BATTERY BASICS

A BEGINNERS GUIDE

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Contents

- Motivation
- Electrochemical driving force
- Electrolytes-Briefly

Motivation

Society is undergoing a rapid and enormous change in energy production and use with electrification of transportation, communications and storage.

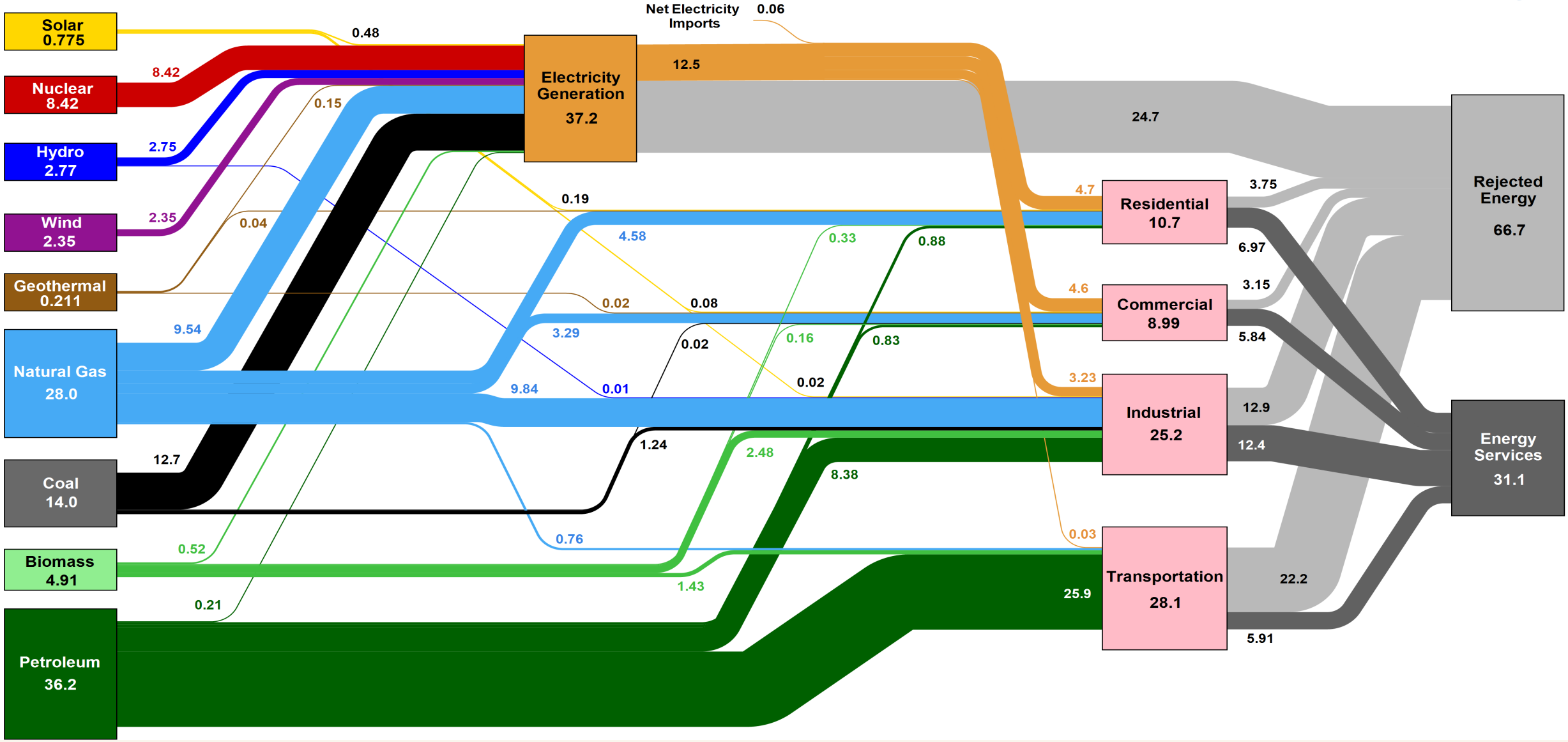
This "revolution" is creating an enormous demand for individuals trained in the design, production and assembly of all types of batteries and at all levels of expertise.

There are no simple, established mechanisms whereby entry level individuals (including students) can gain the expertise needed to become functioning workers in the battery field.

Our goal is to provide a detailed introduction to batteries beginning at the most basic levels, moving to more sophisticated learning opportunities as needs require.

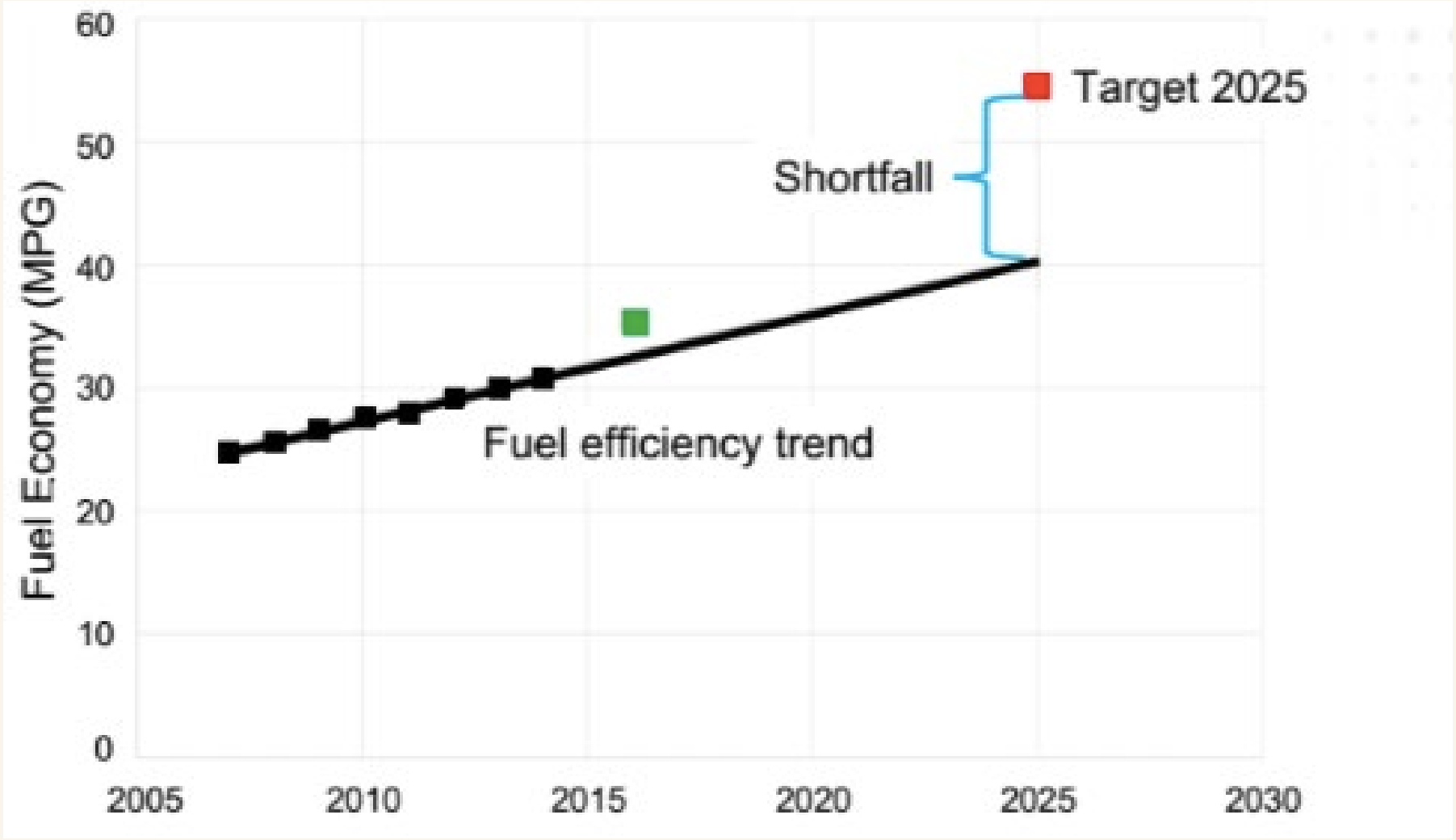
Estimated U.S. Energy Consumption in 2017: 97.7 Quads

