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Electrochemical Energy Storage via Batteries: Prospects and Limitations

Aninda J. Bhattacharyya
Solid State and Structural Chemistry Unit
Division of Chemical Sciences
Indian Institute of Science, Bengaluru, INDIA

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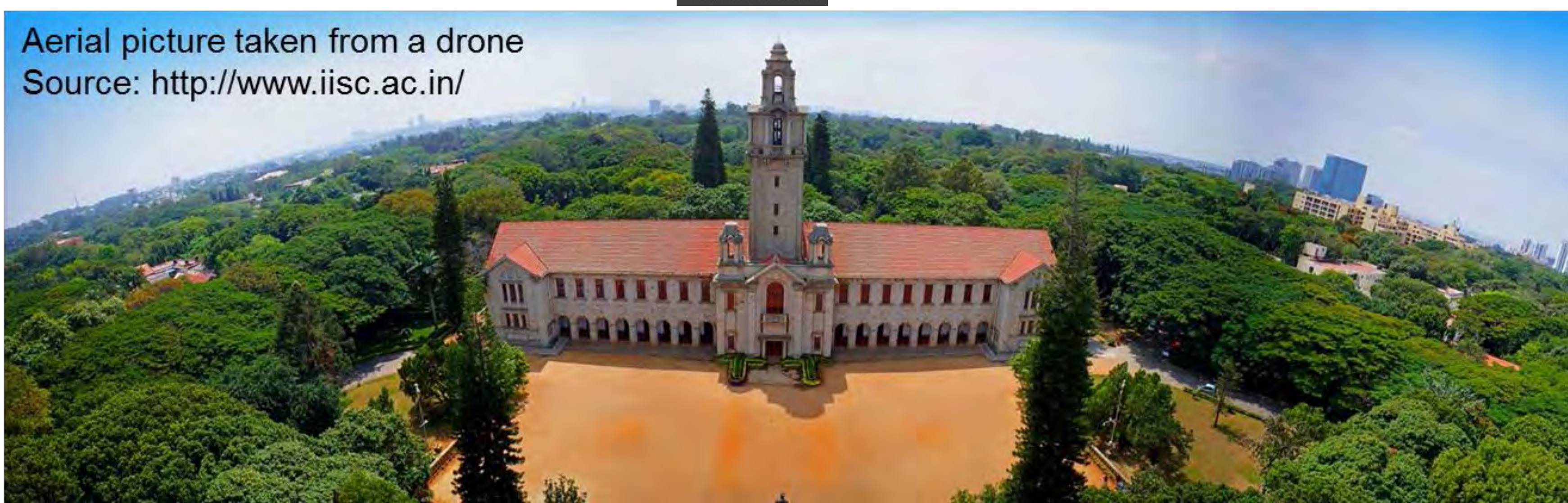


Group Research @ SSCU-IISc, Bengaluru

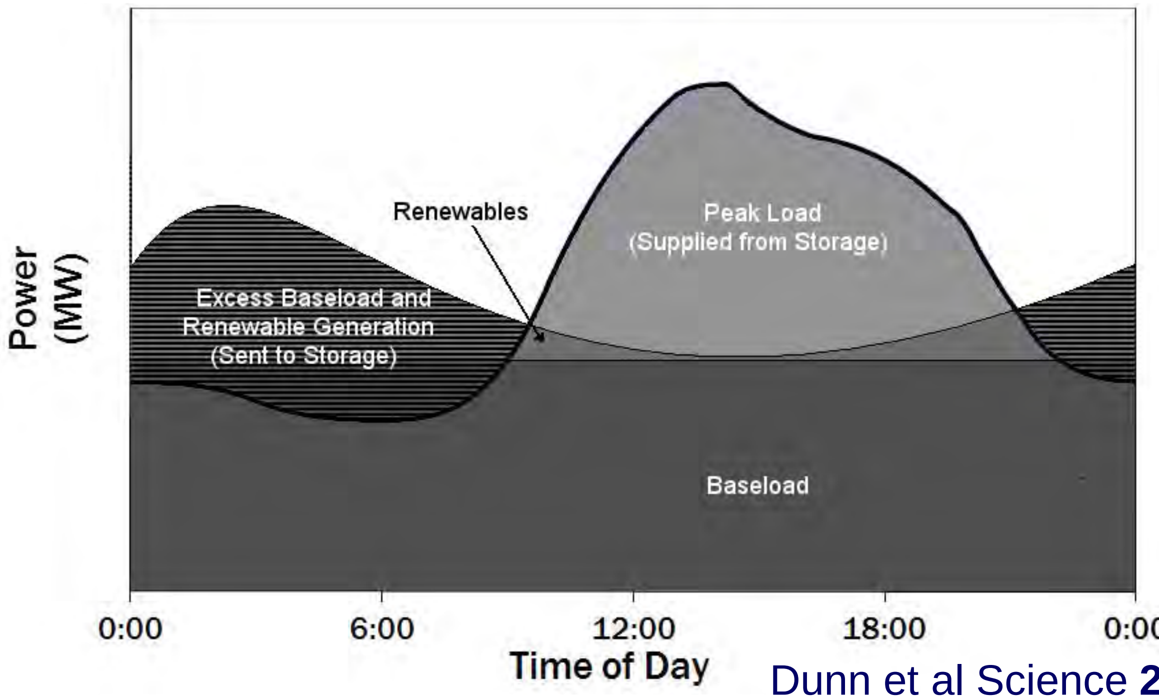
Experimental Physical & Materials Chemistry

- diverse electrochemical processes (in chemistry & biology): energy harvest & generation; catalysis; sensing; actuation

Energy

Generation

Storage



Dunn et al Science **2011**, *334*, 928

- prevention of wastage, optimal usage of resources, protection of environment (greenhouse gases), ……….

Energy

Generation

Storage

Mechanical
Electrical
Chemical
Electrochemical

Mechanical: flywheels, CAES, **pumped hydro**
(1-20000 MW; few (min to h); 10-25 yr; 70-90 %)

Electrical: **Superconductive electromagnetic (SMES)**
(1 MW; 1 - 30 min; 20 yr; > 90 %)

Chemical: **Hydrogen**
(10 MW, >10 h; > 40-50 %)

