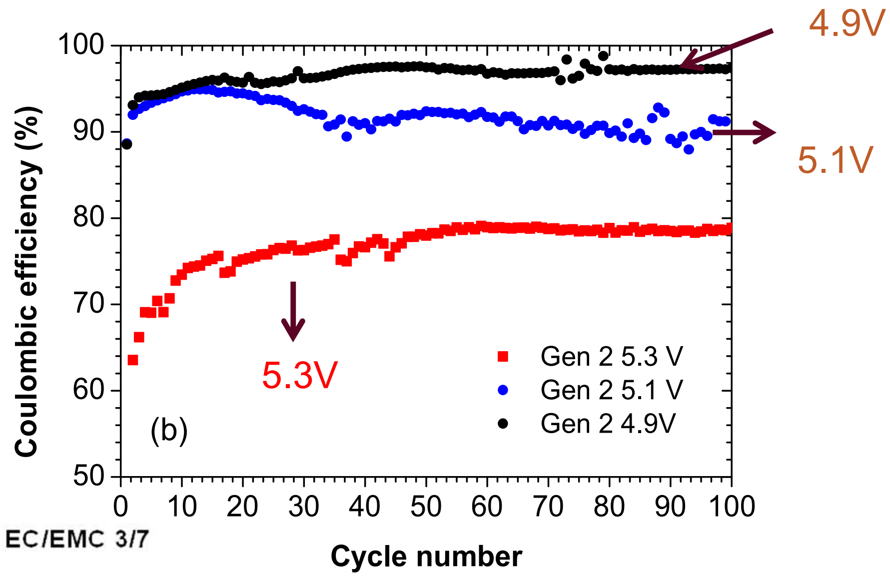
Nail test for FCG cell



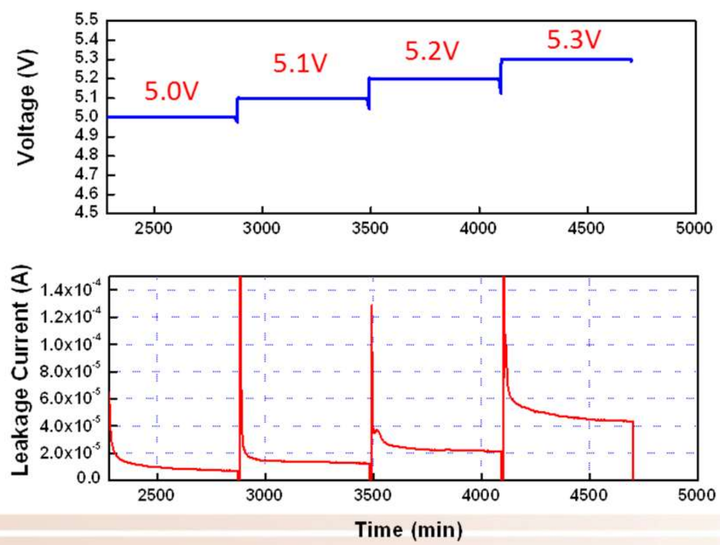
High Voltage electrolytes are needed to enable high energy cathode materials

4.80V $LiNi_{0.5}Mn_{1.5}O_4$ / Graphite Couple 1MLiPF6/EC;EMC

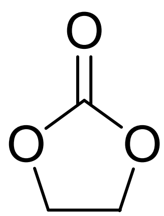




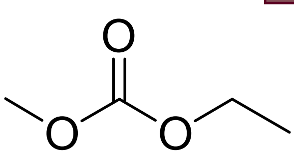
1.2M $LiPF_6$ EC/EMC 3/7



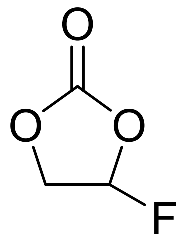
Fluorinated solvenst as potential electrolyte for high voltage and high energy cathodes



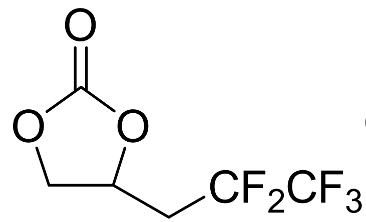
EC



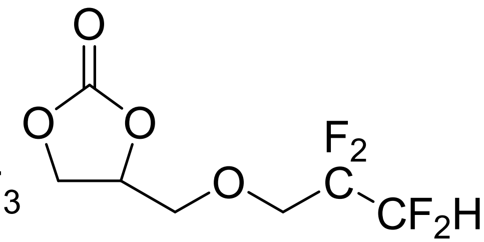
EMC



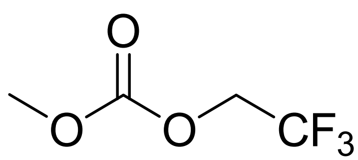
Fluoro-EC



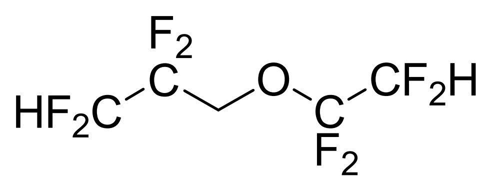
Fluorinated Alkyl-EC



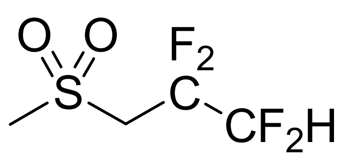
Fluorinated Ether-EC



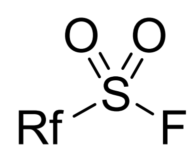
Fluorinated Linear Carbonate



Fluorinated Ether

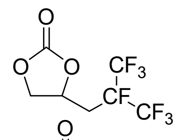
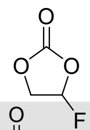
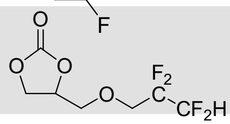
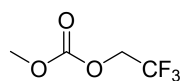
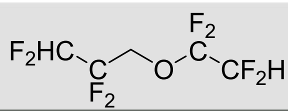


Fluorinated Linear Sulfone



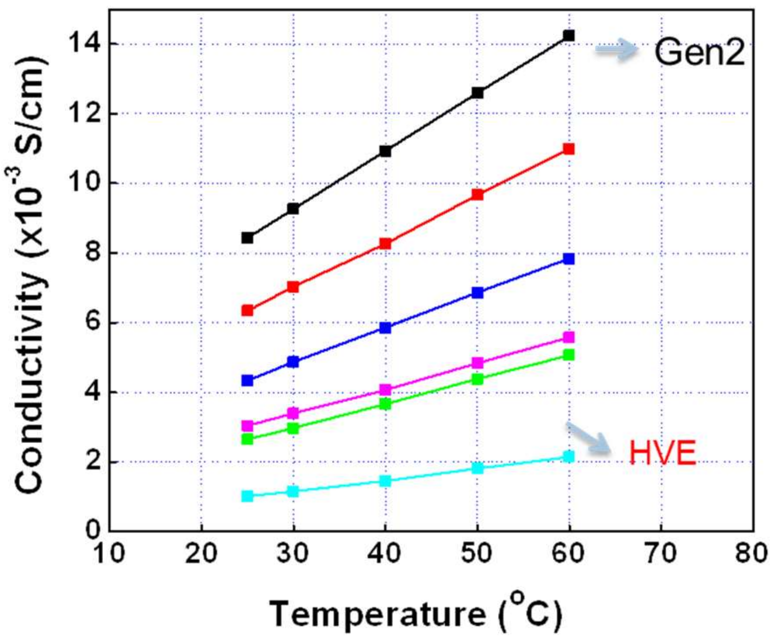
Fluorinated Sulfone

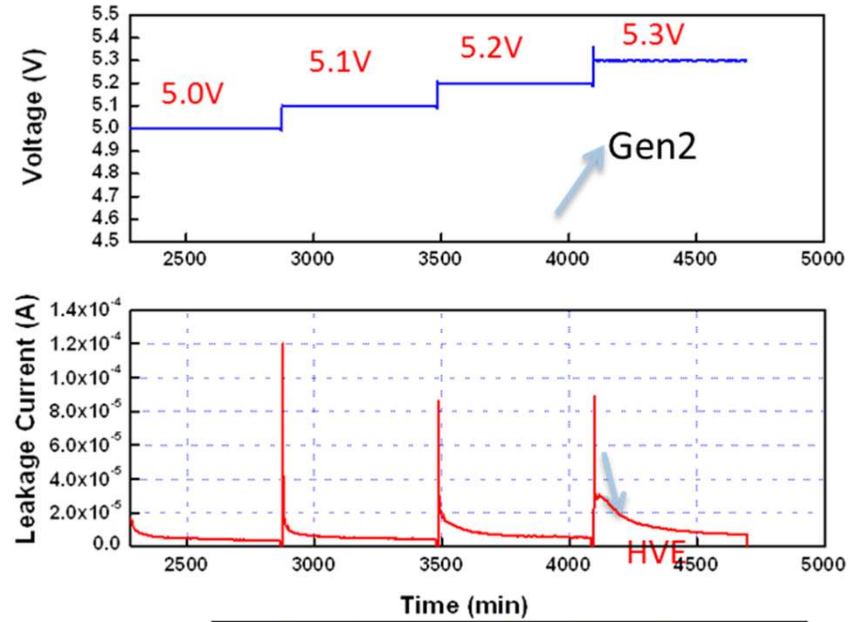
DFT Calculation to Predict the Oxidation Stability of Fluorinated Carbonate Compounds

Code Name	Chemical Structure	P_{ox} [a] / V	P_{red} / V
FCC-1		6.97	1.69
FEC		7.16	1.63
FCC-3		6.93	1.50
FLC-1		7.10	1.58
FE-1		7.29	1.82

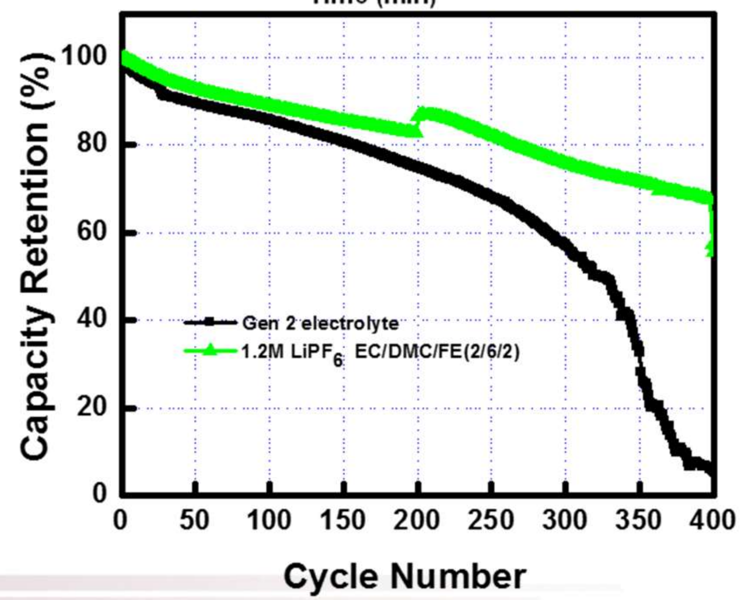
Characteristics of fluorinated High Voltage Electrolyte

$LiNi_{0.5}Mn_{1.5}O_4$ / LTO Couple





[redacted]



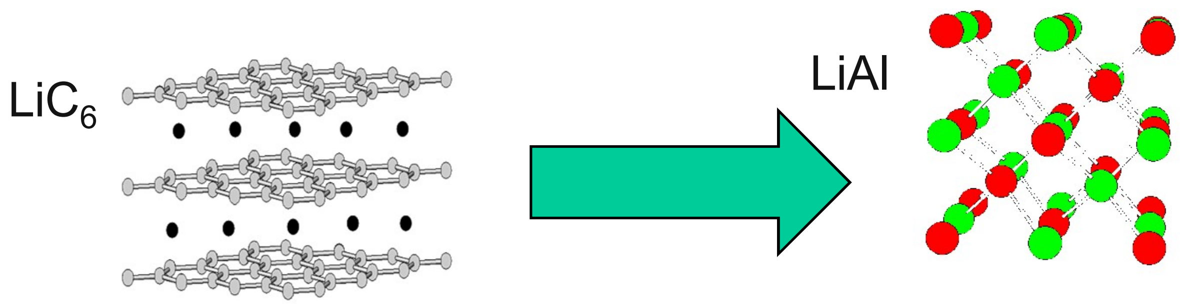
Increase battery Energy by increasing anode capacity

- Non-carbonaceous anode materials : Li – storage metals

  Lithium Alloys : Li_xM (M = Si , Sn , Al , Sb etc)

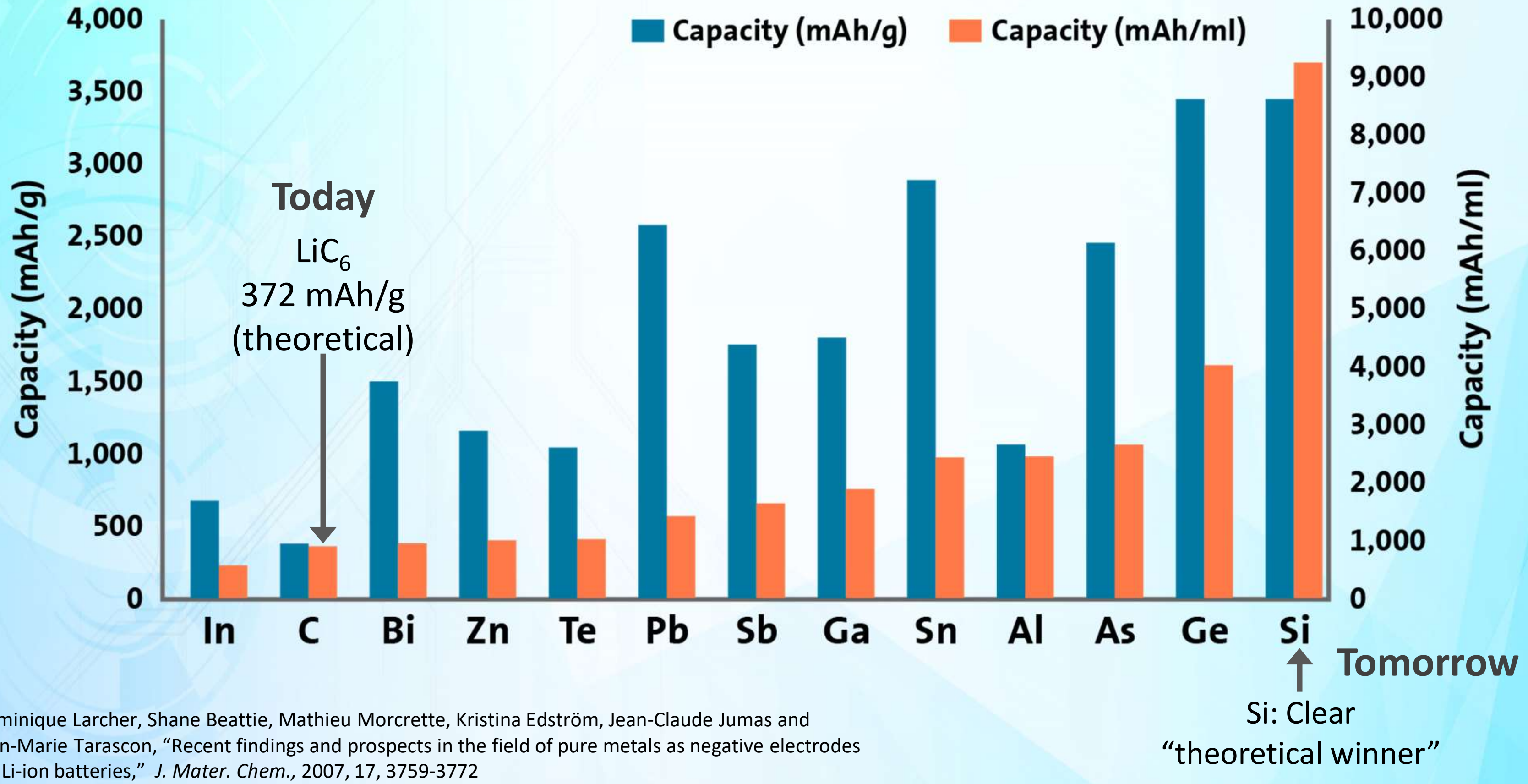
$$xLi + xe^- + M \underset{discharge}{\overset{charge}{\rightleftarrows}} Li_xM$$: Conversion reaction (reversible)