Lawrence Livermore National Laboratory



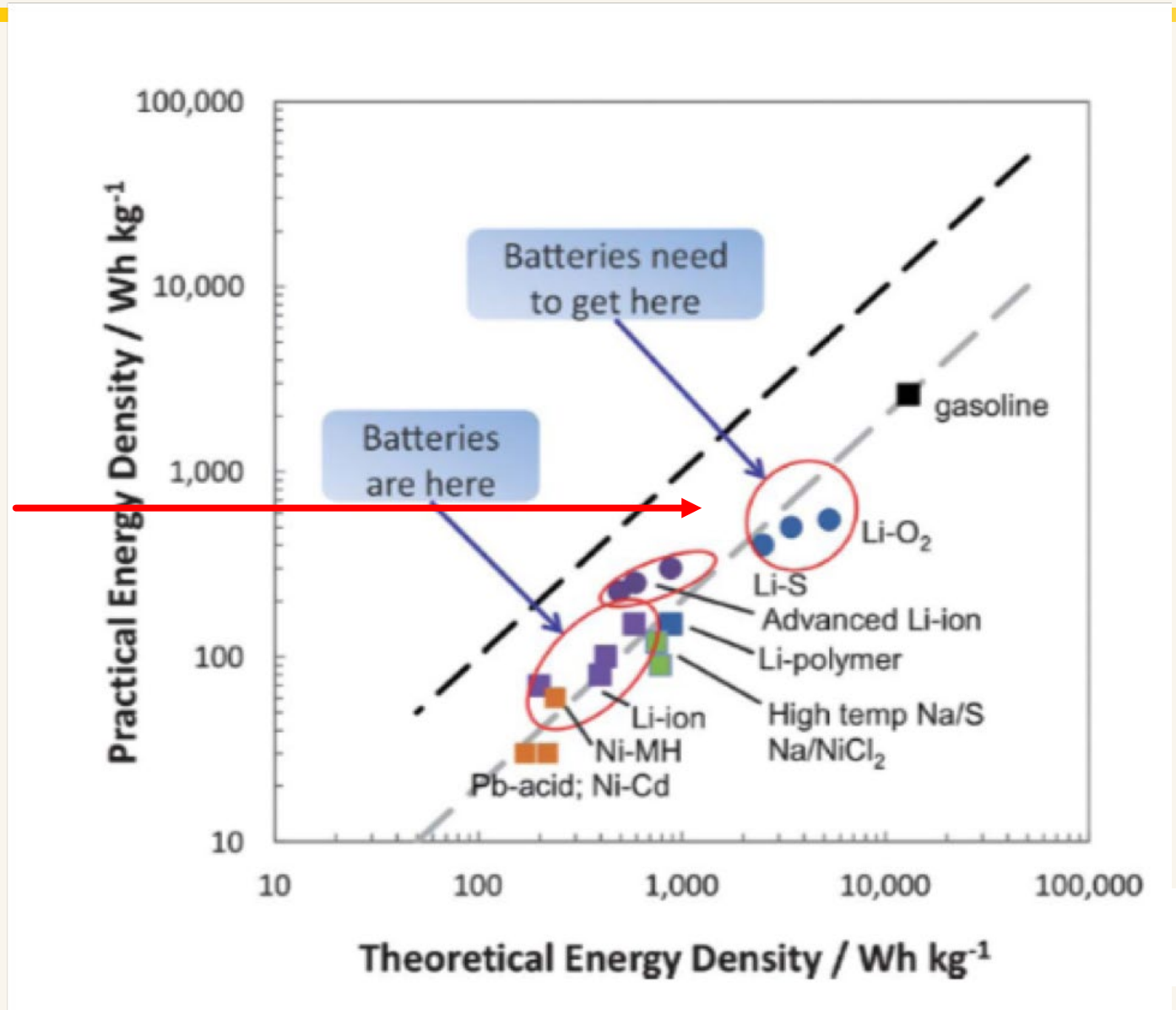
What is driving vehicle electrification?

Fleet-Averaged Light-Duty Fuel Economy—Sales Weighted (UMTRI)



Frontiers of electrochemical energy storage

500



Thackeray, M., M., Wolverton, C. and Isaacs, E. D. 2012. Energy and Environmental Science 5: 7854-7863.

What is a battery = electrochemical storage device?

It provides a mechanism to store energy in chemical form that can be translated into an electric current.

This current can be used to power:

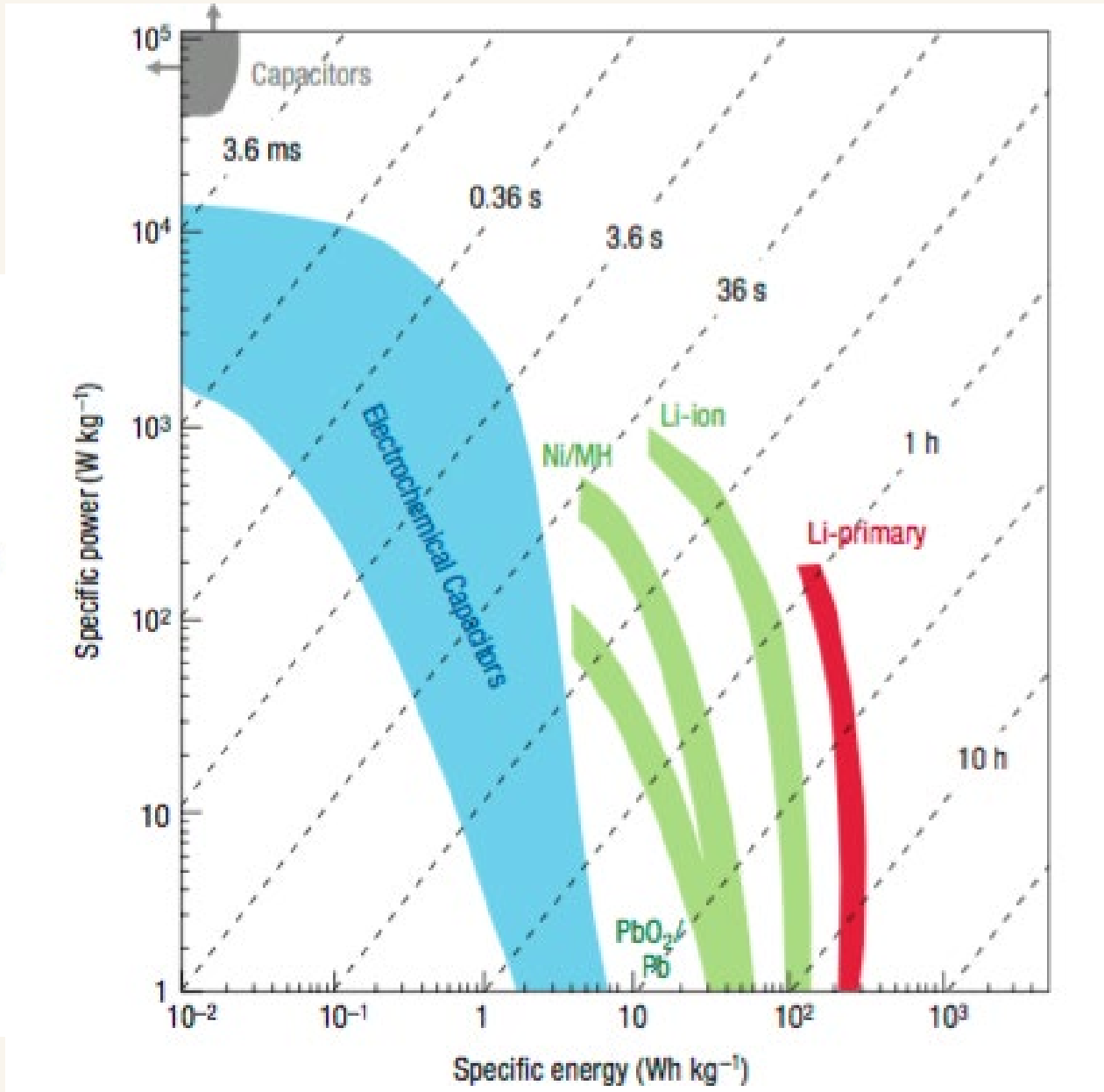
Lighting, electric motors (for vehicles of all types),
electronics (phones, computers, displays), heating, etc.

In order to be useful it must:

- Light weight
- Provide electrical energy rapidly and safely on demand.
- It must be easily restored to its original electrochemical form (rechargeable) easily and rapidly for repeated reuse.

Electrochemical storage devices

- Fuel cells
- Batteries
- Supercapacitors



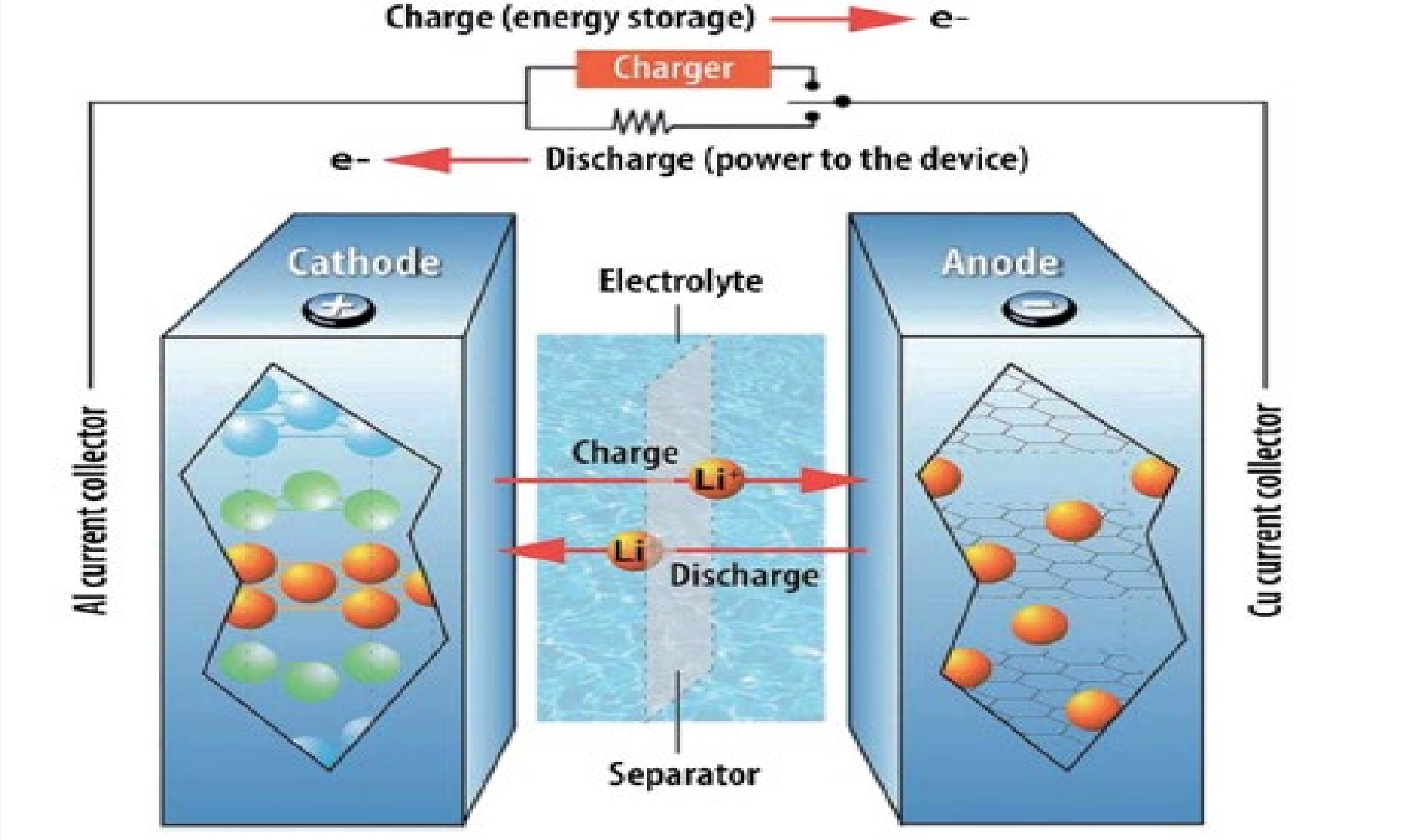
P. Simon and Y. Gogotsi, Nat. Mater., 2008, 7, 845–854.