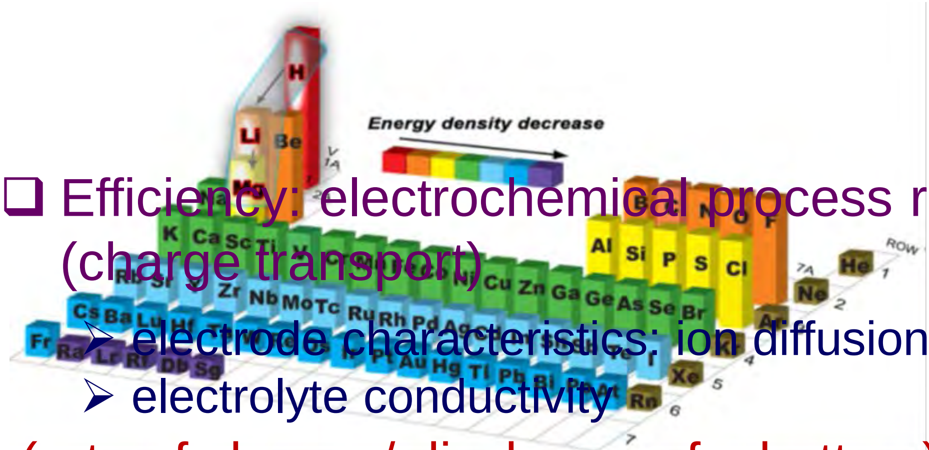
Electrochemical: **Batteries, Supercapacitors**
Secondary (0.5-1 MW; 1-8 h; 7-20 yr; >75%)
Flow (12MW; ≈10 h; 10 yr; > 70%)

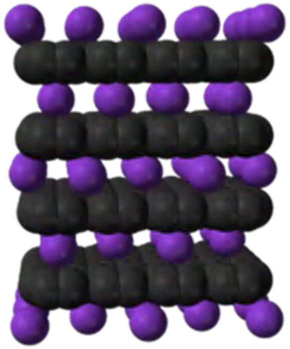
Dunn et al Science **2011**, *334*, 928
Soleveichik *Annu. Rev. Chem. Biomol. Eng.* **2011**, *2*, 503

Battery basics*

- Amount of energy storage (Wh.kg^{-1})

$$E_{specific} = V_{OC} \times Capacity = V_{OC} \times \frac{n_{electron}\, F}{a_{MW}}$$



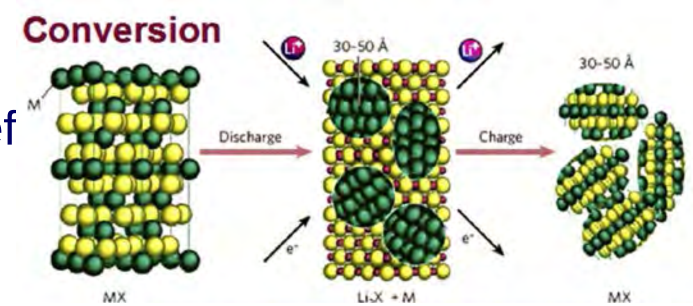


K intercalation in C-Graphite

- Efficiency: electrochemical process rate (charge transport)
  - electrode characteristics: ion diffusion coef
  - electrolyte conductivity

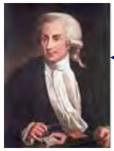
(rate of charge / discharge of a battery)

Peng, Chen *Coord Chem. Rev.* **2009**, 253, 2805



*(Physical) Chemist point of view

Electrochemical devices…..Genesis



Franklin (1748); Coining of "battery"

Galvani (1780-86): Principles of battery function

(Zn-Cu) Voltaic pile: Volta (1800)

Laws of electrolysis: Faraday (1834)

Daniel Cell (1836)
Pb-Acid Battery: Gaston Plante (1859)

Lechlanche (1866)

1899-1964
Dry Zn-C: Gassner (1881)
Ni-Cd: Junger (1899)
Alkaline-Mn: Urry (Eveready-1949)
Duracell (1964)

Li-ion battery: Sony (1991)

2000-…: Li/Na/Mg/Al/Ca…..

H_2/O_2 Gas Battery William R. Grove (1839)
(highlighted by Wilhelm Ostwald, 1896)

Coining of "Fuel Cell" : Charles Langer, Ludwig Mond
(1889) (FC with air and coal gas)

H_2-O_2 FC: Francis Bacon (1932) (→ 5 KW system, 1959)

Capacitors (GE, 1950s (GE)

Supercapacitors: Conway (1999)

Electrochemical devices…..Genesis

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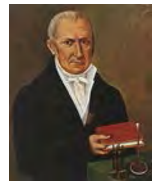

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Duracell (1964)

Evolution time-line for Li-ion: 1977-89

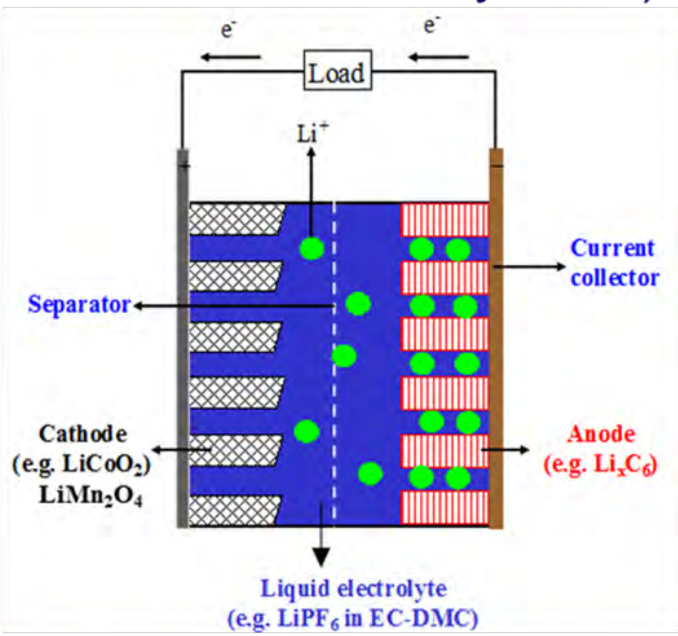
Heller, Basu, Goodenough, Mizushima, Yazami, Thackeray, Yoshino, Manthiram

Li-ion battery: Sony (1991)

2000-…: Li/Na/Mg/Al/Ca…..

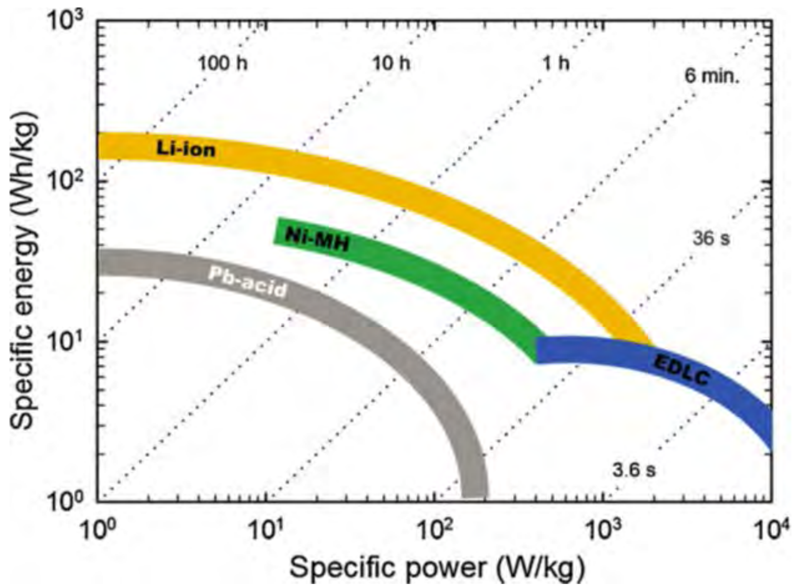
Rechargeable batteries: Lithium-ion (LiB)