- Metals that alloy with Li



										He
					B	**C**	N	O	F	Ne
					Al	**Si**	P	S	Cl	Ar
Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Ru	Rh	Pd	Ag	Cd	In	**Sn**	**Sb**	Te	I	Xe
Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Ru

HIGH CAPACITY ELECTRODES: LITHIATED SI



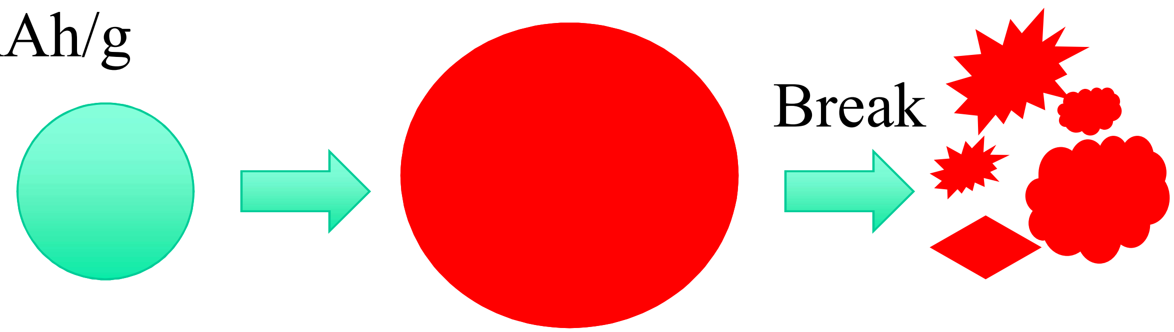
Dominique Larcher, Shane Beattie, Mathieu Morcrette, Kristina Edström, Jean-Claude Jumas and Jean-Marie Tarascon, "Recent findings and prospects in the field of pure metals as negative electrodes for Li-ion batteries," *J. Mater. Chem.,* 2007, 17, 3759-3772

Increasing the Energy by Replacing Graphite with Si-based Anodes

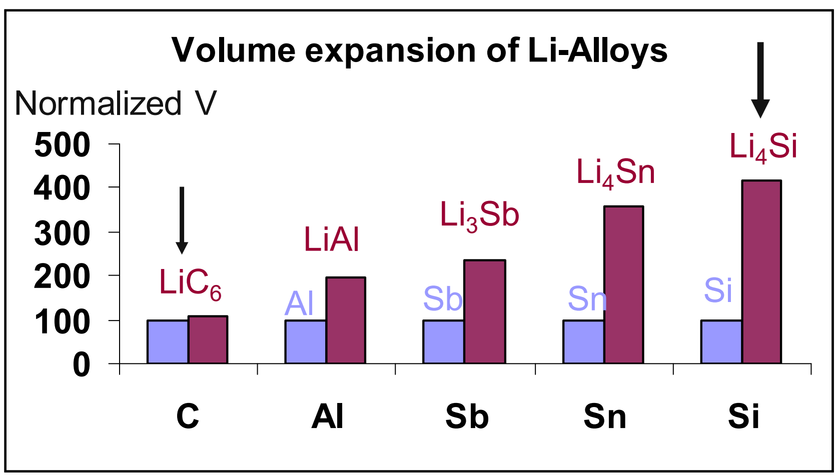
$$Si \longleftrightarrow Li_{4.4}Si \quad 4200\ \text{mAh/g}$$

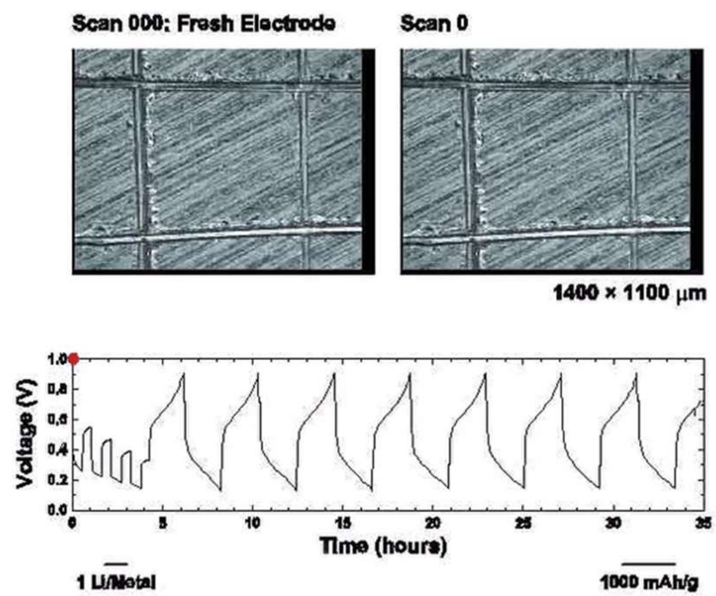
$$C_6 \longleftrightarrow LiC_6 \quad 370\ \text{mAh/g}$$

Individual particle:



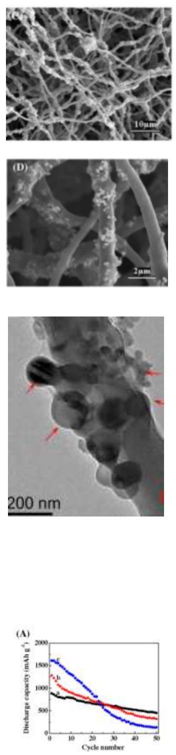
For Si: volume expansion to 4 times





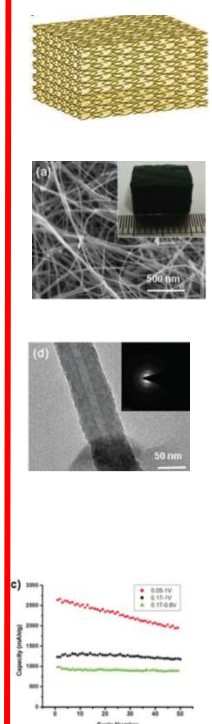
Many Fundamental design concept based on silicon and carbon as anode: Major Issue Scalability!

Si particles embedded and attached on carbon fibers



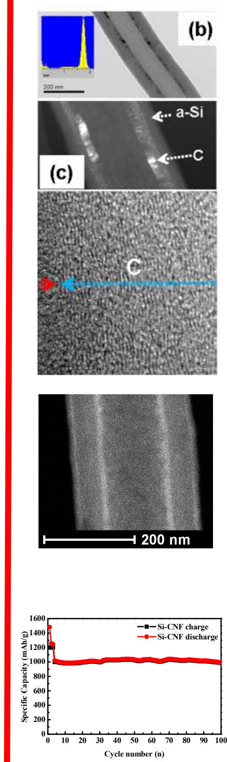
Cycles 50

Si–Carbon Nanotube Coaxial Sponge



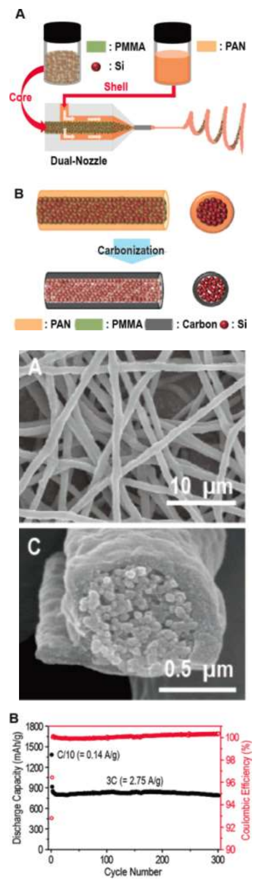
50

a-Si coated on carbon Nanotube Coaxial Sponge



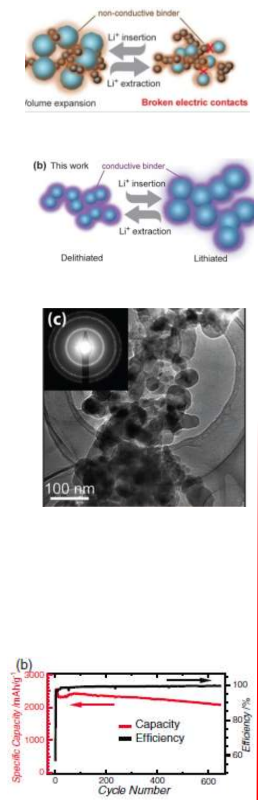
100

Si nanoparticles wrapped by a carbon sheath



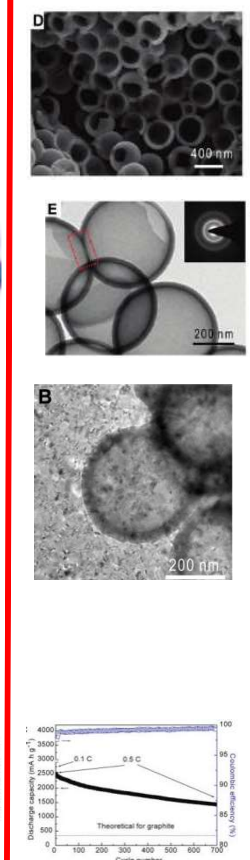
300

Si nanoparticles bounded by conductive polymer



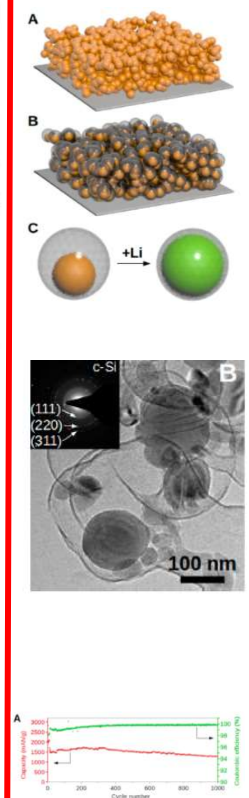
600

Interconnected Silicon Hollow Nanospheres



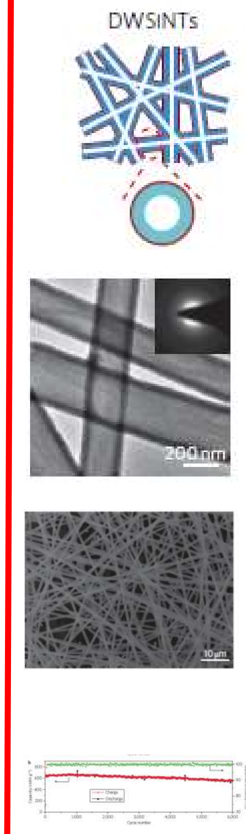
700

Yolk shell design of Si in carbon



1000

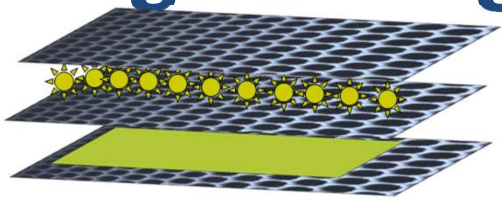
Double wall Si nanotube with oxide

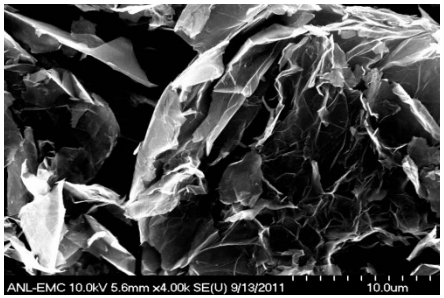


6000

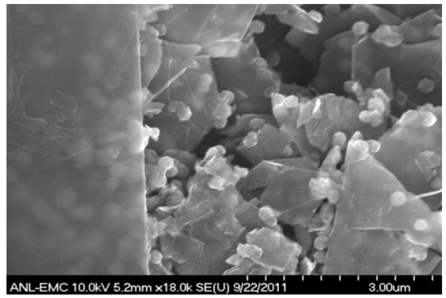
Tae Hoon Hwang et al, Nano Lett. 2012, 12, 802–807;
Liwen Ji et al, Carbon, 4 7 (2 0 0 9) 3 2 1 9 –3 2 2 6; Yao Y, et al. (2011), Nano Lett., 11, 2949–2954 (2011); Gao Liu et al, Adv. Mater. 2011, 23, 4679–4683; Liangbing Hu et al. Adv. Energy Mater. 2011, 1, 523–527, Wu et al, Nature Nanotechnology, 2012, Liu et al, Nano Letters, 12 (2012) 3315.