Batteries

- Definition
  - A battery is a storage device used for the storage of chemical energy and for the transformation of chemical energy into electrical energy
  - Batteries consist of groups of two or more electric cells connected either serial for voltage or in parallel for current.
- Two major types:
  - Primary batteries
  - Secondary batteries

Components of a typical battery

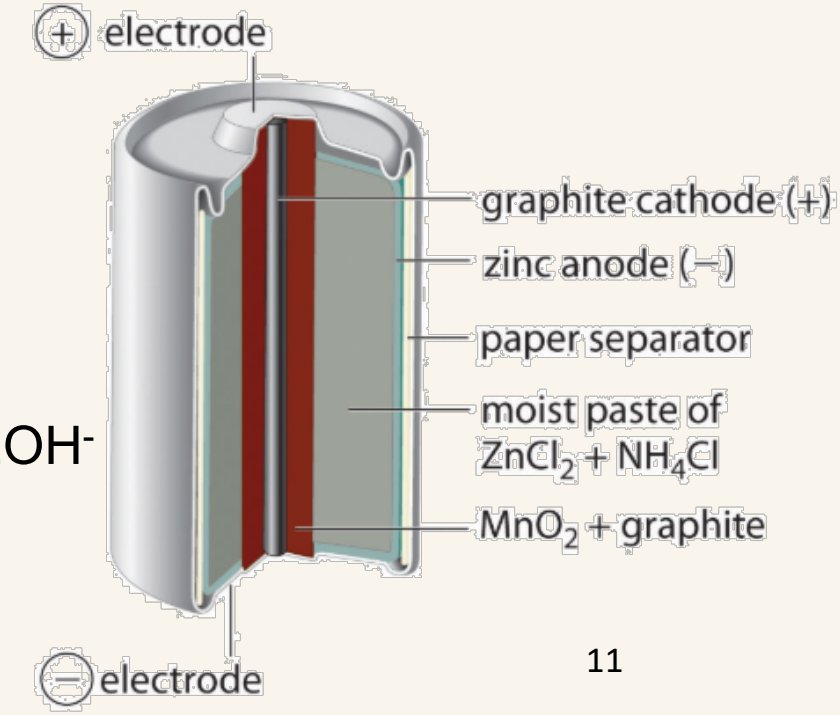
1. Cathode
2. Anode
3. Electrolyte



From: M. Osiak, et al," J. Mater. Chem. A, 2014, 2, 9433–9460

Primary Batteries

- Definition
  - In primary cells, the chemical reaction occurs only once
  - Source of direct current power
- Voltage ranging from 1.25-1.50 V, used in torches, radios, watches etc.
- Low-cost, but short life
- $Zn\text{-}MnO_2$ cell (dry cell)
  - Oxidation at anode: $Zn(s) \rightarrow Zn^{+2}(aq)+2e^-$
  - Reduction at cathode: $2MnO_2(s)+H_2o+2e^- \rightarrow Mn_2O_3(s)+2OH^-$
  - Voltage: 1.5 V

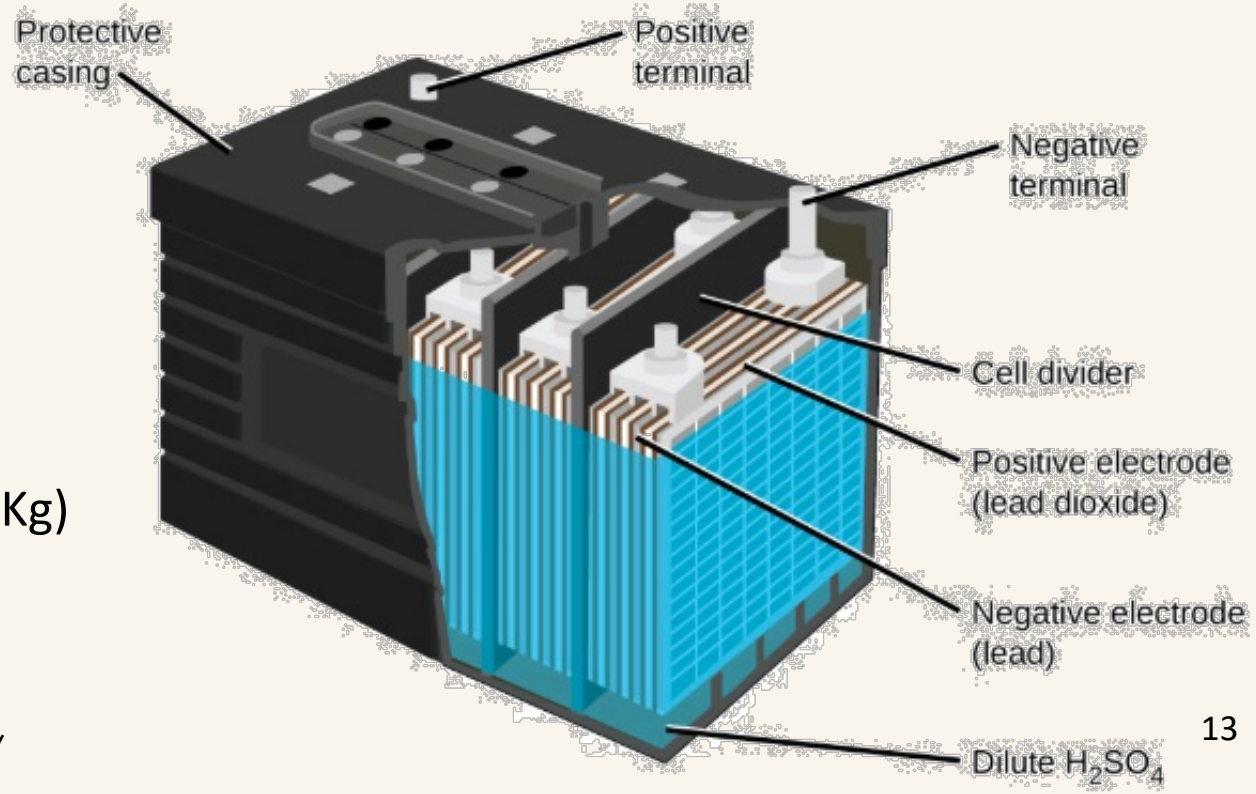


Secondary Batteries

- Definition
  - In secondary cells, the chemical reactions are reversible
  - These cells can be recharged by electric current
- Secondary cells are widely used in electric and hybrid vehicles, smart phones, digital cameras, laptops, etc.

Lead acid battery

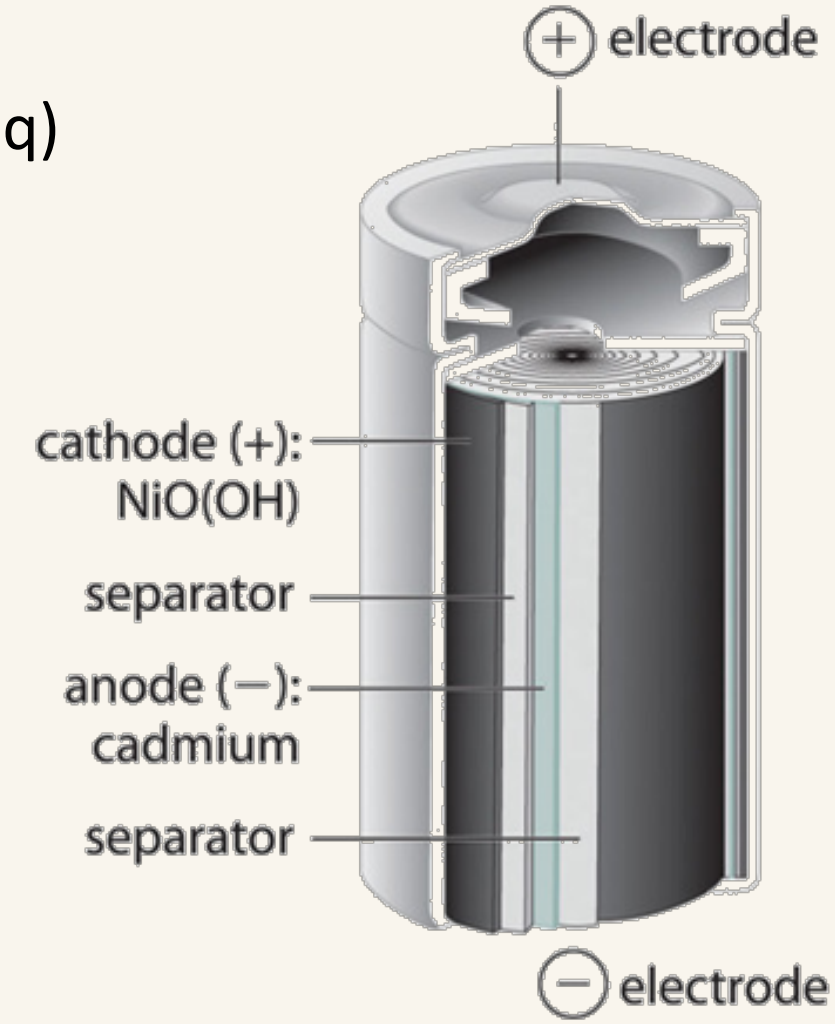
- At anode: $Pb\ (s) + SO_4^{2-}\ (aq.) \rightarrow PbSO_4\ (s) + 2e^-$
- At cathode: $PbO_2\ (s) + SO_4^{2-}\ (aq.) + 4H^+\ (aq.) + 2e^- \rightarrow PbSO_4\ (s) + 2H_2O$
- Voltage: 2 V, used for railways, power stations (stand-by supplies)
- Advatages:
  - Reliable - constant potential
  - Inexpensive
  - Rechargeable, portable
- Drawbacks:
  - Low life cycle
  - Low energy density (30 ~ 40 Wh/Kg)
  - Use of H_2SO_4 is dangerous