"Rocking chair" Li-ion Battery
(Commercial Launch: Sony, 1991)

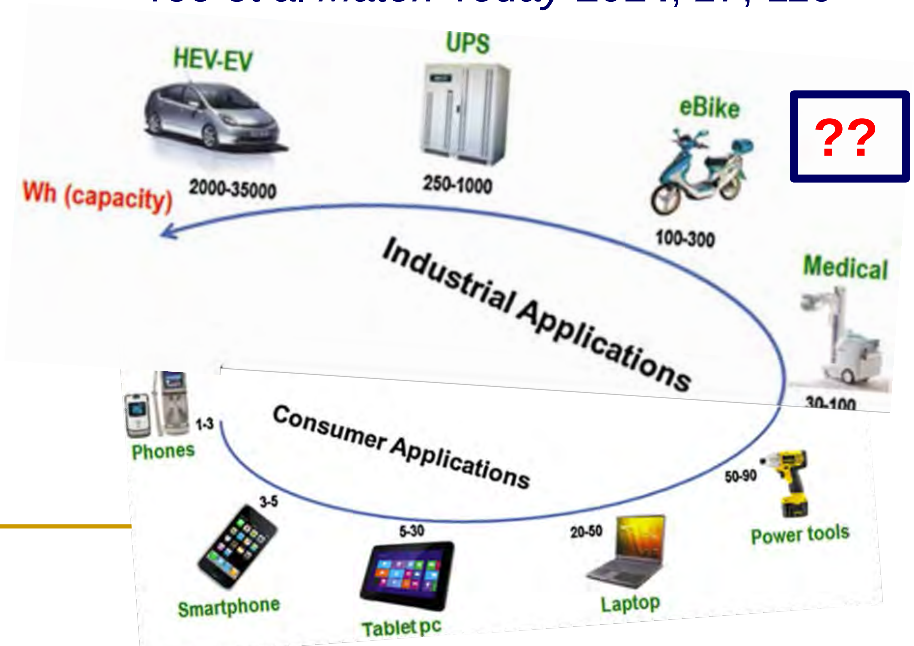


- $0.5\ C_6Li + Li_{0.5}CoO_2 \leftrightarrow 3C + LiCoO_2$
- Practical specific energy: 140 $Whkg^{-1}$

< 1 e^- rev. process



Yoo et al *Mater. Today* **2014**, *17*, 110



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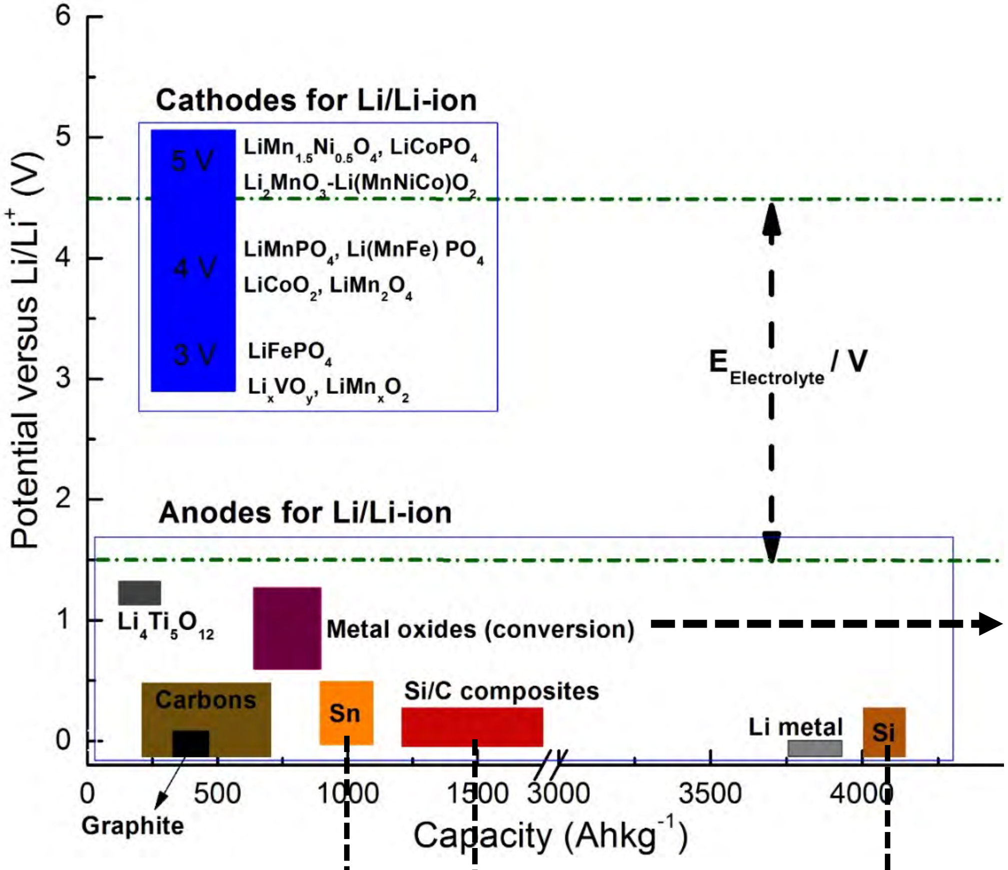
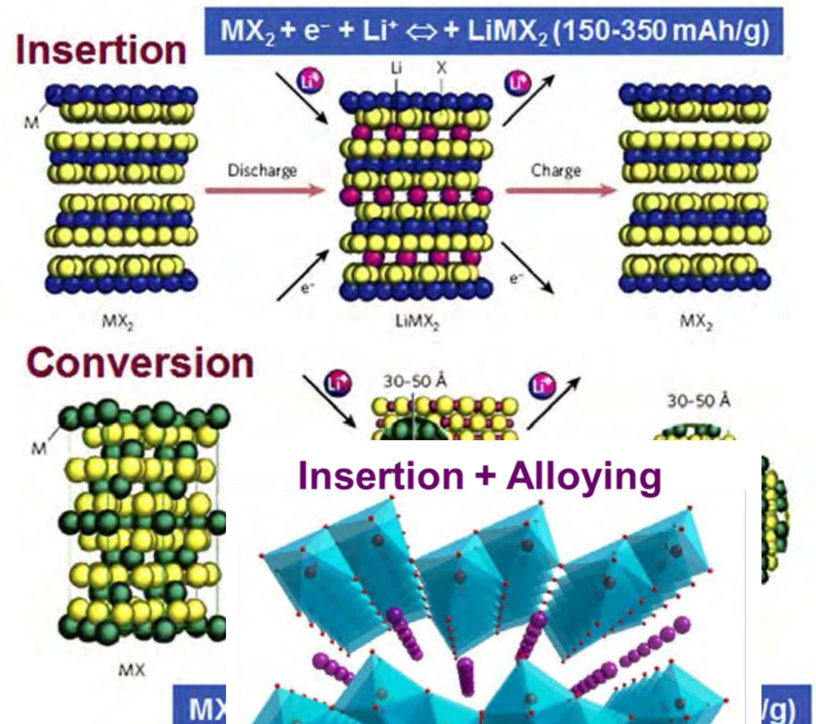
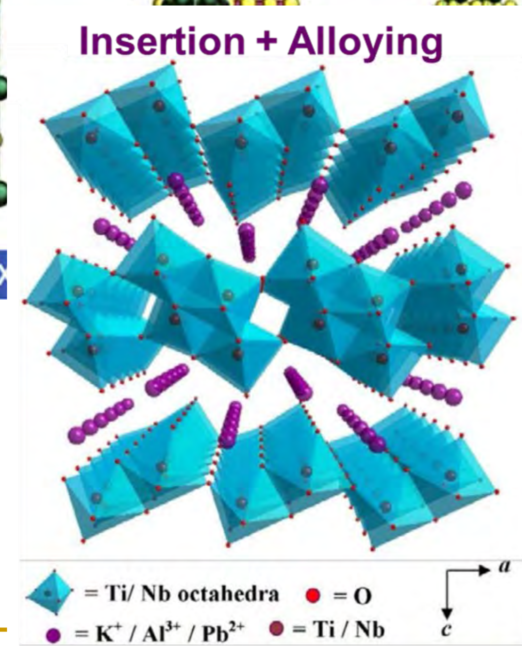
Large LiBs: High performance, cost effective, safe