High Energy Si-graphene based Anodes

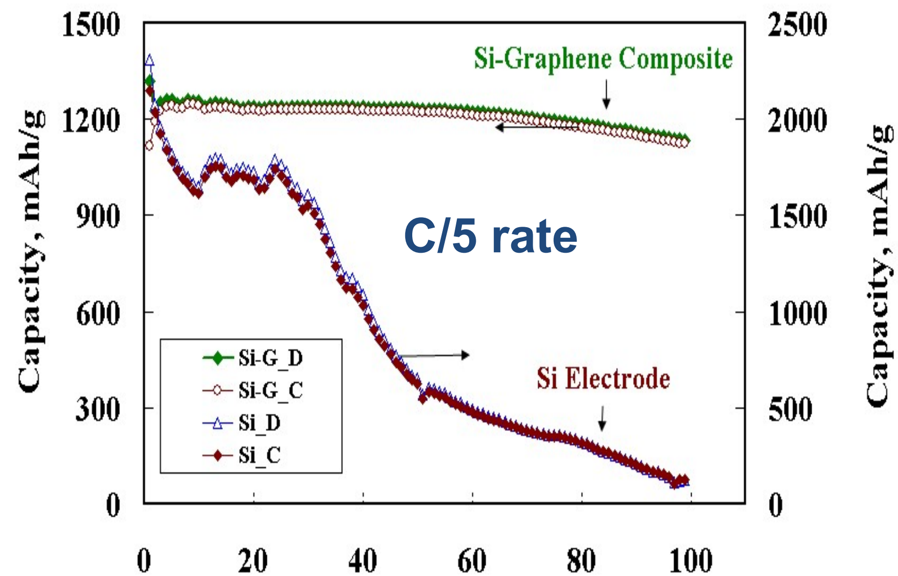




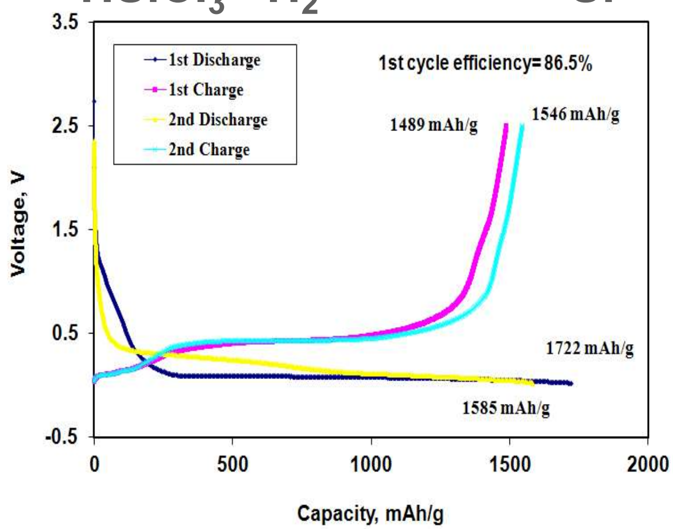
Graphene

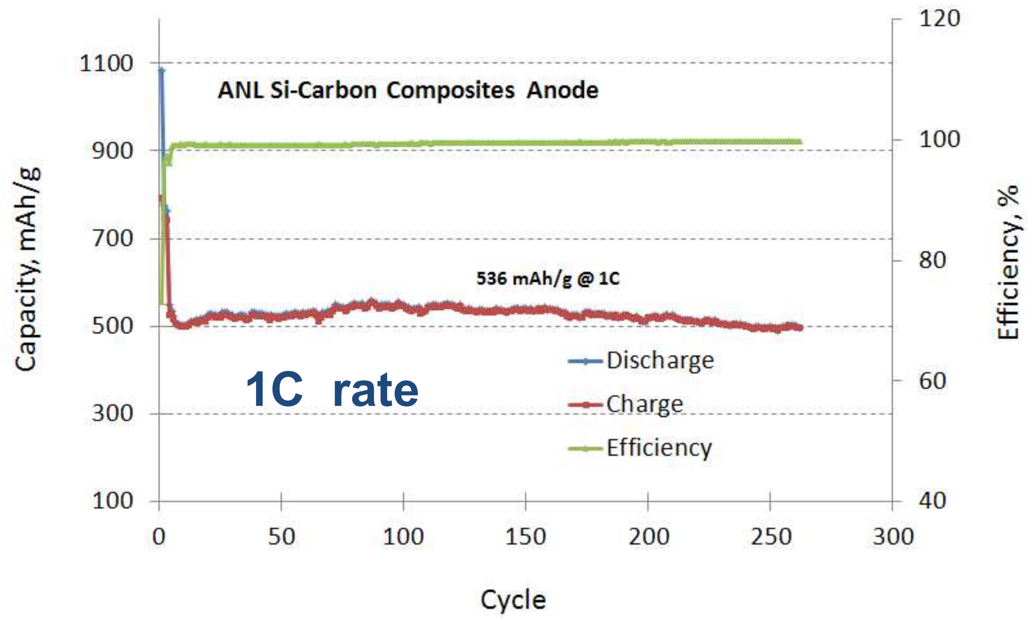


Si-Graphene

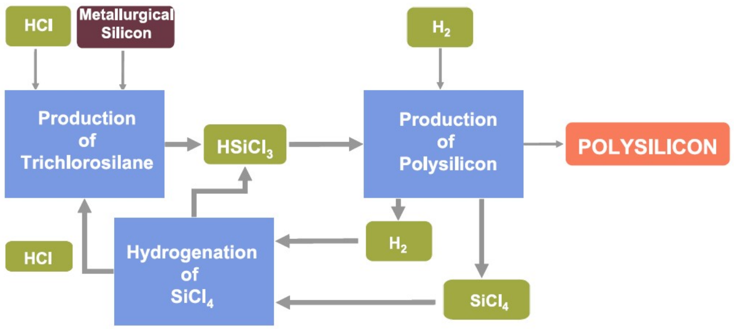


$HSiCl_3 + H_2$--------- $Si + 3HCl$





Integrated process for silicon can be used to scale up Si-Graphene composite anode

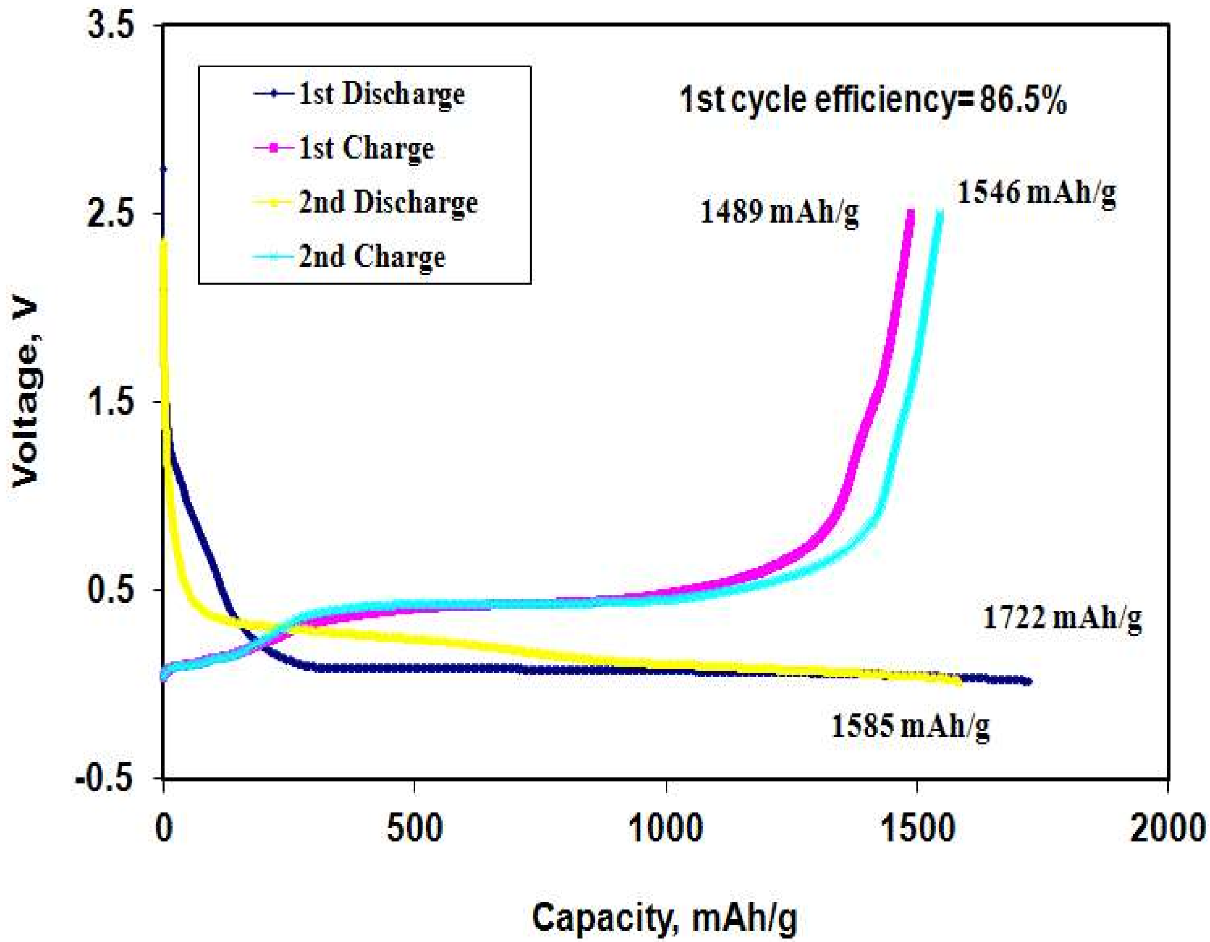


$$SiCl_4(g) + 2H_2(g) \rightleftharpoons Si(s) + 4HCl(g)$$

$HSiCl_3 + H_2$--------- $Si + 3HCl$

- **Trichlorosilane(TCS) Siemens Reactors**
  - Hemlock
  - Wacker
  - Mitsubishi
  - Tokuyama
  - MEMC
  - Newcomers e.g. M. Setek, OCI (ex DCC), GCL, Nitol, LDK etc.
- **Silane Siemens Reactors**
  - REC
- **Fluid Bed Reactors (Granular)**
  - MEMC (Silane based)
  - REC (Silane based)
  - Wacker (TCS based)
- **Upgraded Metallurgical (UMG)**
  - Elkem
  - Others e.g. Timminco, 6N.

Major challenges for Si anode is poor efficiency in the first



Major challenges of efficiency in First scyle when switching to Si or Sn based anode

- Graphite anode has a capacity of about 350 mAh/g. (CE:90%)

- Silicon, tin and alloys based material provide 700-3000 mAh/g capacity (CE:60-80%) (need significant excess of cathode to compensate for the large irreversible loss at the anode)

Solution to Large Irreversible loss in Si based Anode

- Partially replace $Li_xM_yM'_zO_u$(160 mAh/g) by a material "Li_2O" (with a capacity of ~ 1650 mAh/g).

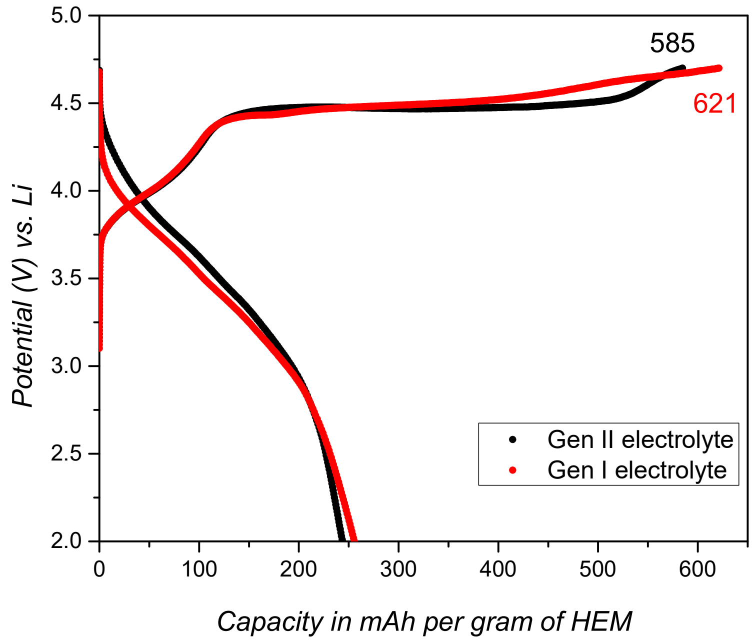
- No need of large cathode extra weight for silicon anode.

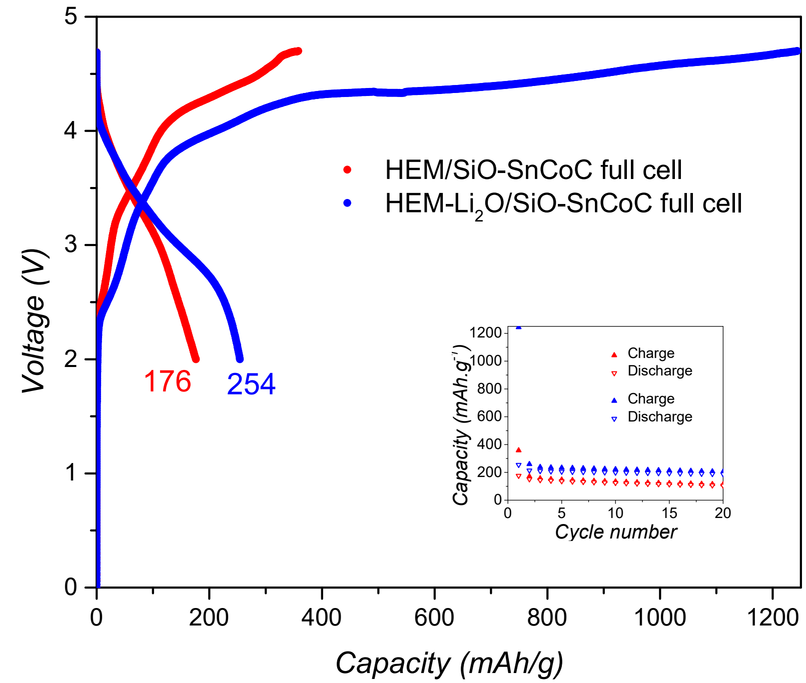
5% of the high capacity Li_2O material can do the job

ANL Patent: K. Amine et al. US 9,012,091 ; April 21, 2015

Li_2O as source of pre-lithiaion

HEM and Li2O are hand mixing



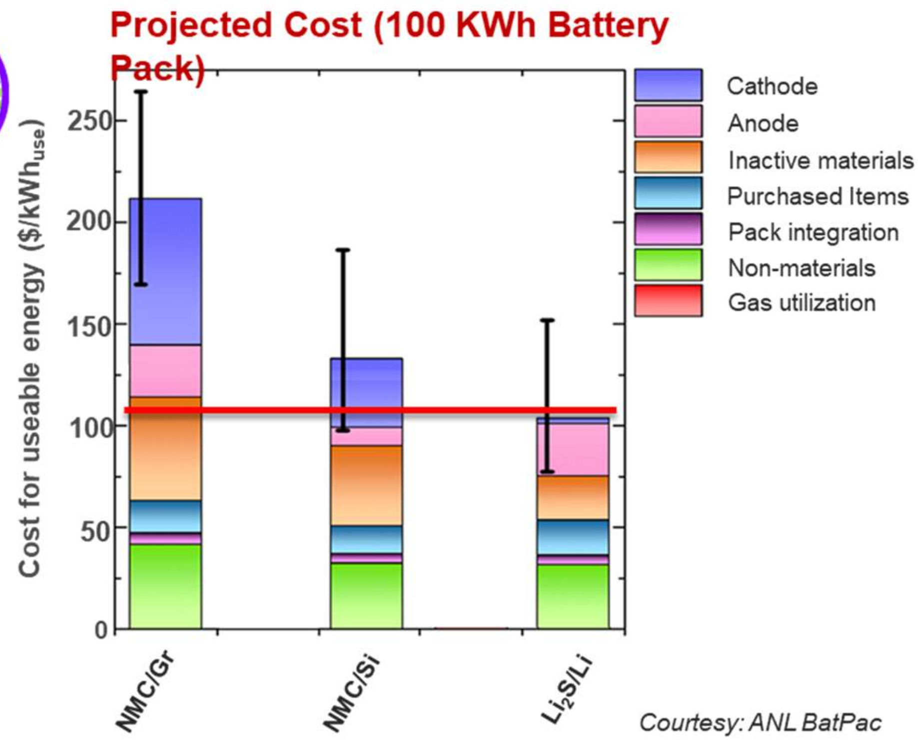


- Higher capacity is obtained with HEM-Li_2O/Li half-cell . (2 times the capacity of he HEM material).

First-cycle voltage profile versus capacity and cycling performance (inset) of HEM–Li_2O/SiO-SnCoC and HEM/SiO-SnCoC full cells.