https://byjus.com/chemistry/lead-acid-battery/

Nickel–cadmium cell

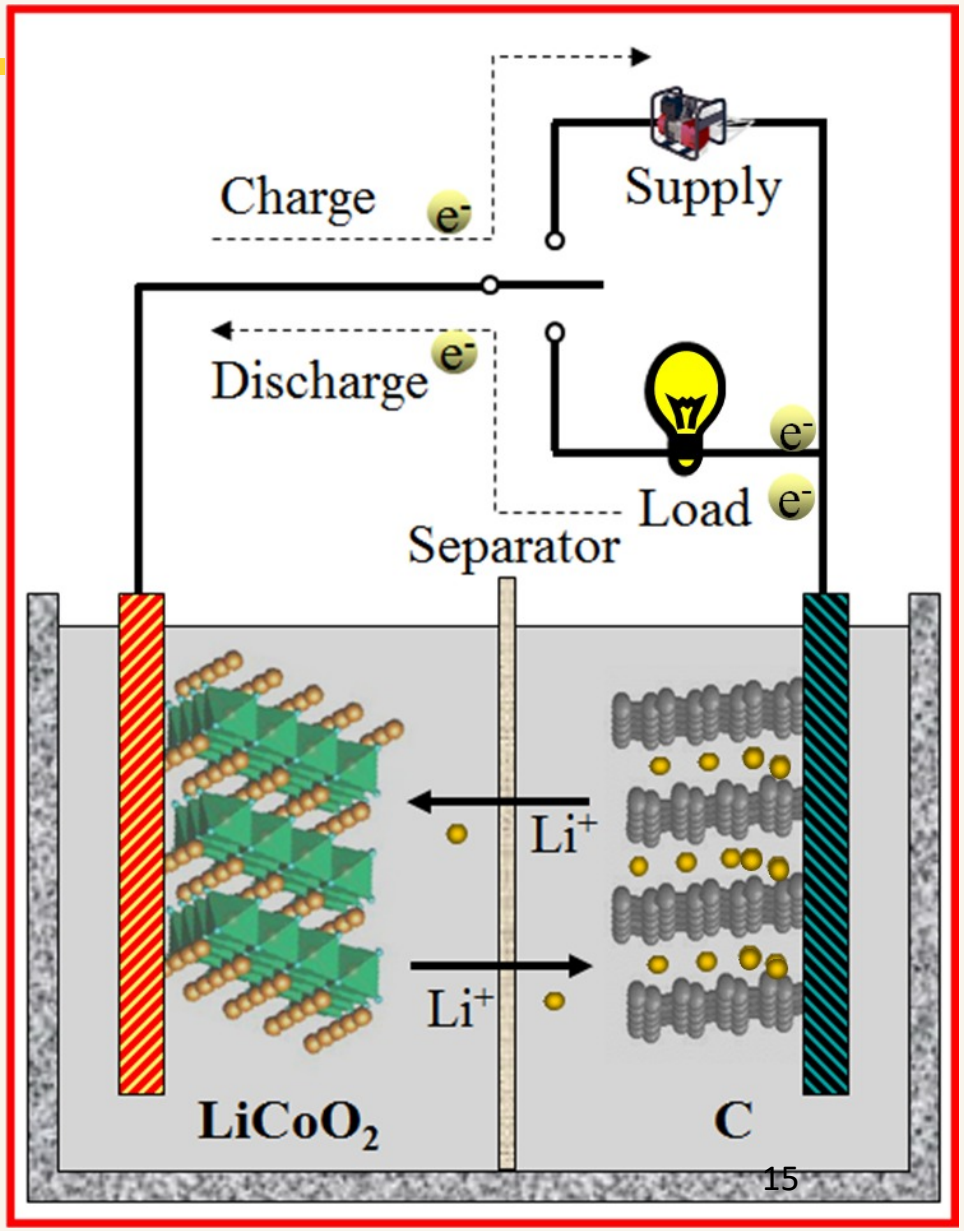
- At Anode: $Cd\ (s) + 2OH^-\ (aq) \rightarrow Cd(OH)2\ (s) + 2e^-$
- At Cathode: $NiO(OH)\ (s) + 2H_2O + 2e^- \rightarrow 2\ Ni(OH)_2 + OH^-(aq)$
- Voltage: 1.4V
- In small electronic calculators, electronic flash units, etc.
- Advantages:
  - Rechargeable
  - High energy density
- Drawbacks:
  - Self discharge (20-30 % per month)
  - Memory effect
  - Toxicity of cadmium



https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_(Zumdahl_and_Decoste)/11%3A_Electrochemistry/11.5%3A_Batteries

Li Ion Battery

- At anode: $xLi^+ + xe^- + 6C \leftrightarrow Li_xC_6$
- At cathode: $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^+ + xe^-$
- Compared to Ni-Cd batteries:
  - No memory effect
  - Higher voltages (~3 ×)
  - Self discharge <5 % per month



D. Deng, *Energy Science & Engineering*, **2015**, 3, 5, 385-418

What is the source of the electrochemical driving force that allow batteries to operate?

What is the source of the electrochemical driving force?

The chemical driving force across a battery, ΔG (Gibbs free energy), can be defined as:

The ease with which the anode material gives up electrons = ease of oxidation

Group I & II metals are easily oxidized to M^{+} or M^{2+}

The ease with which the cathode material picks up electrons = ease of reduction
Group 16 & 17 most easily reduced to form E^{1-} and E^{2-}

The mass of these elements defines their utility for battery applications, lower mass/e^{-} means higher energy density.

Thus, Li, Na, Mg are the lightest and most easily oxidized metals

Oxygen and sulfur are the lightest and most easily reduced elements.

Halogens are easier…but not practical…

Relation of the Gibbs energy with chemical potential

Chemical driving force across battery is ΔG = chemical potential between two electrodes.

Expressed as the difference in standard Gibbs free energy/mol of reaction.

Basically $\Delta G_{free\ energy}$ of products and reactants that occur at neutral electrodes.

$$\Delta G_{reaction} = -zFE = \Delta\mu$$

Z = the charge number of mobile ion

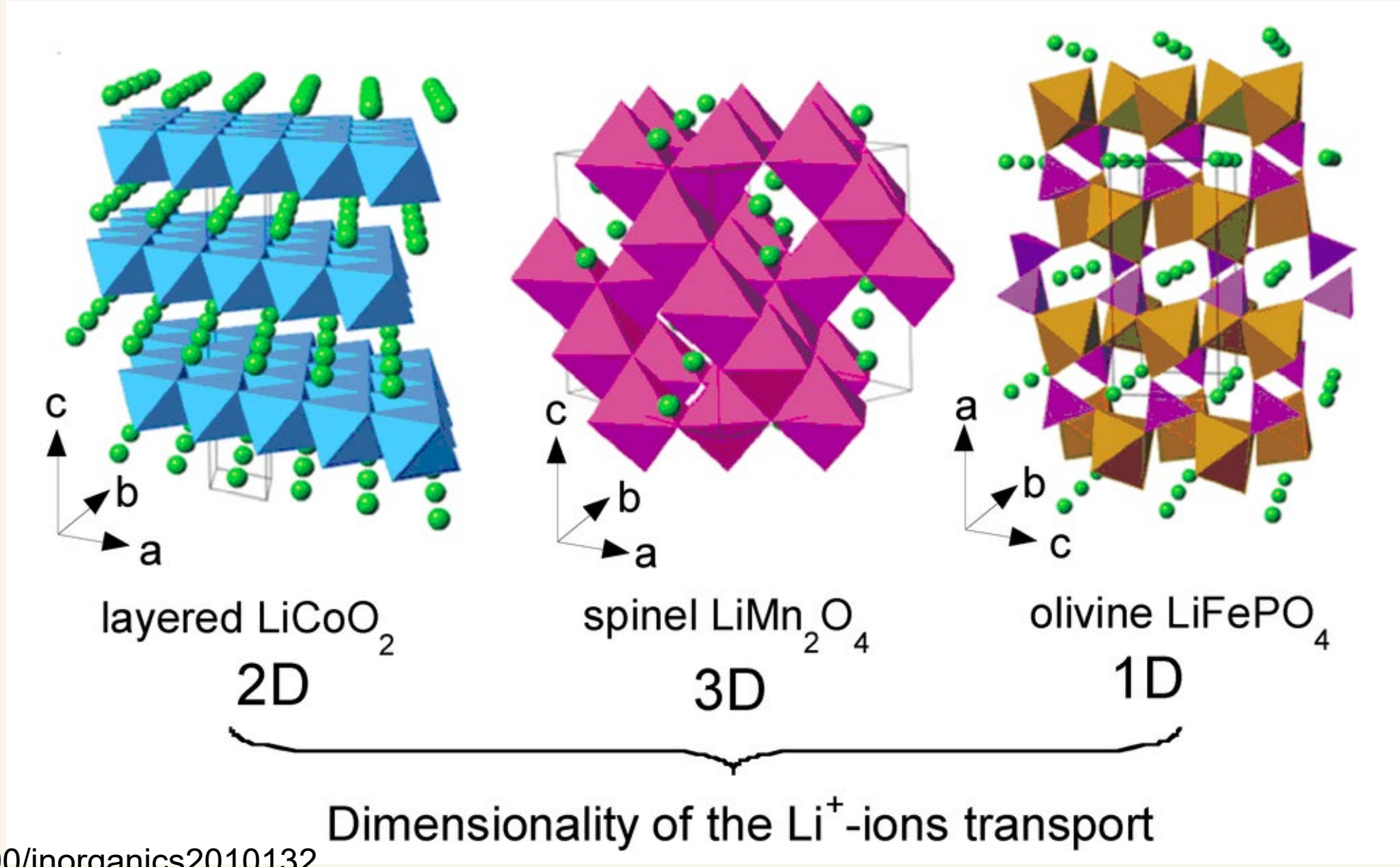
F = Faraday's constant 96,500 coulomb/mol