- Materials exploration: (higher operational voltage, higher storage)







Alloying

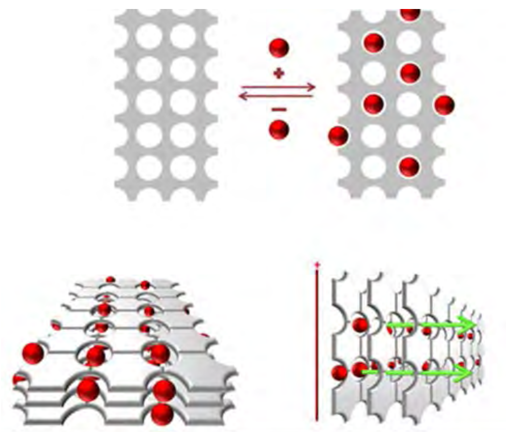
$Sn + xe^- + xLi^+ <=> Li_xSn$; $x \rightarrow 4.4$ >900mAh/g

$Si + xe^- + xLi^+ <=> Li_xSi$; $x \rightarrow 4.4$ > 4000mAh/g

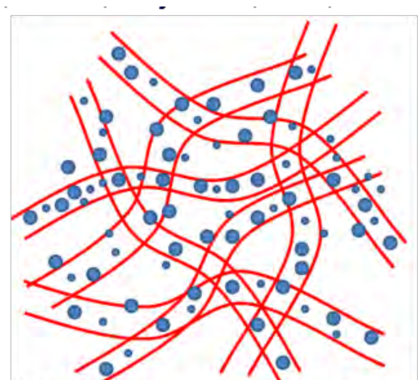
Suman Das et al *Chem. Asian J.* 2018, 13, 299-310

Improved LiBs

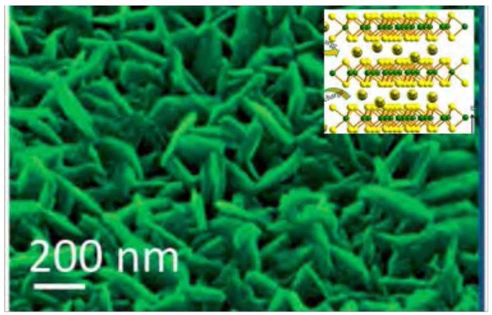
- Materials exploration: (higher operational voltage, higher storage)
- Tailored architectures: manipulating charge transport @ small length scale



$g\text{-}C_3N_4$ (3D ion conductor)



Electrospun C-Sn-alloy

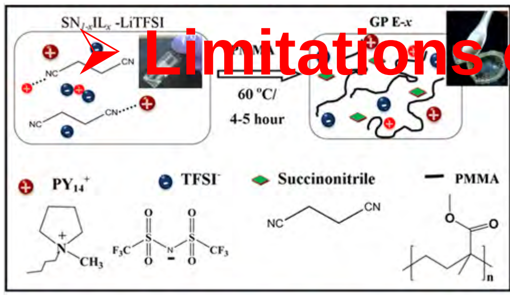


Nano-wall networks in ALD-grown MoS_2 films

Improved LiBs

- ➢ Materials exploration: higher operational voltage, higher storage
- ➢ Tailored architectures: manipulating charge transport @ small length scale
- ➢ Newer electrolyte designs: Liquid → Solid-like ion conductors

Gel (linear) polymer electrolytes

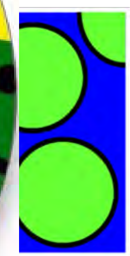


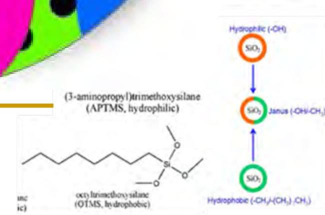
S. Sen, Sneha M. AJB, *J. Phys. Chem. B* 2016

➢ **Limitations of LiBs: functionality…. cost**

S. Sen *et*
Patel, AJB
Patel, Gna
AJB

hybrid liquid electrolytes





Adv. Mater. 2004
Adv. Mater. 2008
J. Phys. Chem. C 2009
Energy Environ. Sc. 2011
J. Phys. Chem. B 2010
J. Phys. Chem. Lett. 2012
J. Phys. Chem. B 2015

Improved rechargeable batteries…cost, safe, sustainable

Beyond Li-ion → Earth abundant and cheaper

Element	Crustal composition	E^0 / V	$mAhg^{-1}$	$mAhml^{-1}$
Li	0.002	-3.0	3861	2062
Na	2.4	-2.7	1166	1128
Mg	2.1	-2.4	2205	3833
Al	8.1	-1.7	2980	8046
Ca	3.6	-2.9	1337	2073
K	2.8	-2.9	685	591
Zn	0.008	-0.8	820	5851
Be	0.002	-1.9	5948	11003
Pb	0.001	-0.13	258	3000