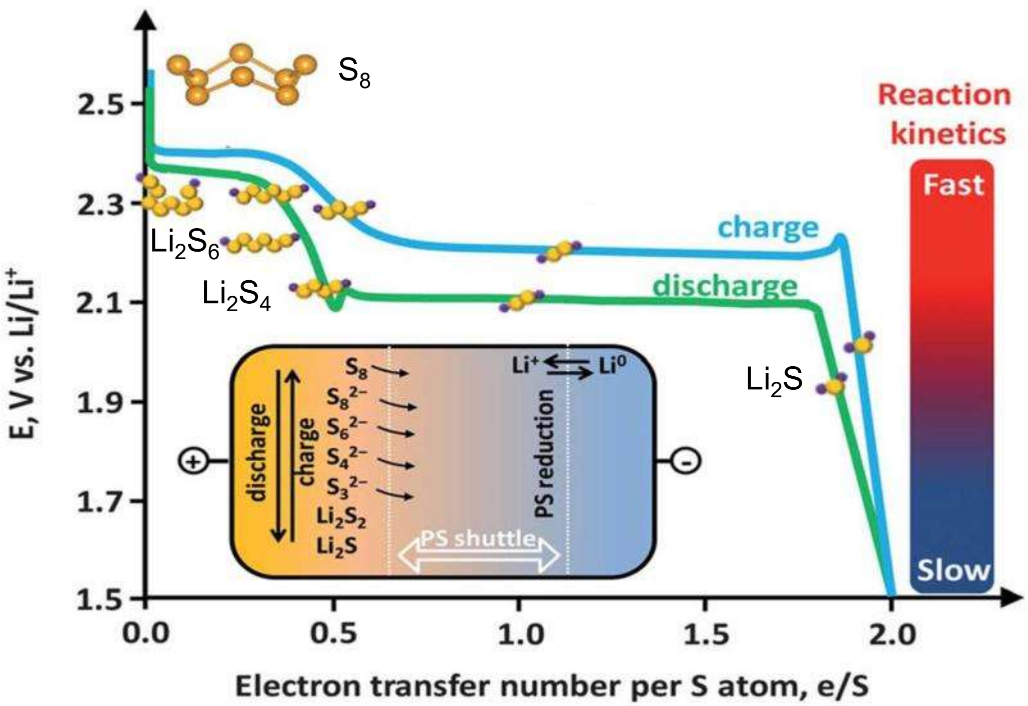
Projected Cost of Battery pack using different technology

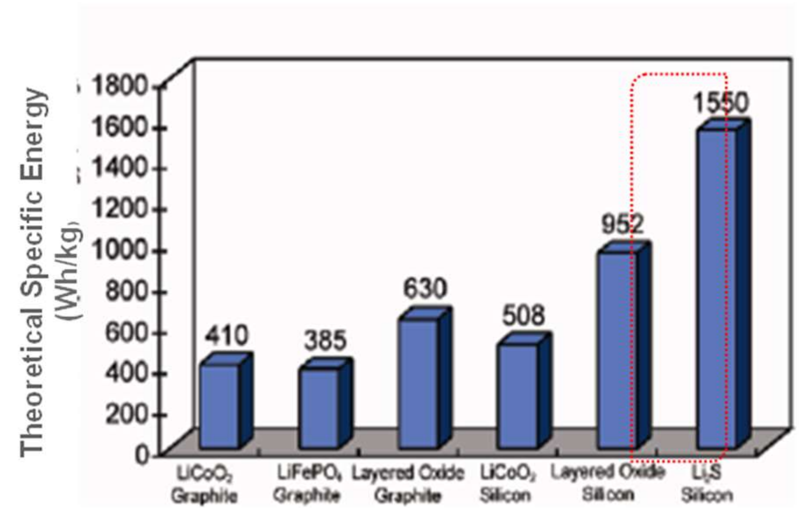
Techno-economic modeling of grid and transportation batteries

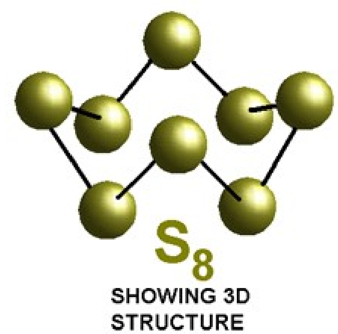


Courtesy: ANL BatPac

The lithium- sulfur battery



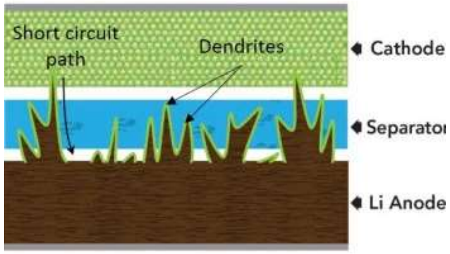




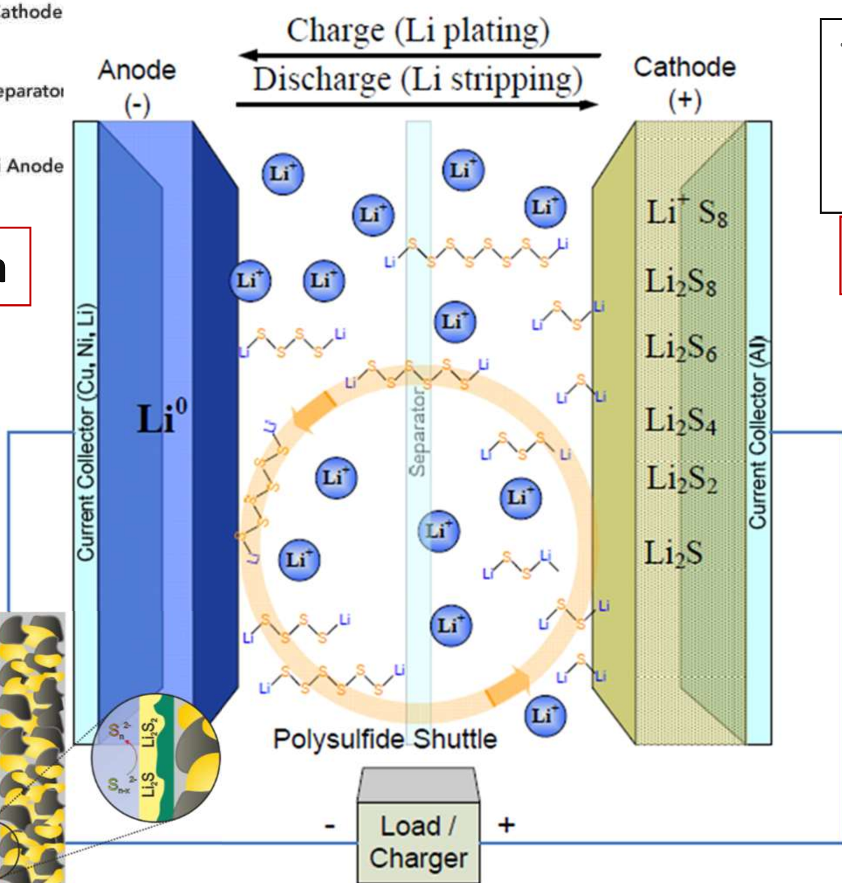
Two-electron reaction
1,672 Ah/kg; 2,500 Wh/kg
Abundant, environ. benign

$S + 2Li^{+} + 2e^{-} \leftrightarrow Li_2S$

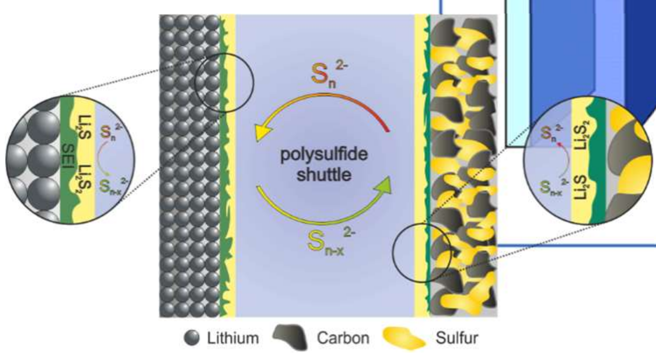
Challenge Issues



Li dendrite growth



Lithium Sulfur Battery



Polysulfide shuttle

The high resistance of sulfur (~10^{-30} S cm^{-1}) and the intermediate products.

Low Conductivity of S and Li_2S

Low mass-loading of sulfur

Self-Discharge

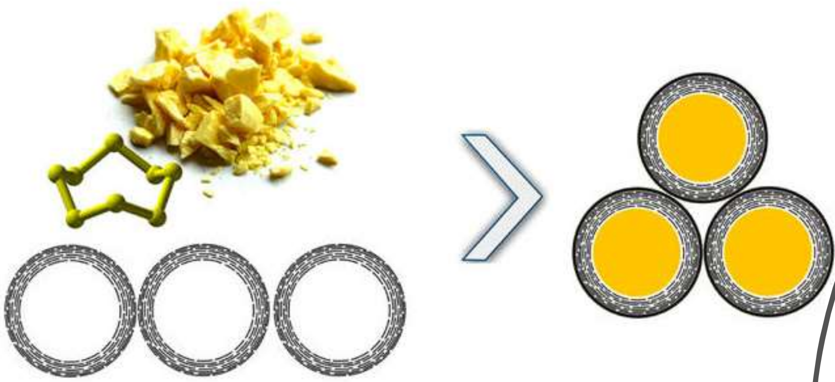
The volume expansion when sulfur is fully converted to Li_2S is as large as 80%.

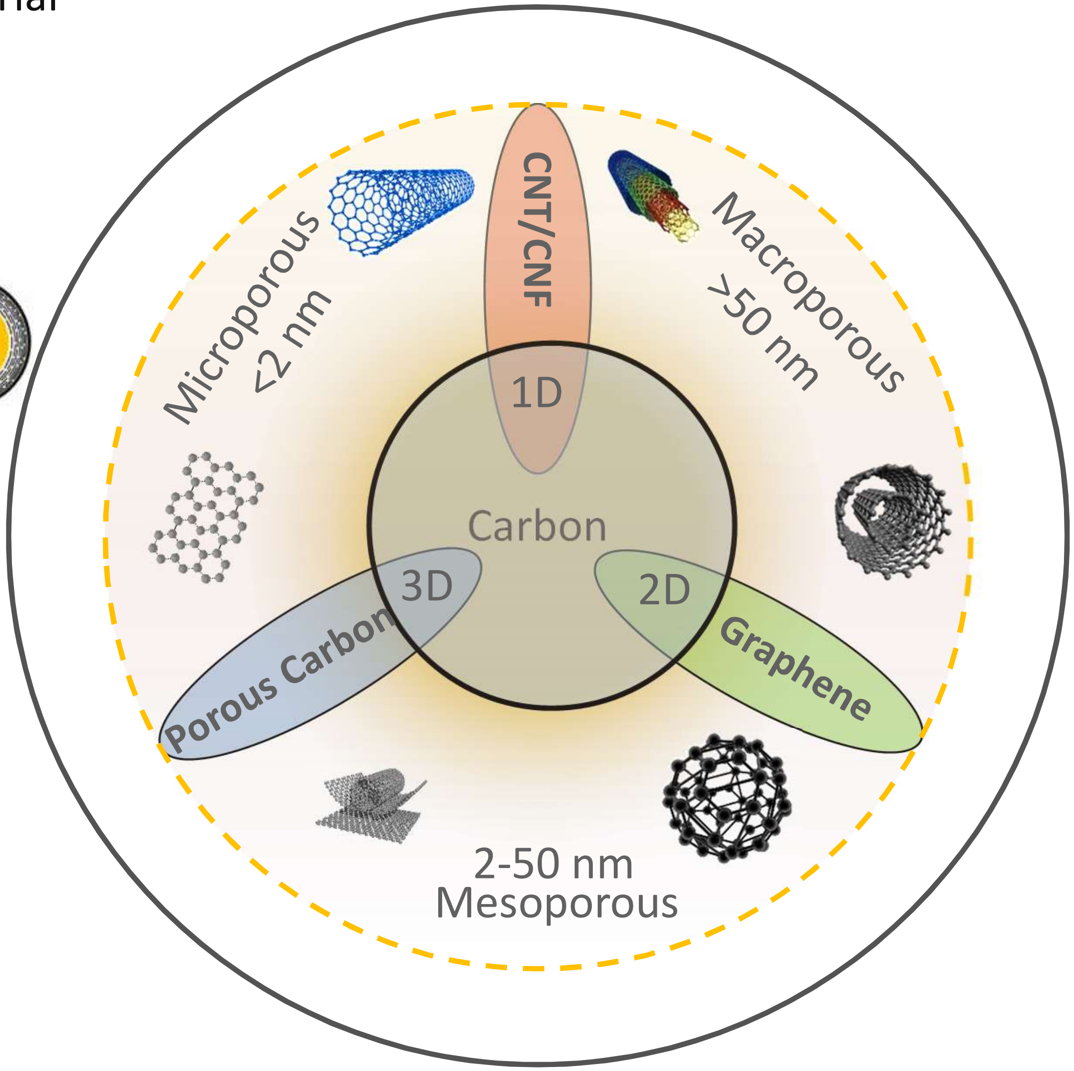
Cathode Volume Change

Y. S. Su, et al. Chem. Rev. 2014 ,114 , 11751 .
L. F. Nazar, et al. Nat. Commun. 2014 ,5 , 4759 .
K. Amine, et al. Adv. Energy Mater. 2015, 5, 1500408.

Current Solutions

Mix Sulfur with different Carbon Material



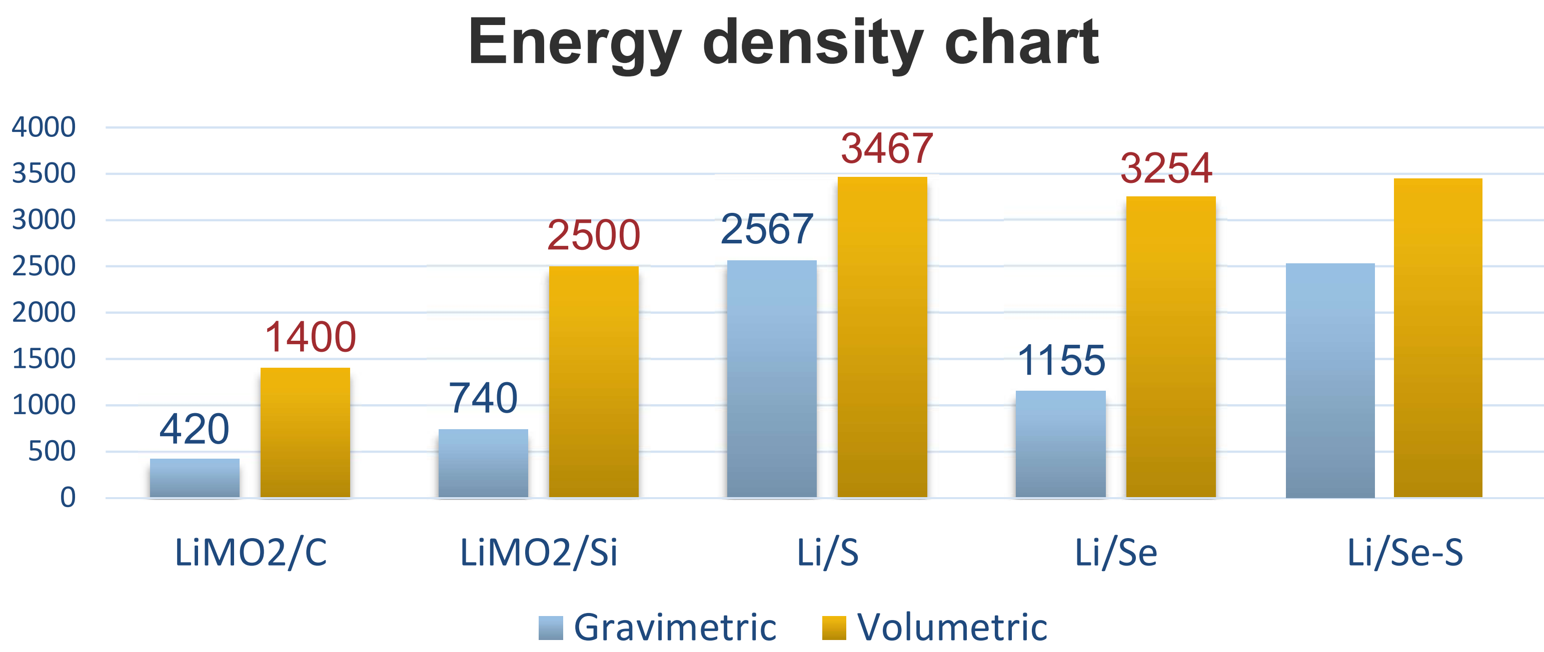


Advantages of Carbon materials:

- Enhance the active material utilization of the sulfur cathode.
- Immobilizing the active material.
- Constraining/trapping the dissolved polysulfides.
- Accelerating the charge transport.
- Absorbing/ channeling the liquid electrolyte.