E = Voltage between electrodes

$\Delta\mu$ = chemical potential – ability to be oxidized/reduced

The $G_{free\ energy}$ depends on the battery chemistry which relies on the electrodes

Typical cathode materials



doi:10.3390/inorganics2010132

Selection criteria for cathode

- High redox potential (values)
- High specific capacity (mAh/g values)
- Reversibility
- Mixed conductor ($\sigma_{m_+} = \sigma_{e^-}$)
- Good stability with respect to electrolyte system(s)

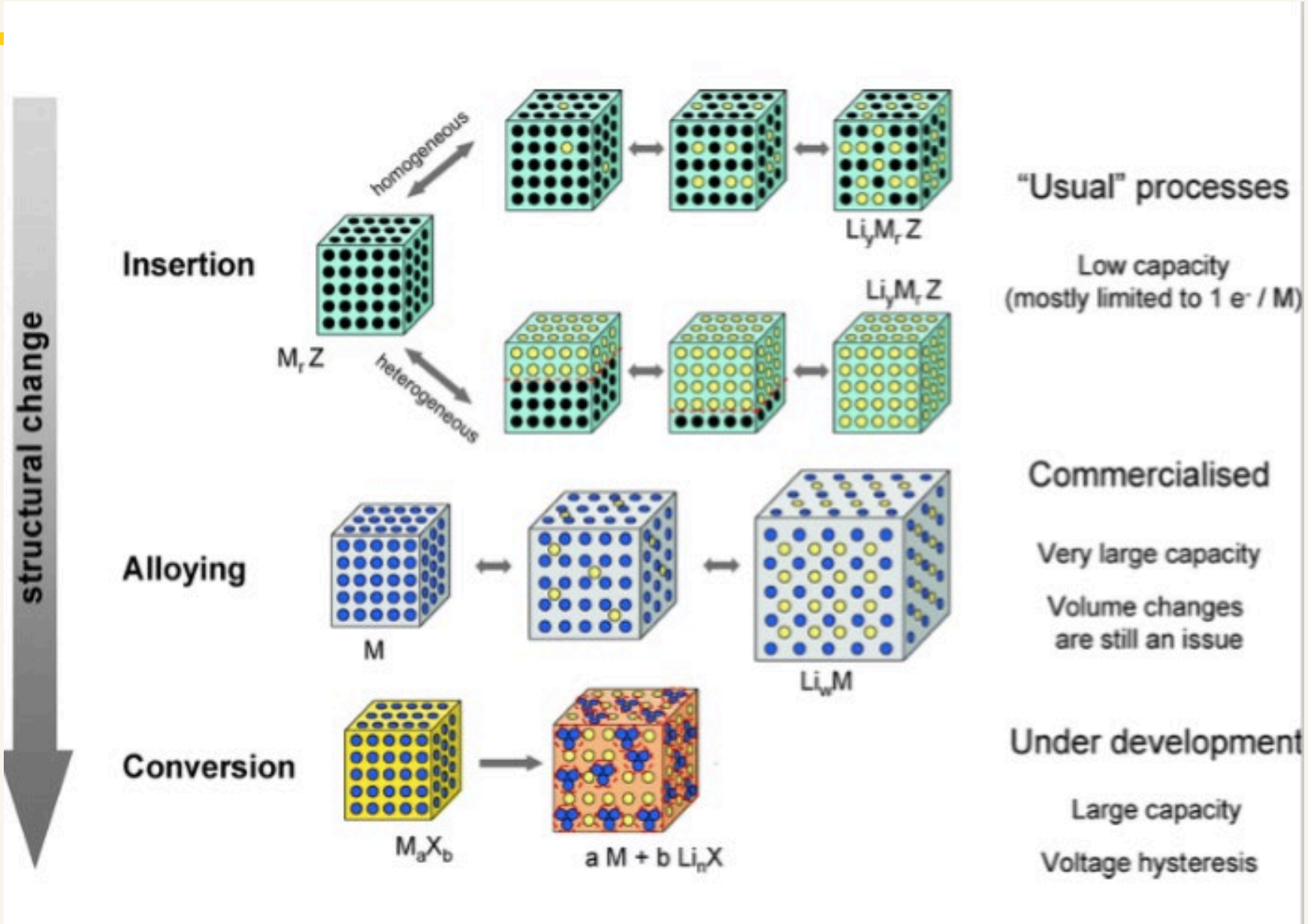
Typical anode materials

Anode	Reversible Specific capacity (mAh/g)	Irreversible Specific capacity (mAh/g)	Average Voltage (V)
Graphite	372	15-30	0.2-0.1
SnO_2	782	711	0.7-0.4
SnO	875	398	0.7-0.4
Sn	993(805*)	-	0.7-0.4
Si	4,211(2,109*)	-	0.4-0.1
Li	3,862	-	0.0

Define irreversible, asterisk?

Categories of anodes

- Intercalation
- Li metal
- Insertion
- Conversion (alloy)



Selection criteria for anode

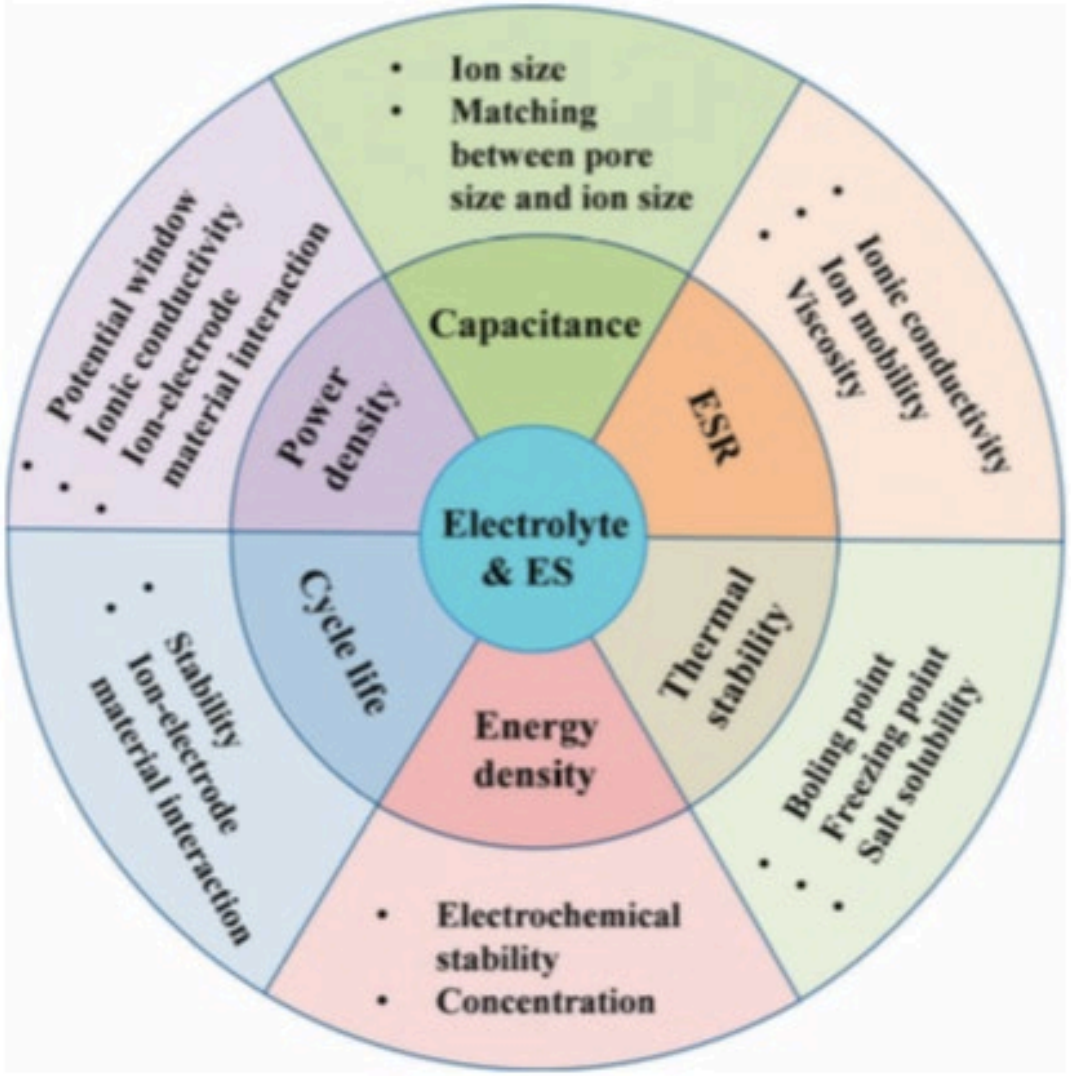
- Low redox potential values
- High specific capacity (mAh/g values)
- Reversibility
- Mixed conductor ($\sigma_{m_{+}} = \sigma_{e}$-)
- Constant voltage