Na-based

$>1\ e^-$ process

Higher valency

- Mg^{2+}, Ca^{2+}
- Al^{3+}

- lower performance, non-trivial electrochemistry

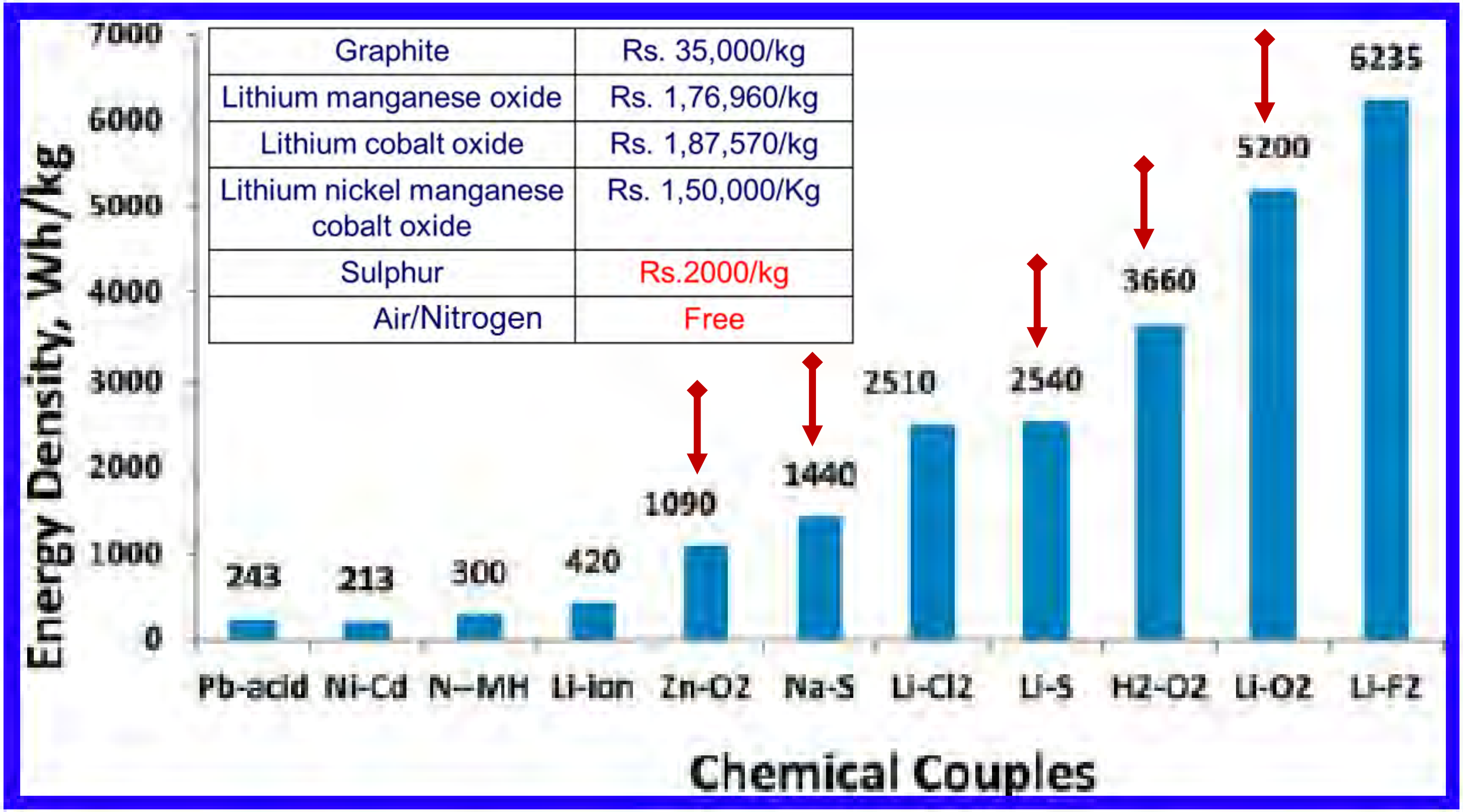
Beyond Li-ion

- **Compound → Elements (+multi-electron processes)**

- Specific energy ($E_{specific}$ $Wh.kg^{-1}$)

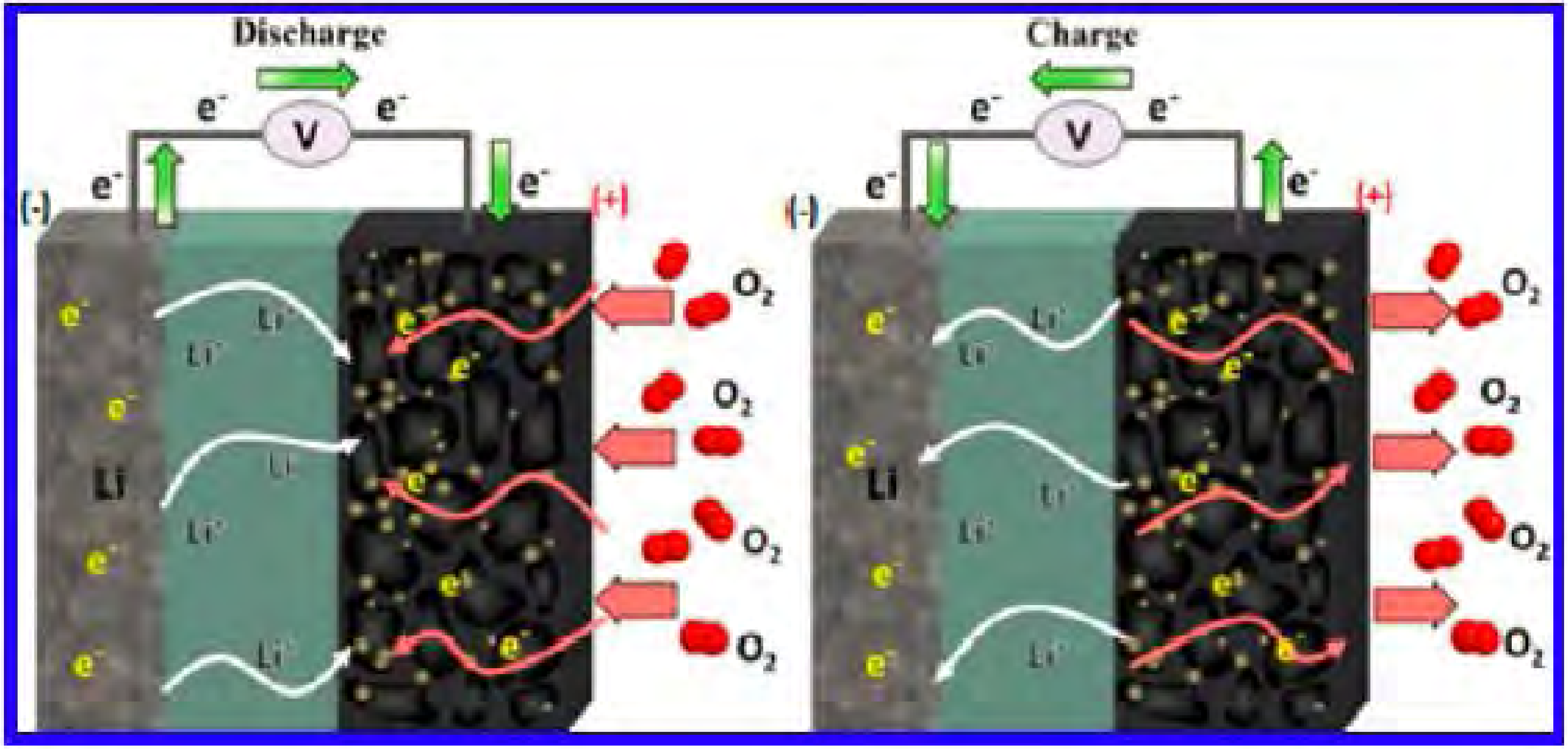
$$E_{specific} = V_{OC} \times Capacity = V_{OC} \times \frac{n_{electron} F}{a_{MW}}$$