Y. -S. Su., et al, Chem. Rev. 2014, 114, 11751−11787.

Novel SeS system as a replacement to Sulfur

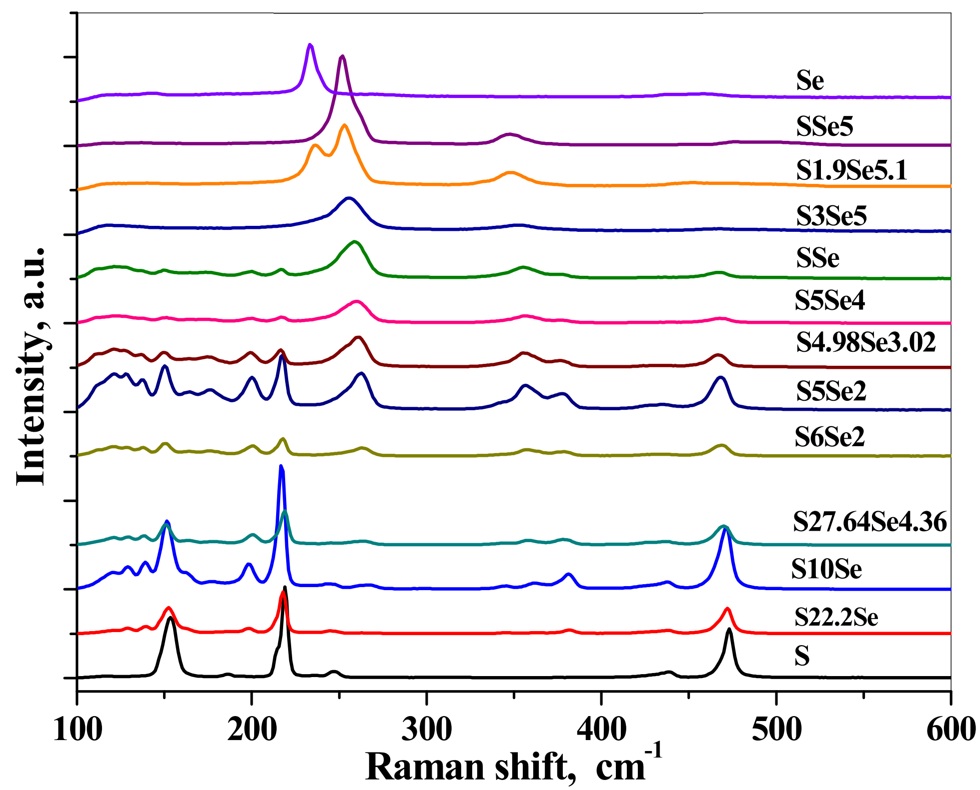


Selenium sulfur systems can lead to:

- Comparable energy density to Li/S battery
- High electrical conductivity (1E^{-3} vs. 5E^{-28} S/m for S)
- High active material loading, leading to high volumetric energy density

	Sulfur weight ratio
Se	0
SSe_5	7.5%
$S_{1.9}Se_{5.1}$	13.1%
S_3Se_5	19.6%
SSe	28.8%
S_5Se_4	33.6%
$S_{4.98}Se_{3.02}$	40%
S_5Se_2	50.3%
S_6Se_2	54.8%
S_4Se	61.8%
$S_{27.64}Se_{4.36}$	72.0%
$S_{10}Se$	80.2%
$S_{22.2}Se$	90.2%
S	100.0%

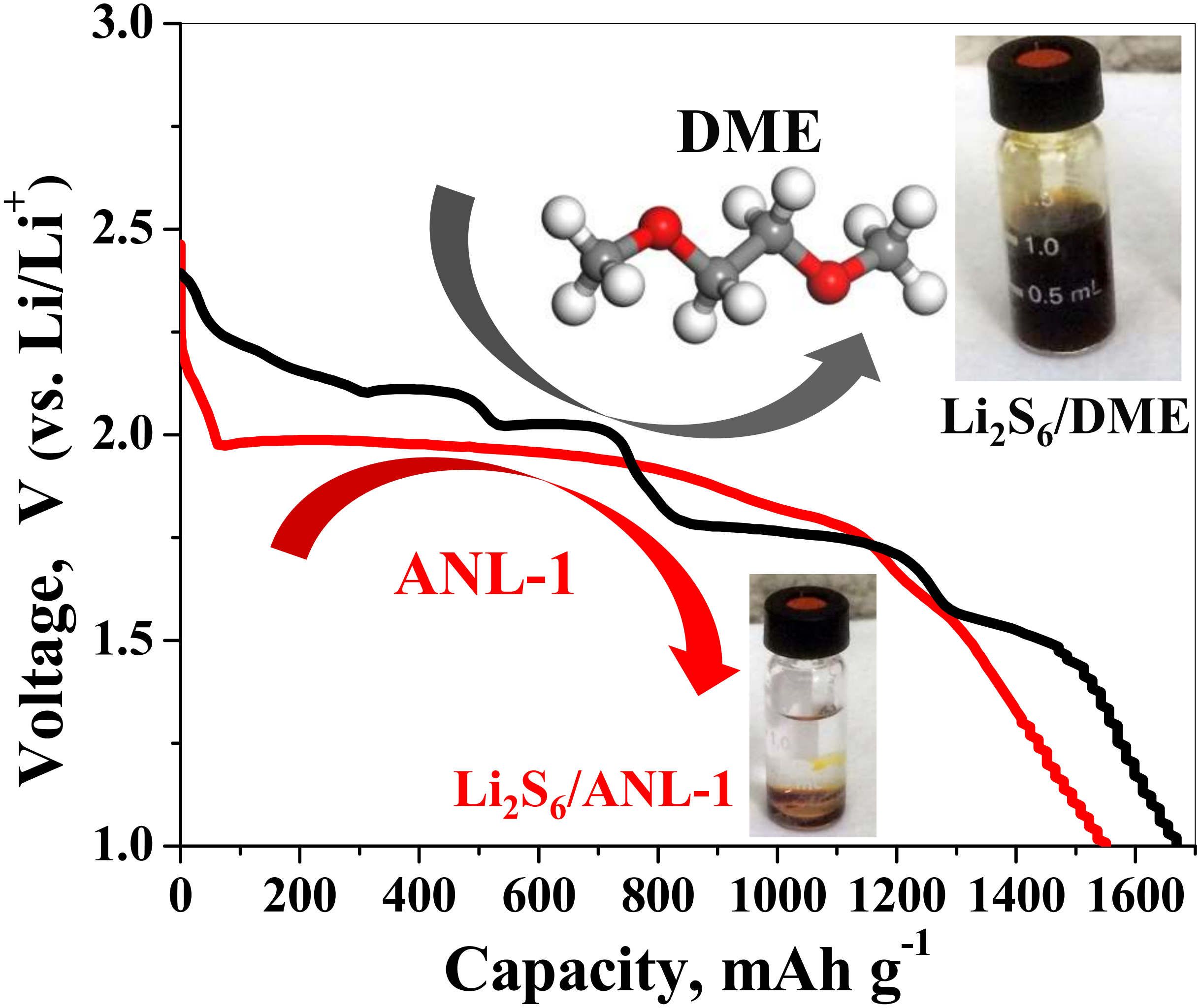
Raman spectra



Li/S_5Se_4 cell in ANL-1 electrolytes compared to DOL-DME

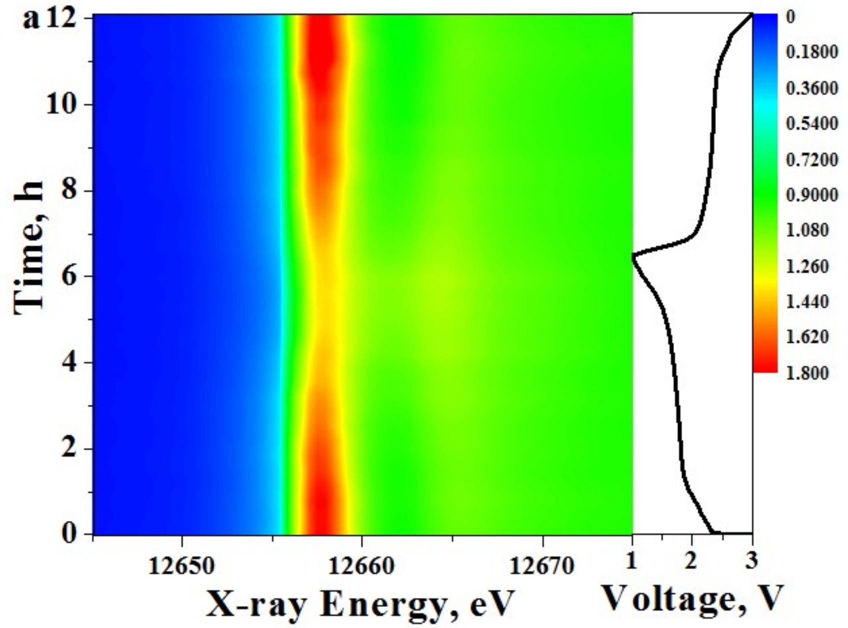
A new electrochemical reaction pathway

"from four plateaus to one long plateau"



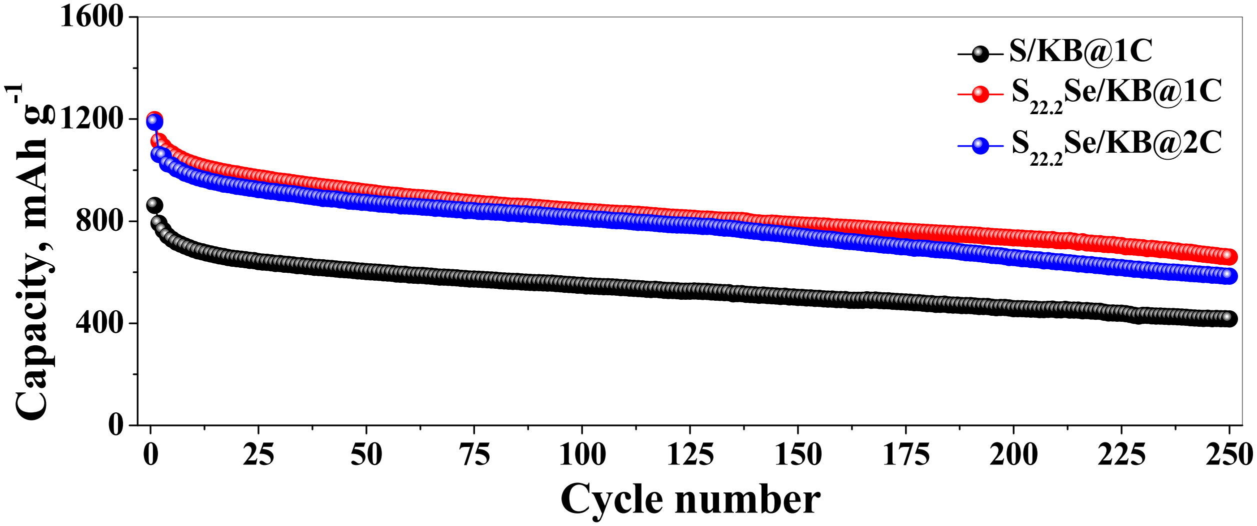
Operando Se K-edge XANES characterization of S_5Se_4/C composite-70 wt.% in ANL-based electrolytes

2D contour plot



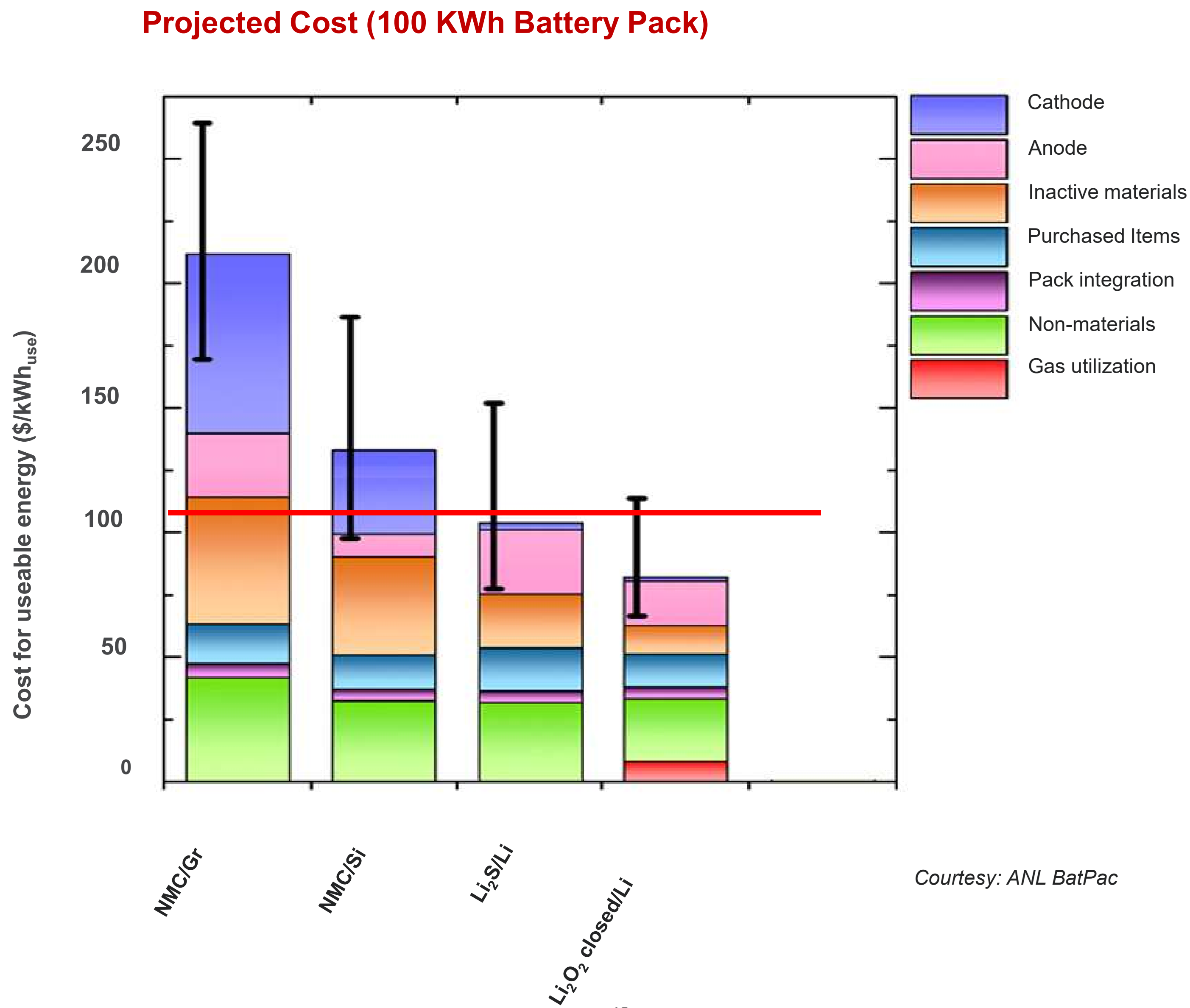
- Se K-edge position did not show clear shifts, but the absorption intensity decreased with discharging and recovered during charging
- The result confirmed that Se-S/KB cathodes undergo a solid-state lithiation/de-lithiation process in the ANL-based electrolyte