Electrolytes

will be described in separate lectures

1. Liquids
2. Solids
3. Polymer
4. Composite or hybrid

Criteria for electrolytes



1. Wide potential window
2. High ionic conductivity
3. Chemically & electrochemically inert
4. Wide operating temperature range
5. Low volatility and flammability
6. Environmentally friendly

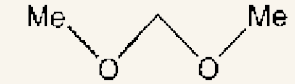
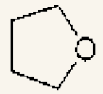
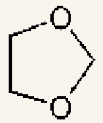
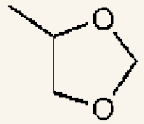
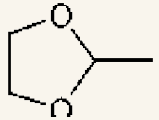
Zhong, Cheng, et al. *Chemical Society Reviews* 44.21 (2015): 7484-7539.

Traditional liquid electrolytes

- Low viscosity, polar liquids capable of dissolving M^{+}/M^{2+} and anions.
- Operational window -40 °C to ≈ 60 °C.
- Typical Li^{+} diffusion rates values
- Low flammability

K. Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” *Chem. Rev*. **2004**, 104, 4303−4417

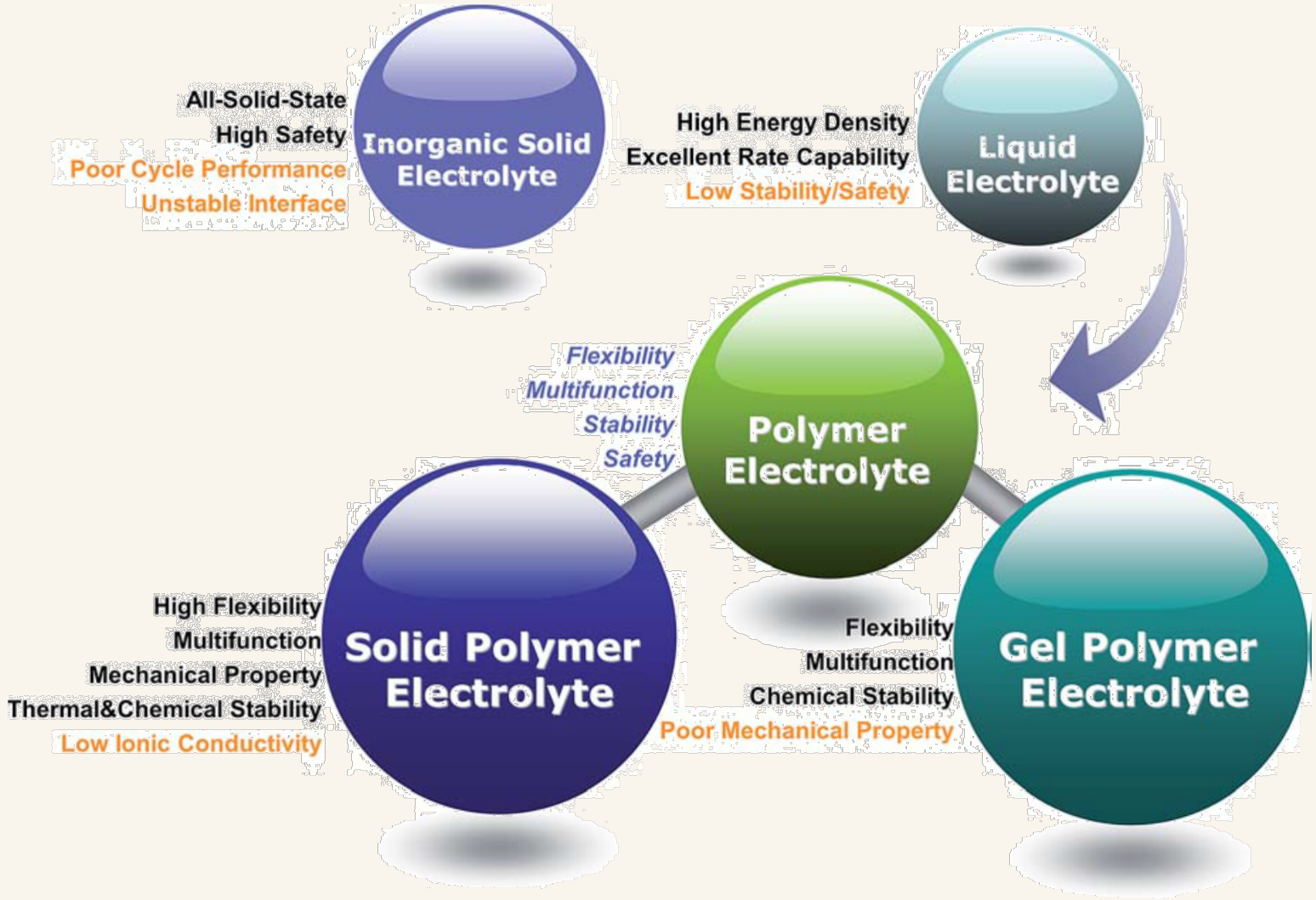
Traditional liquid electrolytes

Solvent	Structure	M. Wt	T_m/ °C	T_b/ °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T_f/ °C	d/gcm^{-3}, 25 °C
DMM		76	-105	41	0.33	2.7	2.41	–17	0.86
DME		90	-58	84	0.46	7.2	1.15	0	0.86
DEE		118	-74	121				20	0.84
THF		72	-109	66	0.46	7.4	1.7	-17	0.88
2-Me-THF		86	-137	80	0.47	6.2	1.6	-11	0.85
1,3-DL		74	-95	78	0.59	7.1	1.25	1	1.06
4-Me-1,3-DL		88	-125	85	0.60	6.8	1.43	-2	0.983
2-Me-1,3-DL		88			0.54	4.39			

K. Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” *Chem. Rev*. **2004**, 104, 4303−4417

Polymeric electrolytes

- Multifunctional
- Flexible
- Good mechanical properties
- Moderate thermal stability
- Safe



Z. Xue, et al., *J. Mater. Chem. A* **2015**, 3, 19218–19253

Polymeric electrolytes

Solid polymer electrolytes (SPE)

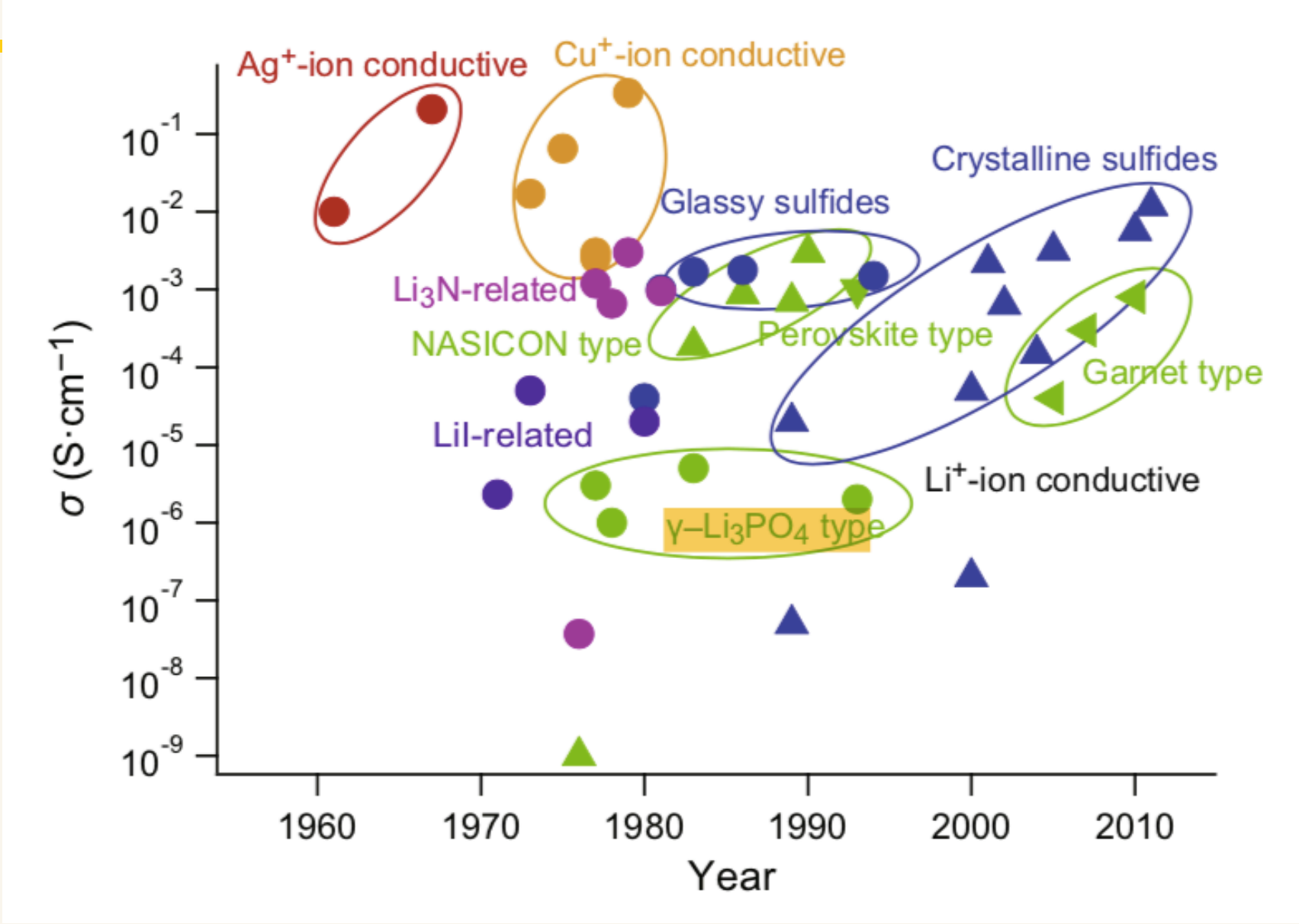
- Polymer matrix + lithium salt
- Good safety, easy fabrication, low cost, high energy density, good electrochemical stability, and excellent compatibility with lithium salts
- But poor ionic conductivity at room temperature (10^{-5}-10^{-1} mS cm^{-1})