Chemical couples



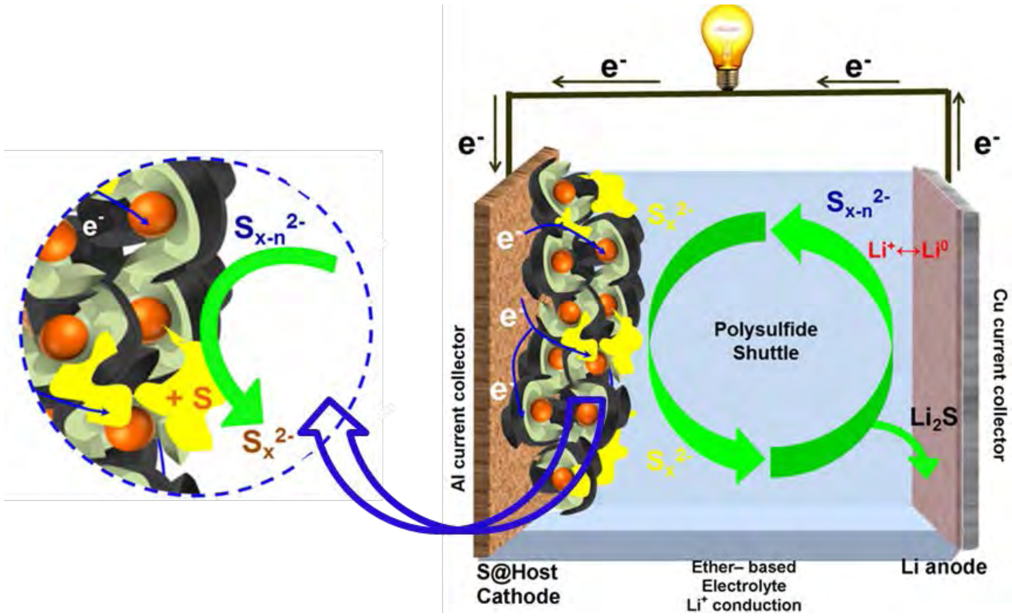
Graphite	Rs. 35,000/kg
Lithium manganese oxide	Rs. 1,76,960/kg
Lithium cobalt oxide	Rs. 1,87,570/kg
Lithium nickel manganese cobalt oxide	Rs. 1,50,000/Kg
Sulphur	Rs.2000/kg
Air/Nitrogen	Free

Metal-air (O_2) battery



Metal: Li, Na, Zn, Mg..

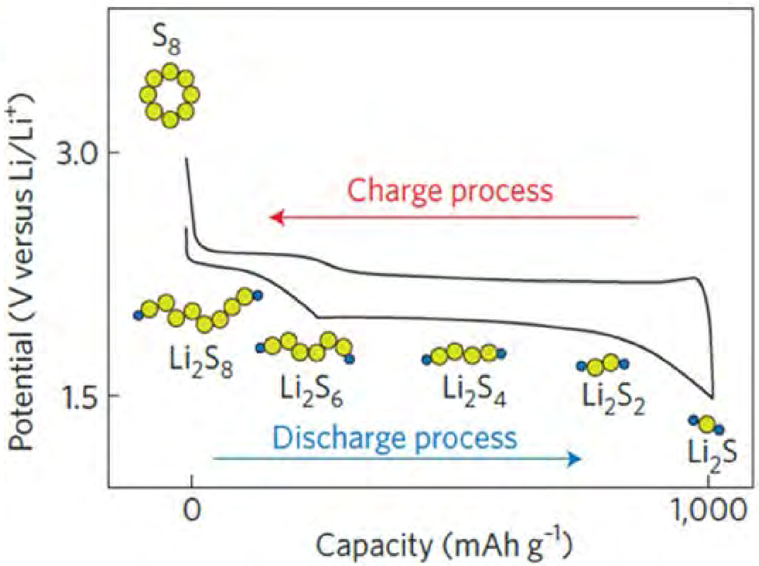
Metal-S battery: Li-S



Anode poisoning

$\Delta V_{cathode}$
(Mg: 36%, Li: 80%, Na: 310%)