Rate performance of $S_{22.2}Se/C$ composite-70 wt.% in ANL-based electrolytes



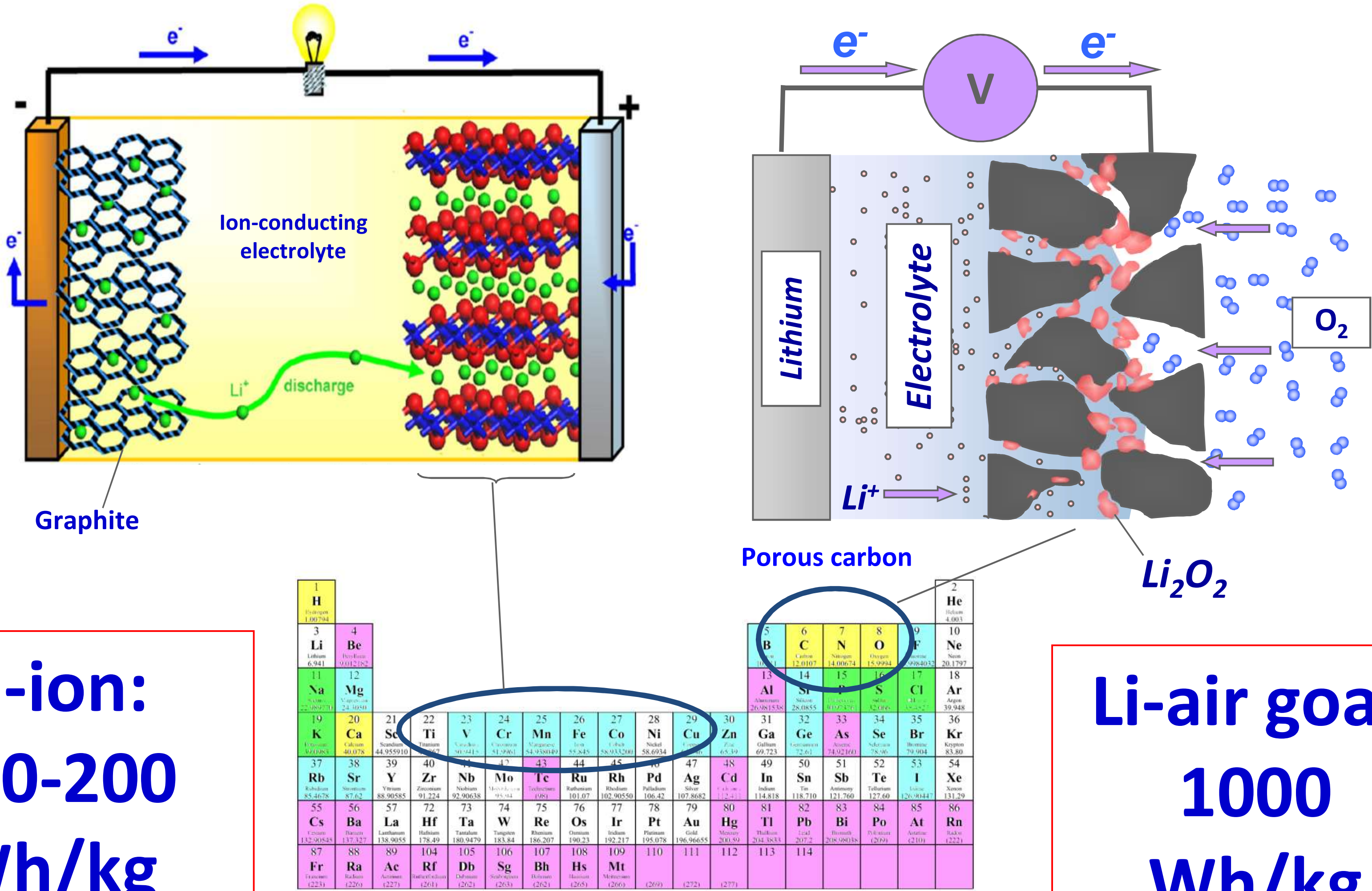
- Se-doped S cathode present higher reversible capacities and better rate capability than S cathode due to better electronic conductivity

Projected Cost of Battery pack using different technology



Courtesy: ANL BatPac

The Holy Grail of Batteries " Li-air"



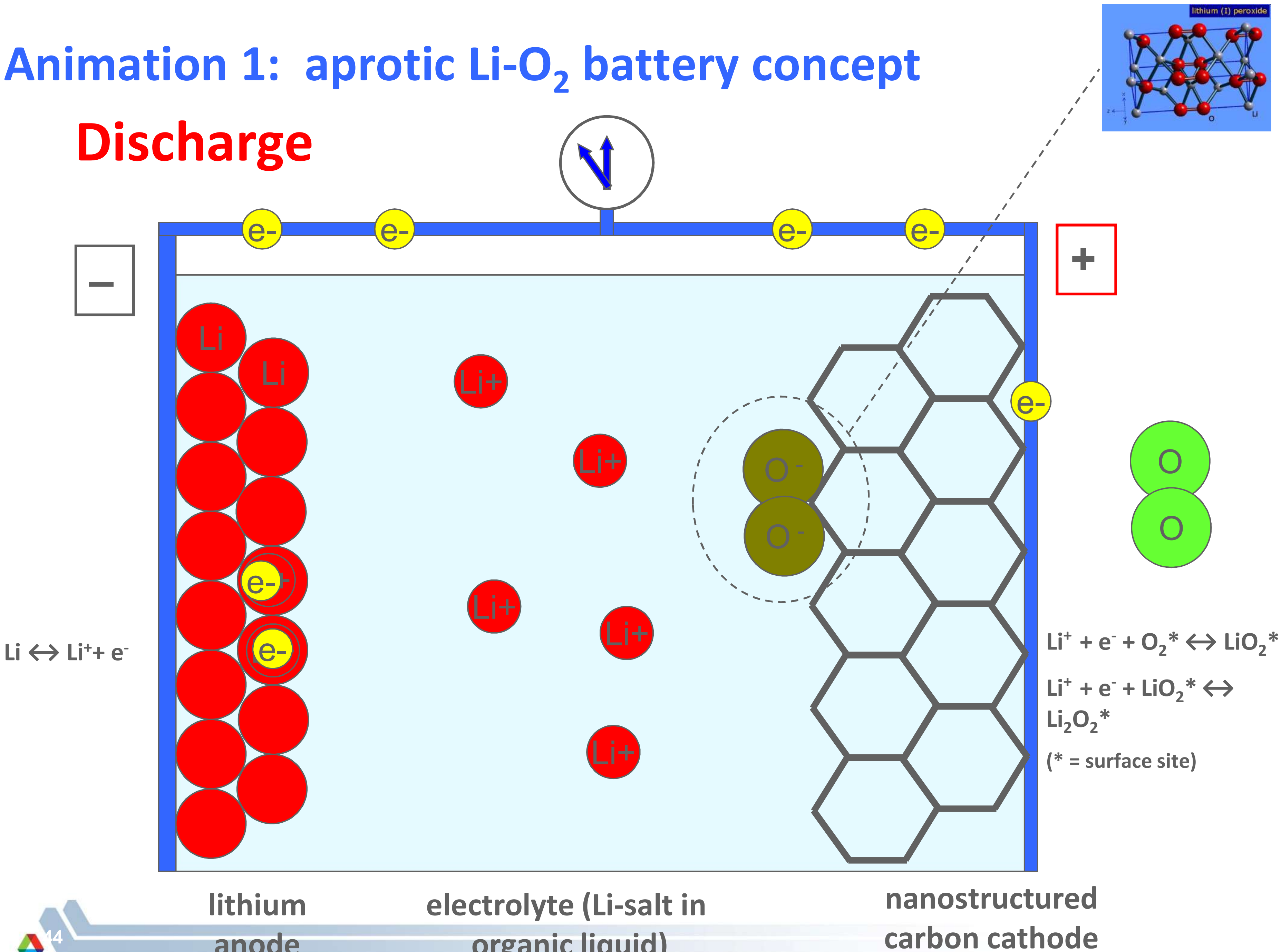
Li-ion: 100-200 Wh/kg

Li-air goal: 1000 Wh/kg (cell)

$$2Li^+ + O_2 + 2e^- \underset{\text{Recharge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2$$

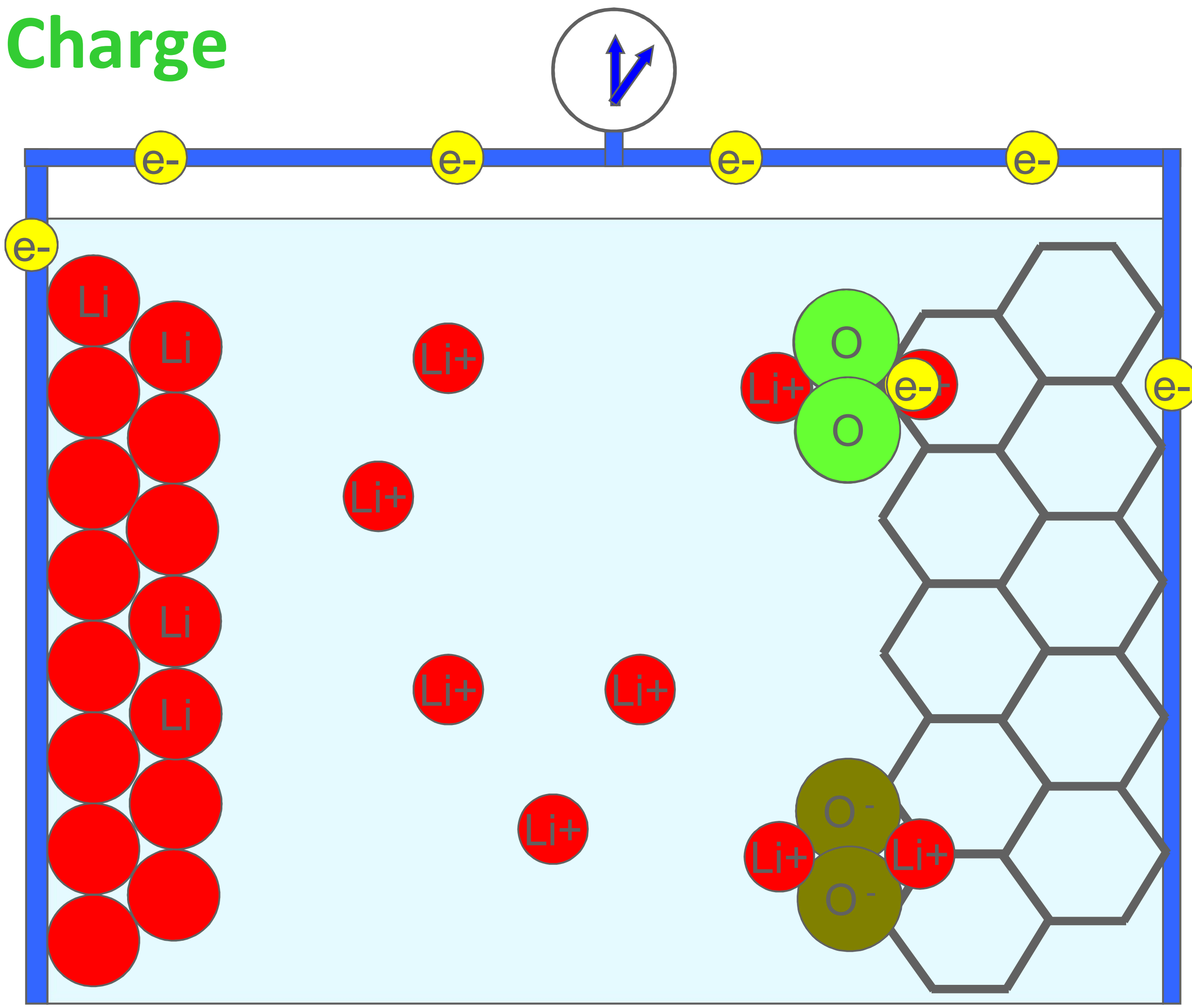
Animation 1: aprotic Li-O_2 battery concept

Discharge



Animation 2: aprotic Li/Air battery concept - CHARGE

Charge



$Li_2O_2 \leftrightarrow LiO_2 + Li^+ + e^-$

$LiO_2 \leftrightarrow O_2 + Li^+ + e^-$

$2Li^+ + 2e^- \leftrightarrow 2Li^0$

Basic Charge/Discharge Reaction of aprotic Li/air

$$2Li^{+} + O_2 + 2e^{-} \underset{\text{Recharge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2$$

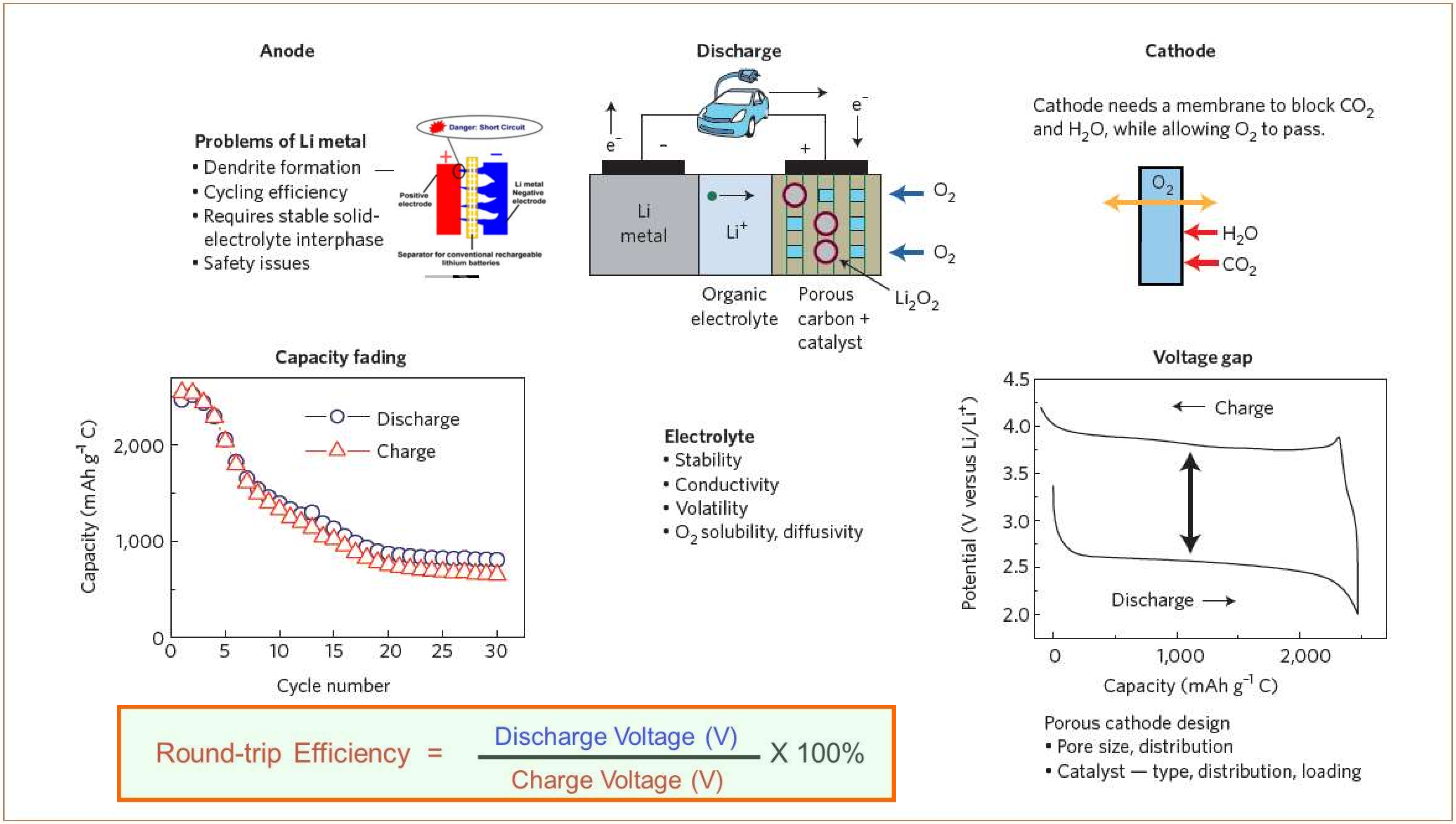
A Li/Air powered car will:

=> Use air while driving

=> Release oxygen while being charged

Major Challenges of Li-O_2 Battery

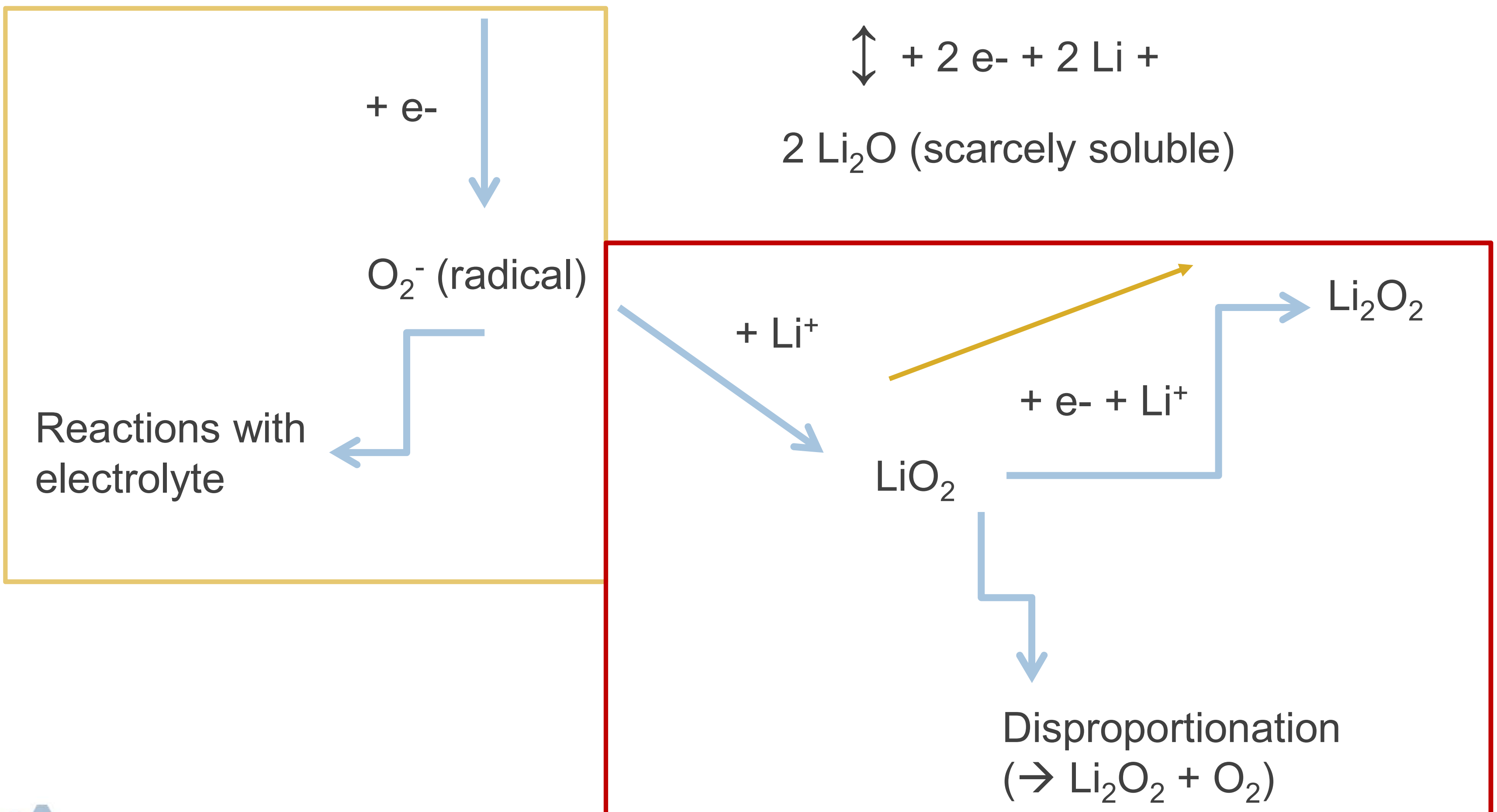
$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$ (solid) $E_{rev} = 2.96\ V_{Li}$



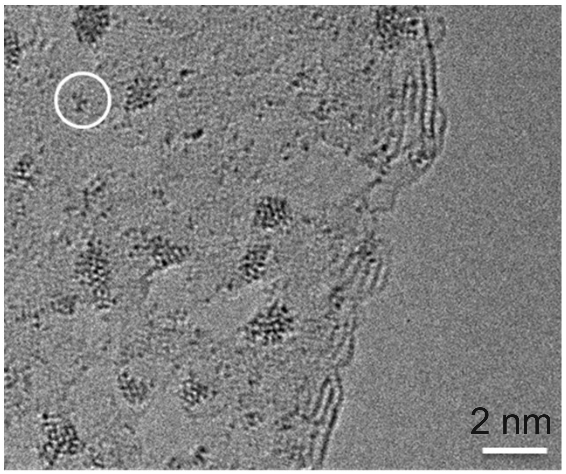
$Li\text{-}O_2$ Battery (Open System):
Electrochemical reaction scheme in Li-air cells

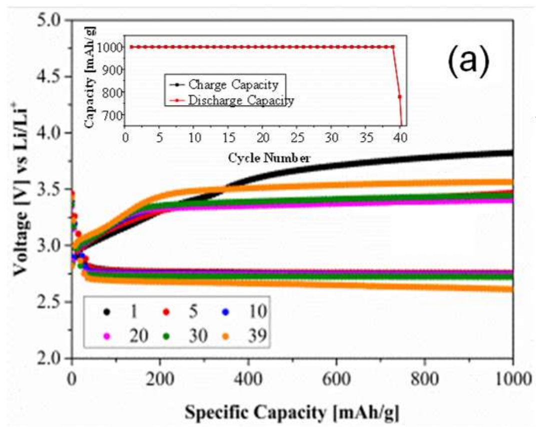
Ideal reaction scheme (on the air cathode):

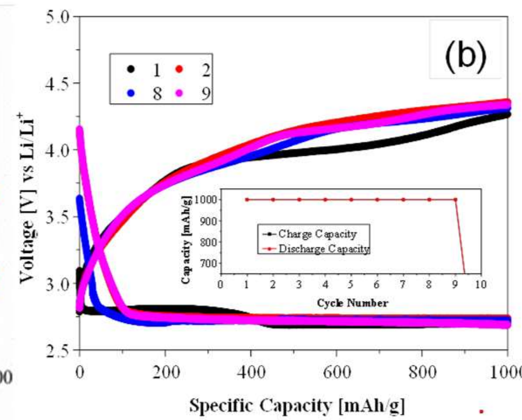
$2\,Li^+ + 2\,e^- + O_2(\text{molecule}) \leftrightarrow Li_2O_2$ (scarcely soluble)



Novel Ir catalyst on reduced graphene oxide (rGO) can stabilize Li2O crystalline phase







Cathode: Ir nanoparticles on rGO

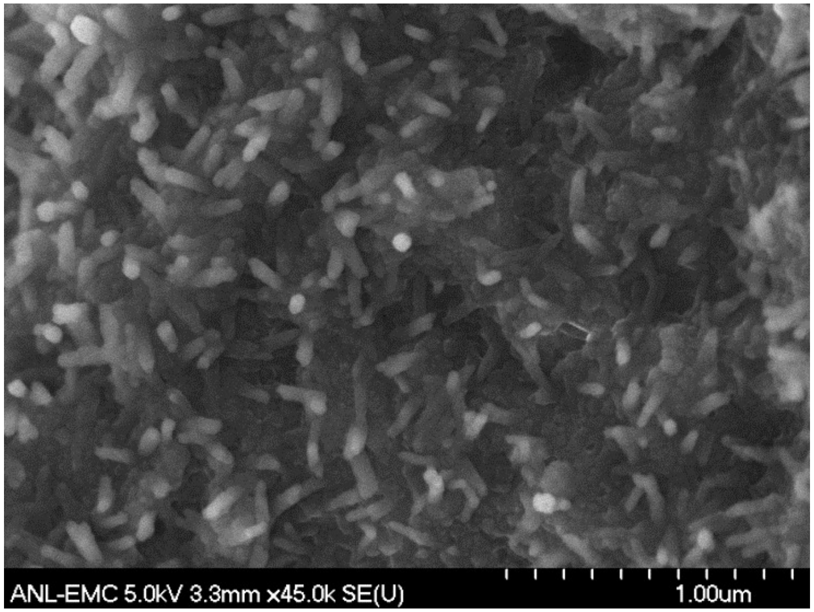
Ir-rGO

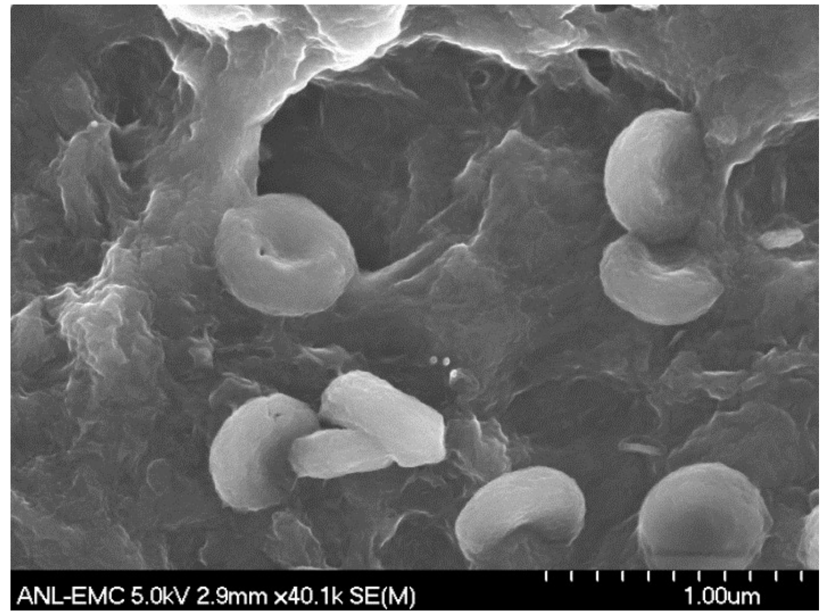
rGO

- The presence of the Ir nanoparticles significantly reduces the charge overpotential from >4 V to under 3.5 V
- Cell configuration: tetraglyme (ether) and LiTFSI electrolyte; lithium anode

Nature, 529, 377–382, 2016

Discharge product - comparison of rGO and Ir-rGO





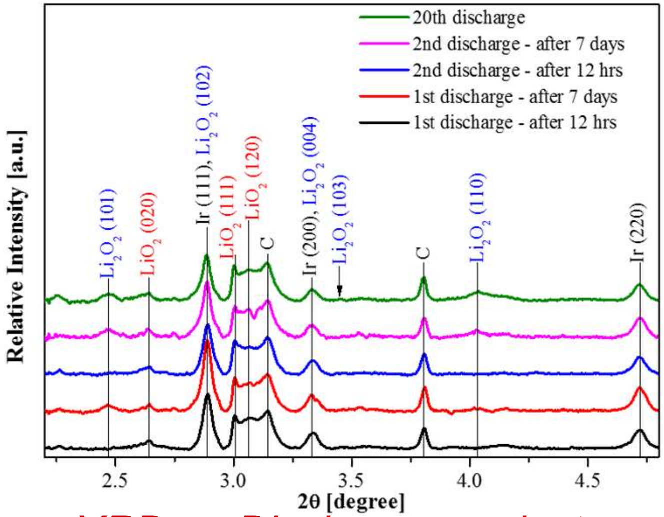
Ir-rGO **rGO**

- Ir-rGO cathode discharge product appears to be nanorods
- rGO cathode discharge product is toroids as is commonly seen in Li-O2 batteries

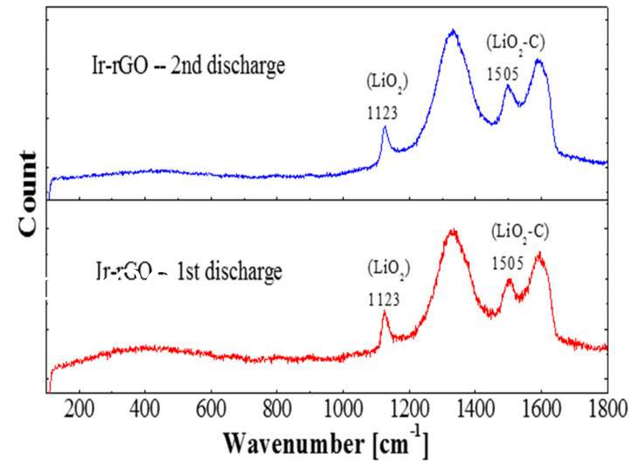
Nature, 529, 377–382, 2016

Stabilize LiO_2 (lithium superoxide)

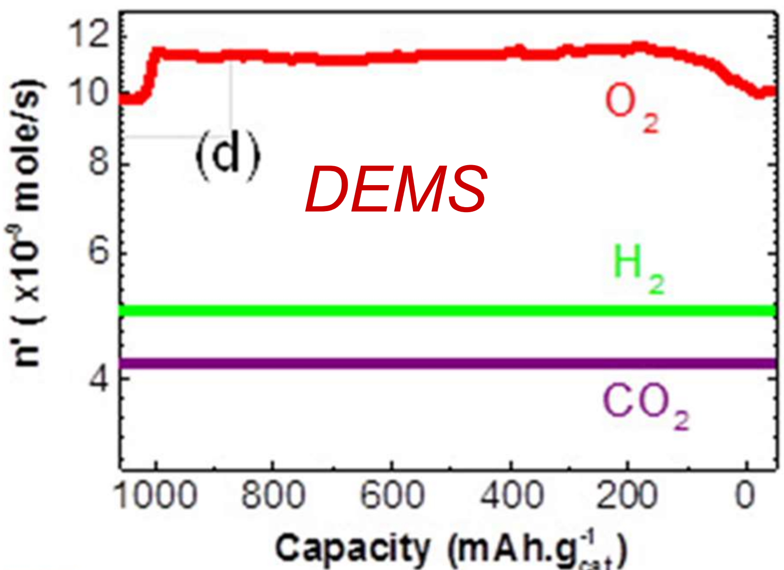
------- Ir on rGO promotes the formation of LiO_2 only!