Polymeric electrolytes

Gel polymer electrolytes (GPE)

- Incorporate liquid plasticizer and/or solvent into a polymer–salt system
- Conductivity can reach 1 mS cm^{-1}, but poor mechanical strength and poor interfacial properties

Progress with solid electrolytes



K. Takada, Progress and prospective of solid-state lithium batteries, Acta Mater. (2013).

Advantages of solid-state electrolytes

details later in course

- Inorganic solid-state electrolytes enable robust cell chemistries
  - No electrolyte leakage
  - No organics to degrade
  - Improved safety – non-flammable
  - Could enable Li metal and high voltage cathodes (values)
  - Enhanced thermal stability
  - Could be fabricated in air
  - High Li^+ transference numbers values vs:
    - > 0.25 – liquid electrolyte these values are for liquids?
    - > 0.5 – polymer electrolyte

COLLEGE OF ENGINEERING
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Introduction to Battery architecture
Lecture 2

Taylor Brandt, Mengjie Yu, Richard M. Laine, Eleni Temeche, Xinyu Zhang,

Depts of Materials Sci. & Eng. And Macromolecular Sci. & Eng.

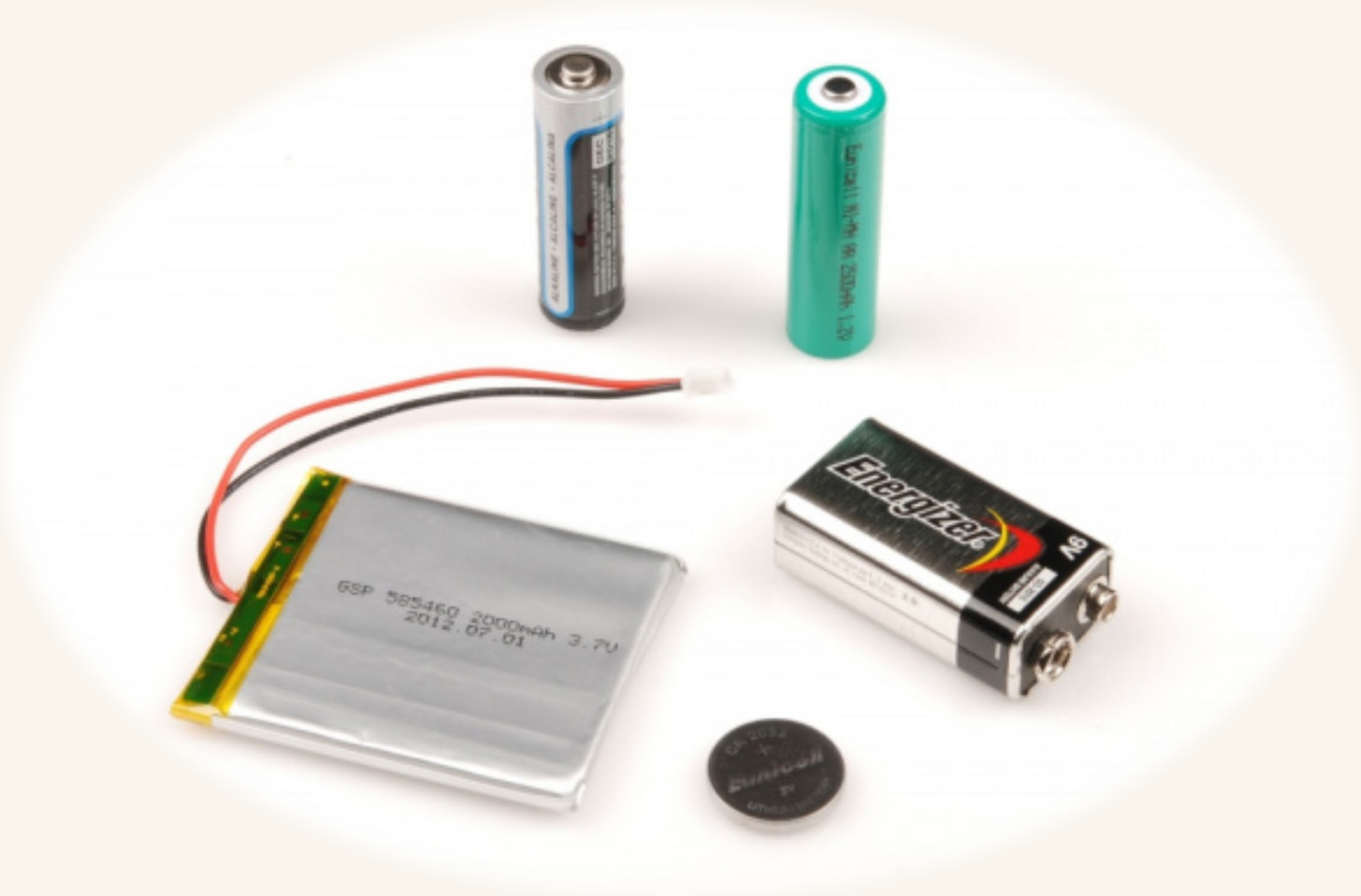
University of Michigan

Content

- Battery Architecture
  - Cell format
- Components in:
  - Coin cell
  - Prismatic cell
  - Pouch cell
- Solid state battery assembly

Cell formats

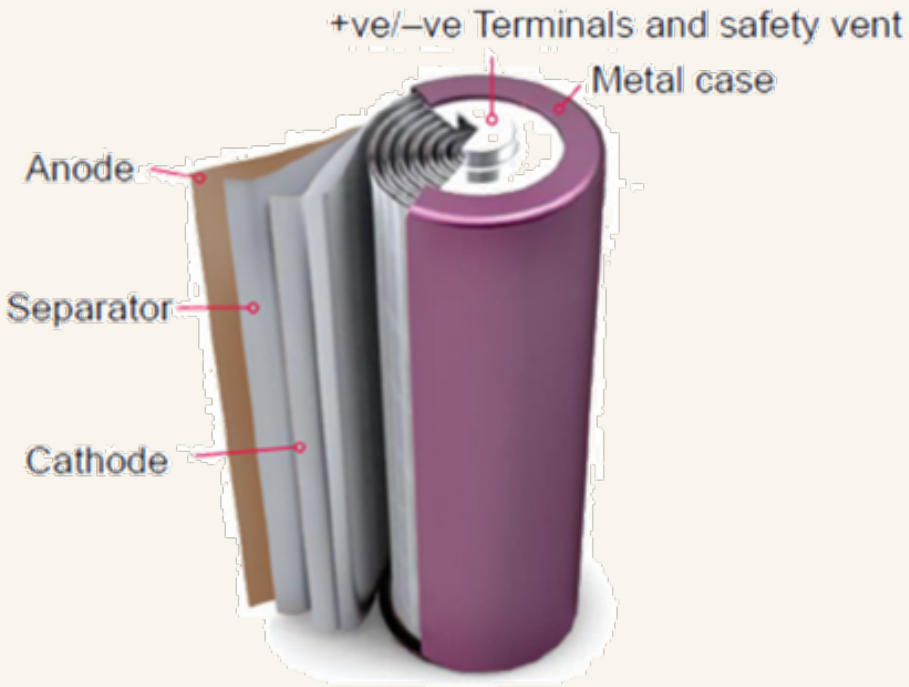
- Cylindrical cells
- Prismatic cells
- Pouch cells
- Coin cells