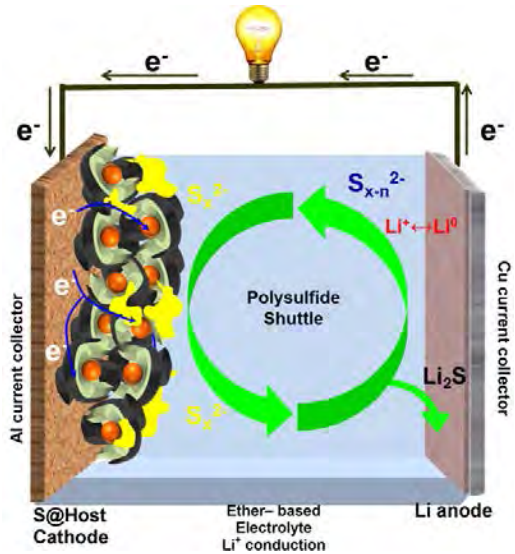
Insulators: S, M_xS

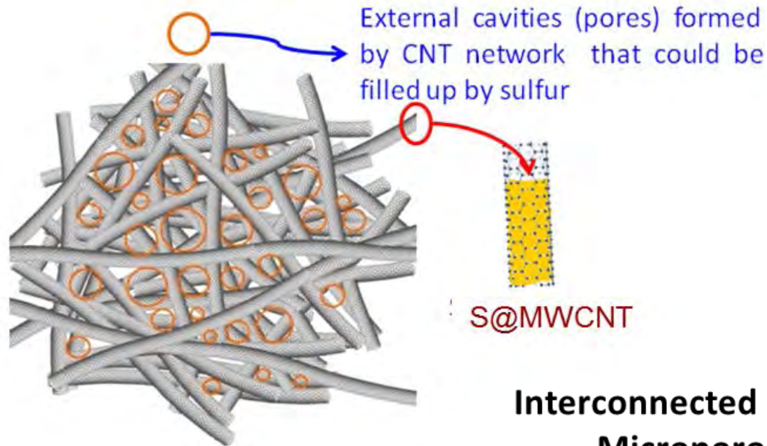


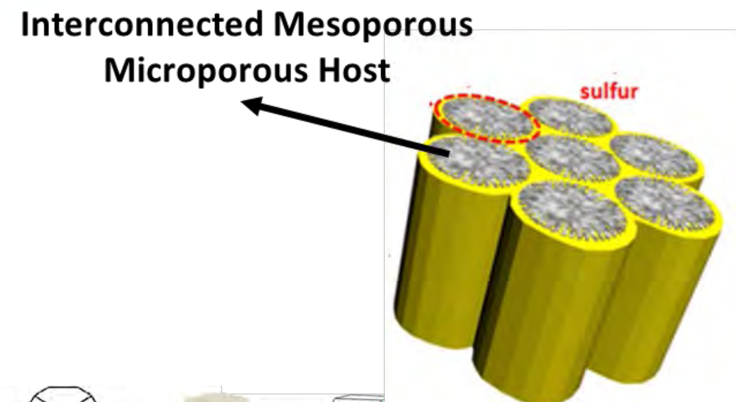
Efficient Li-SBs

- S-cathode scaffolds: high S-load, efficient encapsulants

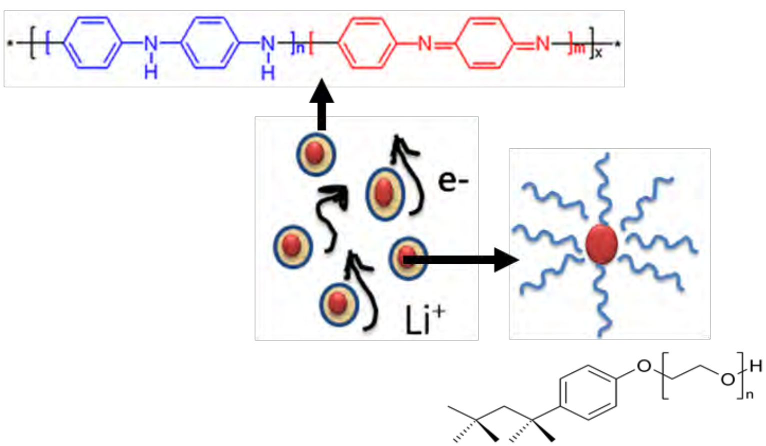
Li-S battery: S-cathode scaffolds

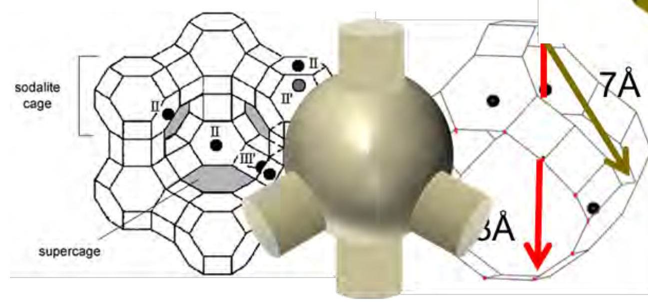






Mixed conducting flexible (organic) S-hosts

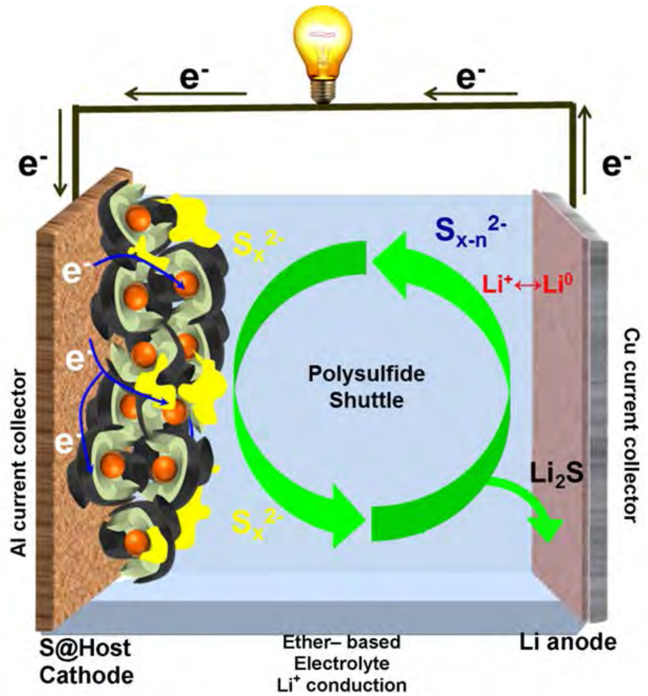




Zeolite NaY: $(Na_2,Ca,Mg)_{3.5}[Al_7Si_{17}O_{48}]\cdot 32(H_2O)$

- ❖ S-content: > 75% (scaffold characteristics)