XRD on Discharge products



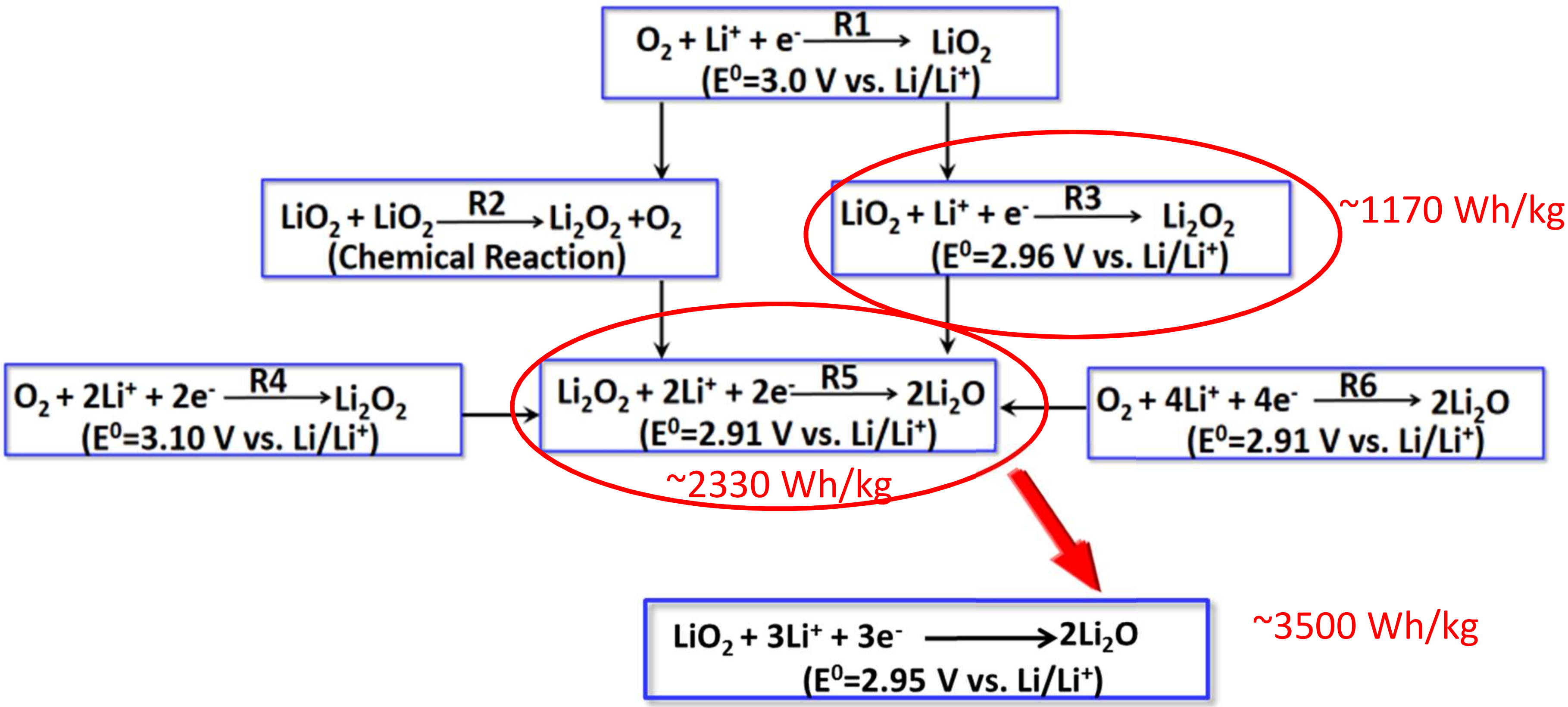
Raman measurement



- DEMS results give a 1.00 e^-/O_2 ratio.
  $LiO_2 \rightarrow Li^+ + e^- + O_2$
- The result supports LiO_2 as the major Li-discharge product.

Nature, 529, 377–382, 2016

Li-O_2 Battery (Close System) - Advantages



- ***High gravimetric energy density and volumetric energy density***
- ***Can reach >500 Wh/kg on the cell level!!***
- ***No O_2 involved in the reactions, avoid the crossover effect***
- ***Use conventional Li-ion configuration***
- ***Minimum electrolyte decomposition issue***

Energy densities of Li-S and Li-superoxide

Cathode	Specific Capacity (mAh g^{-1})	Average Voltage （vs Li/Li^+）	Specific Energy density (Wh kg^{-1})	Volume Energy density (Wh L^{-1})
Li-S	1167	2.15	2510	5196
Li-O_2 (Based Li2O2)	1168	2.75	3212	7387

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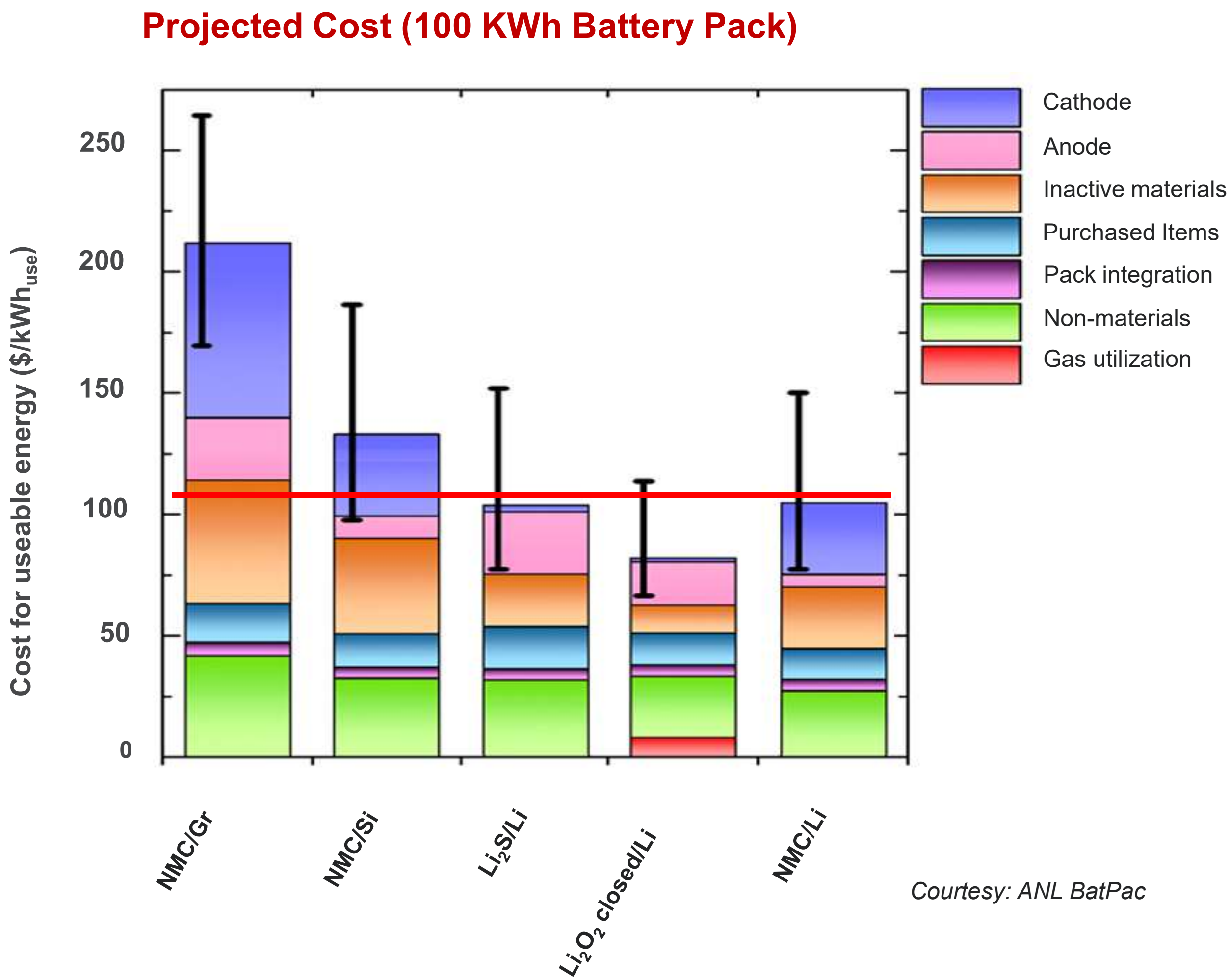
Enabling Lithium metal can Allow for meeting cost target of $100/Kwh using high voltage NMC cathode



Courtesy: ANL BatPac

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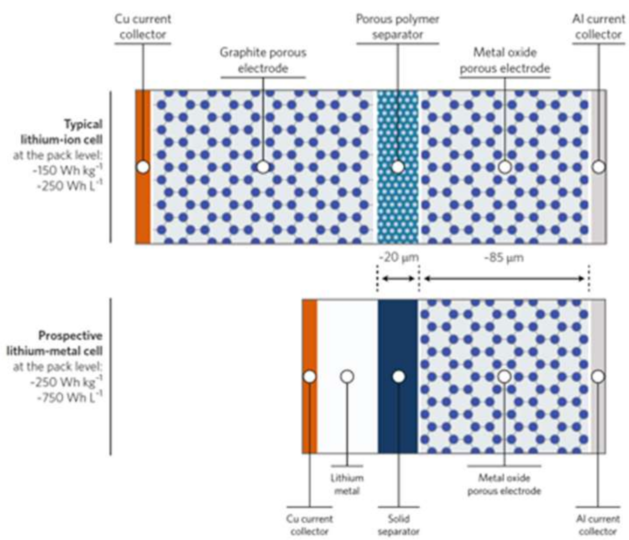
Enabling Lithium Metal using all Solid state battery

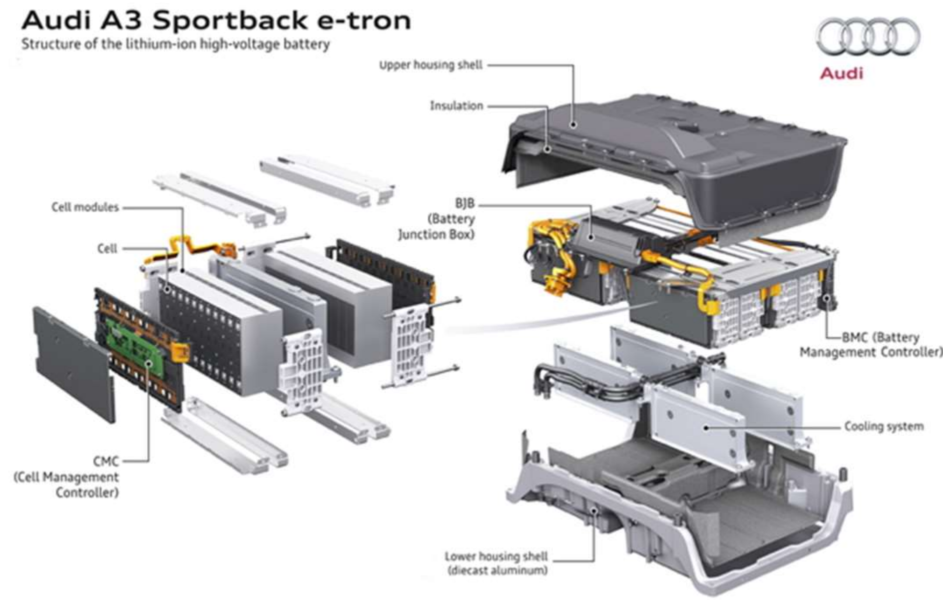
Graphite Anode → **Metallic Li Anode**

~450* mAh/cm^3 → **1,856** mAh/cm^3**



Albertus, Babinec, Litzelman, and Newman. *Nat. Energy* (2017): 1.

*assumes 330 mAh/g, 40% porosity
**assumes 10% un-used excess Li for mechanical compliance

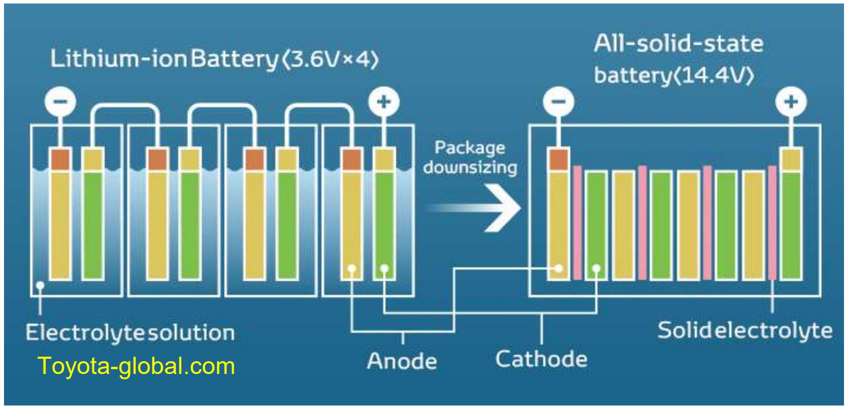


Increase in energy density:

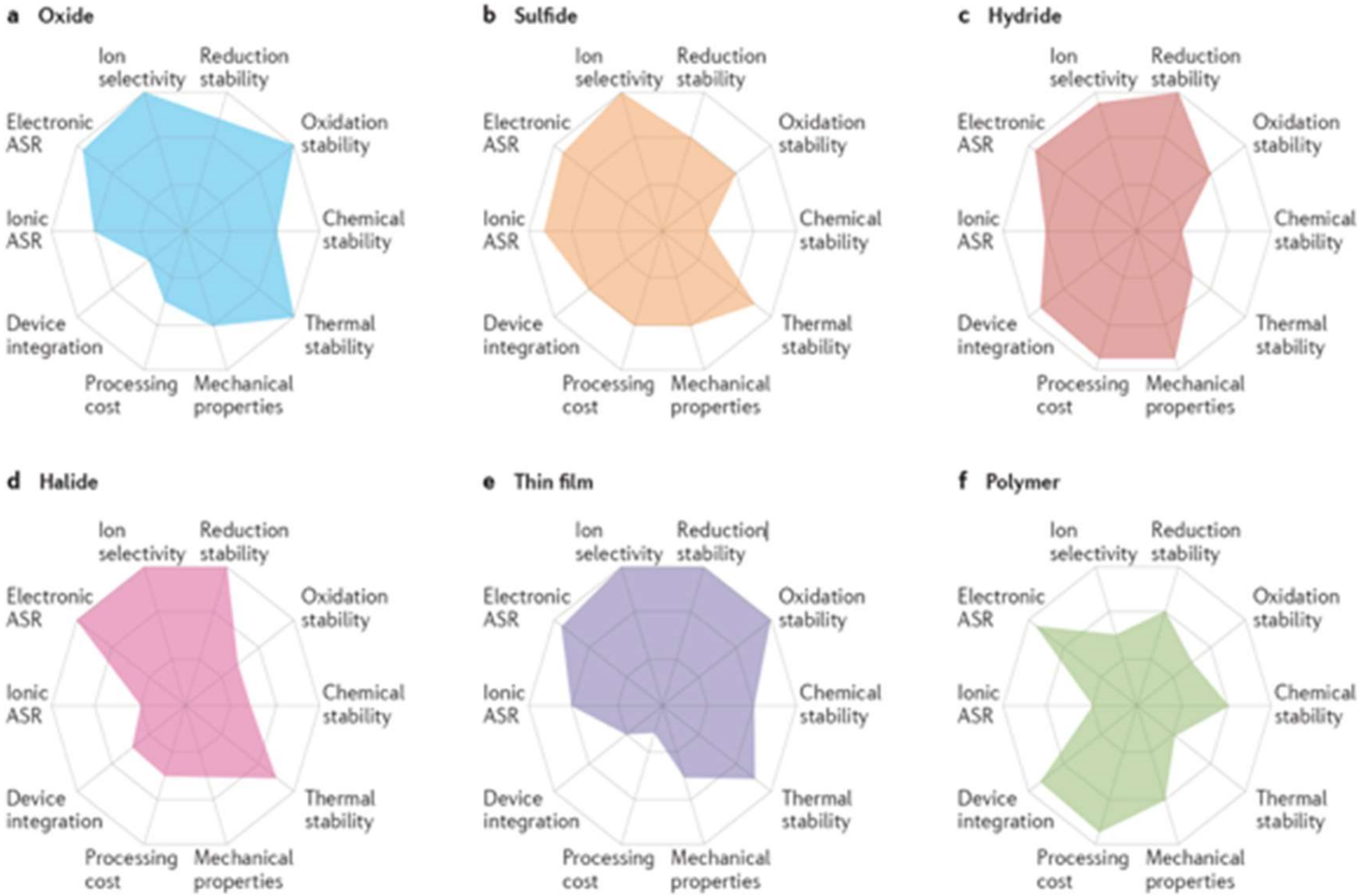
- ❖ Cell level: high energy density of Li
- ❖ Pack level: reduction of peripheral volume

Benefits

- Prevent dendrite formation when Li anode is used
- General safety—possible savings on BMS
- Some materials (certain oxides) have high electrochemical stability window
- High energy storage and power capacity
- Wider operating temperature window
- Bipolar design possible



Solid Electrolyte Materials Comparison



CHALLENGES OF SOLID STATE BATTERY

- Lithium dendrite trough pin holes and grain boundaries
- Interfacial issues at both cathode and anode caused by volume change during charge and discharge
- Processing and manufacturing the solid state electrolyte at a big scale