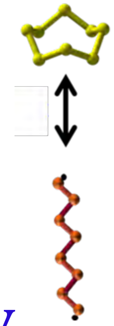
Li-S battery



- ❖ Entrap soluble S_n^{2-} /control anode poisoning
- ❖ ΔV : S → L_2S_n

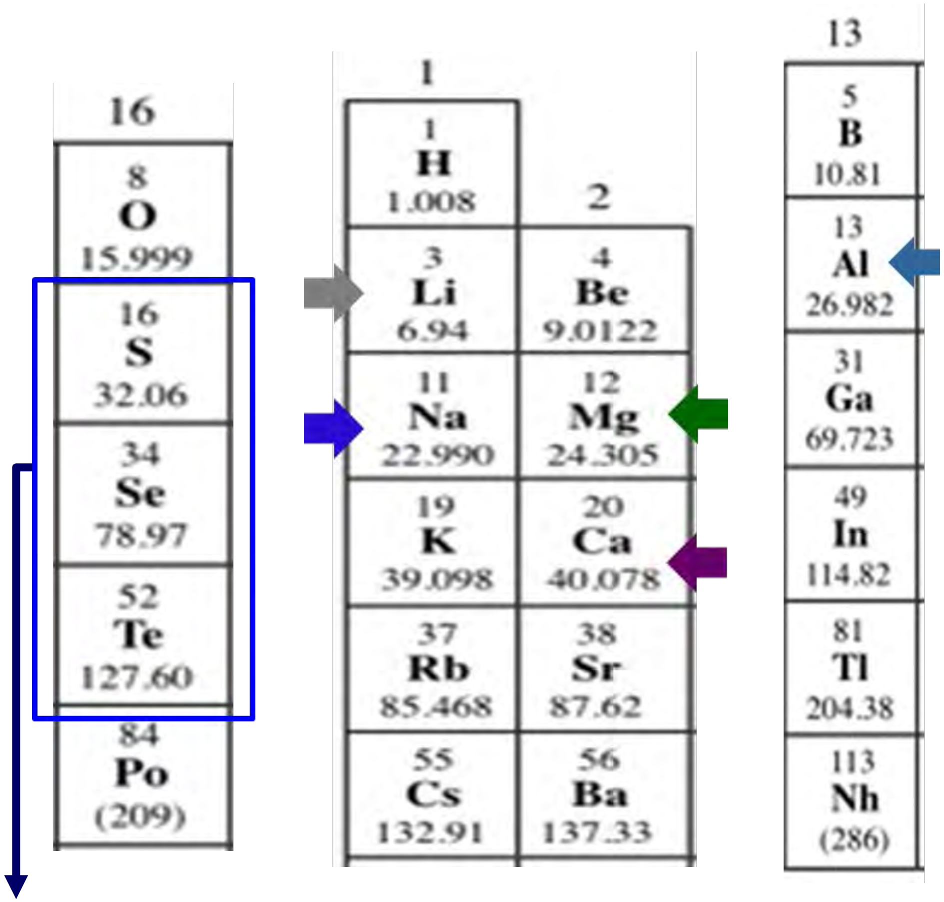
- ❑ Host structure is crucial: S-loading
- ❑ S-conformation → Packing density
- ❑ **S** ↔ M_2S_n : Extent of reversibility

(*in situ* spectroscopy/microscopy + electrochemistry)



	S →	L_2S_8 →	L_2S_6 →	Li_2S_4 →	Li_2S_2 →	Li_2S
$mAhg^{-1}$	1675	4	260	377	687	1165

Metal : Chalcogenide Batteries



Na, Mg, Ca, Al (earth abundant)

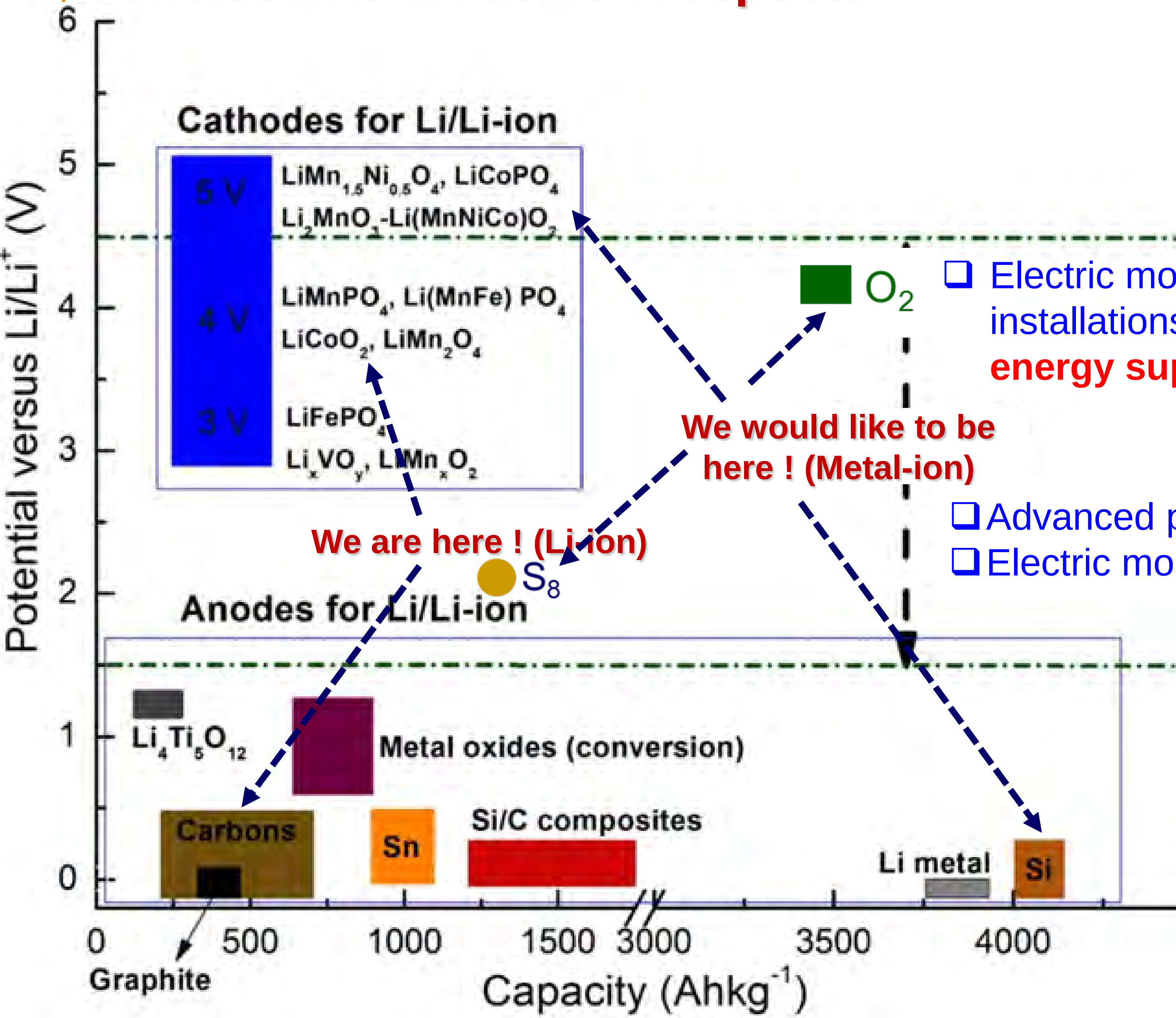
- lower energy output

Several challenges

- sluggish ion motion
- S/S_n^{2-} confinement
- S $\Leftrightarrow$ M_2S_n

- lower specific capacities, higher electrode conductivity, easier manipulation of polychalcogenides

Conclusions & Future Prospects



- Electric mobility, grids, remote installations…**autonomous energy supply system**

- Advanced portable devices
- Electric mobility

Leap forward…. Improved, safer, cheaper batteries

- **Gasoline → Electric mobility**
- **E-chem storage integration with Electric Grid/ Renewables**

- ✓ sustainable, cheaper materials, (new) battery chemistries
- ✓ *in operando* monitoring of battery health, optimizes performance under diverse conditions
- ✓ Theoretical studies:
  - materials discovery
  - modelling battery operations on varying length/time scale
- ✓ Collaborative research

No Mental block !


Thank You...