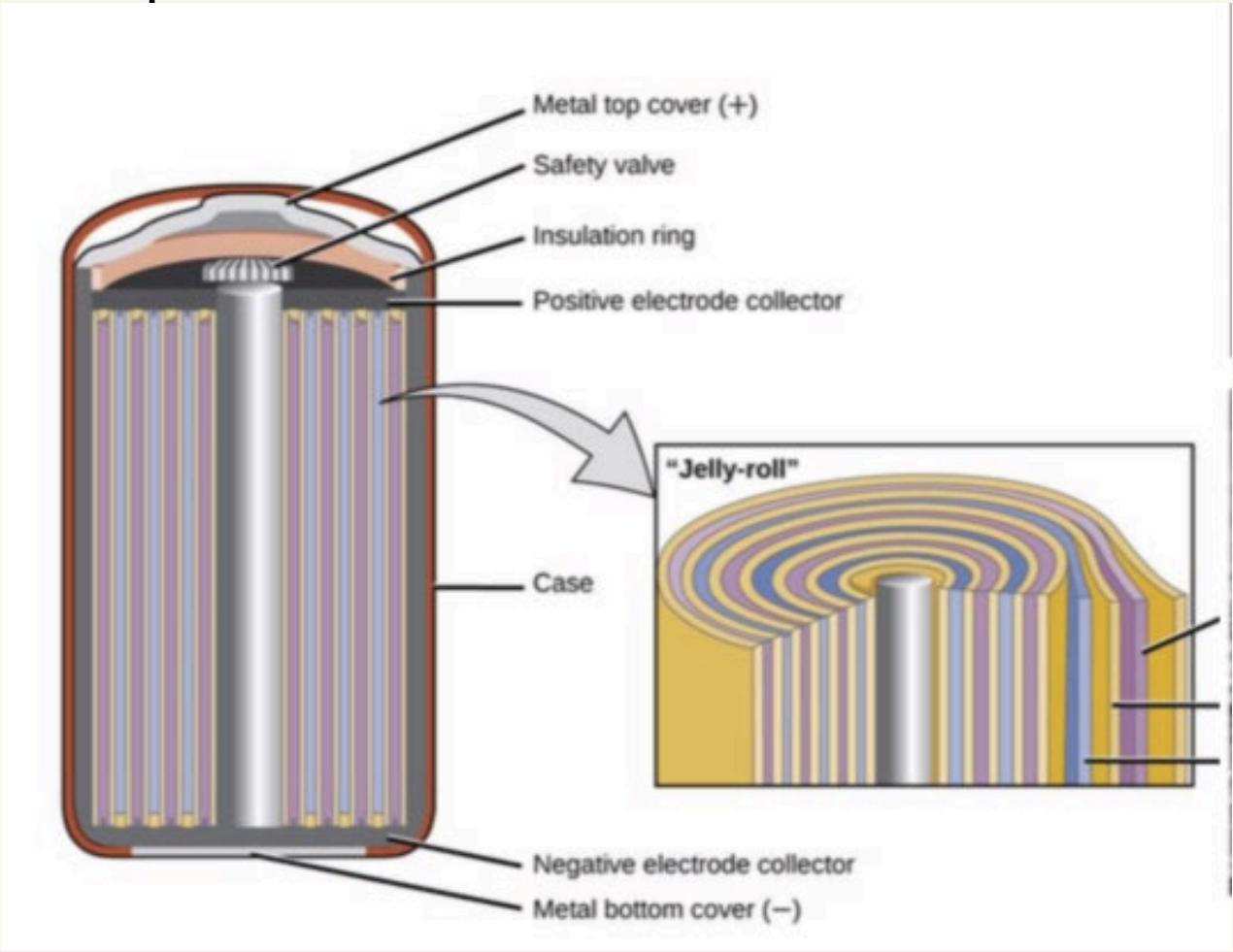


https://learn.sparkfun.com/tutorials/what-is-a-battery/all

Cylindrical Cells—Jelly Roll

- Definition
  - Cell with positive, negative electrodes, and separator in cylindrical container

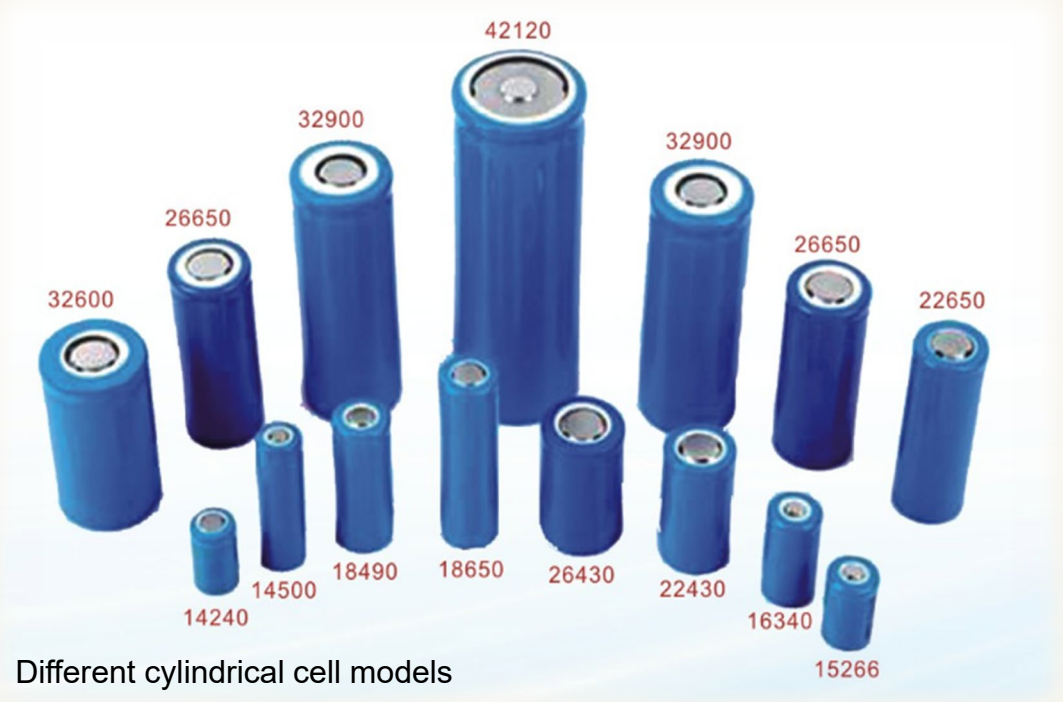




C. J. Cleveland et al., *Dictionary of Energy*, Second Edition; M Zschornak et al., *Physical Sciences Reviews,* **2018**, 20170111; http://nbobattery.com/product/html/?18.html

Cylindrical Cells

- Advantages:
  - Good mechanical stability
  - High energy density
  - Lowest cost to manufacture
  - Mass produced in standard sizes
    - E.g. 18650 cell: 18 mm diameter, 65 mm length
- Challenges:
  - Low packaging efficiency
    - Relative heavy packing material
- Applications:
  - Traditional: power tools, medical instruments
  - New demands: military, drones and electric car

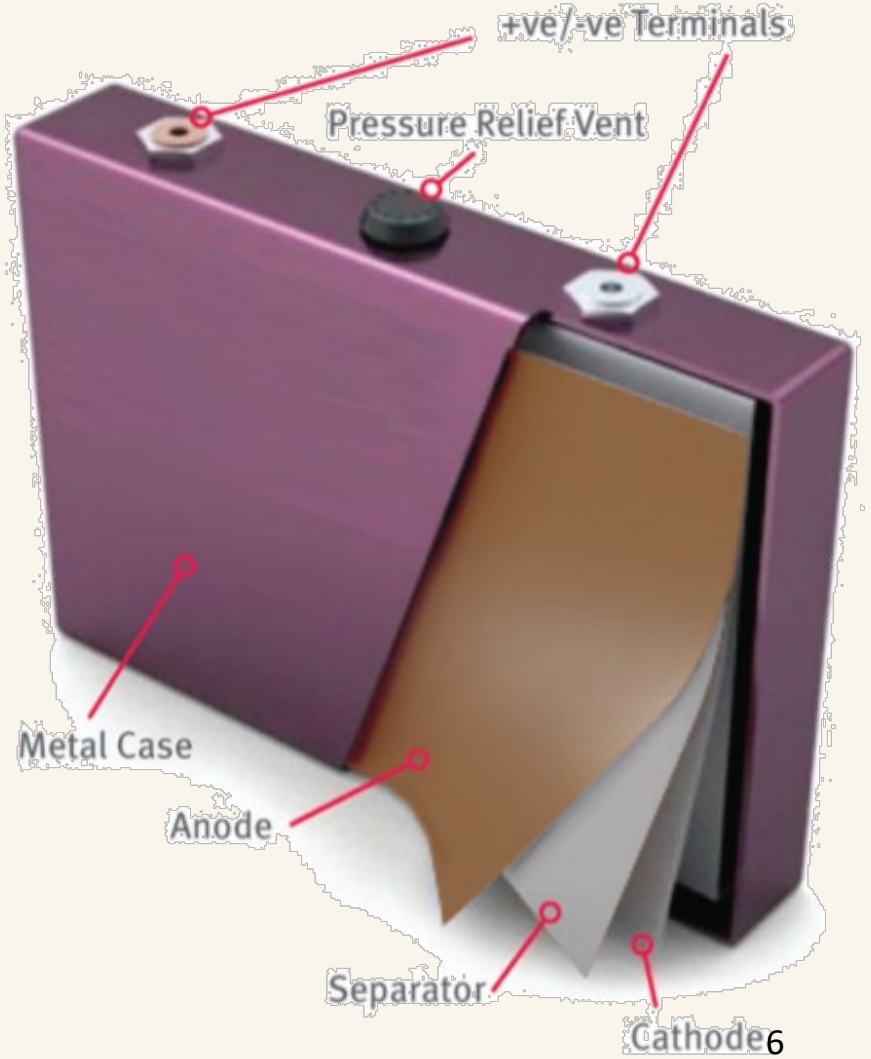


Different cylindrical cell models

http://nbobattery.com/product/html/?18.html

Cell formats prismatic cells

- Definition
  - Cell where positive, negative plates, and separator, stacking in prismatic container



C. J. Cleveland et al., *Dictionary of Energy*, Second Edition
M Zschornak et al., *Physical Sciences Reviews,* **2018**, 20170111
https://www.vpwllc.com/prismatic-cells/

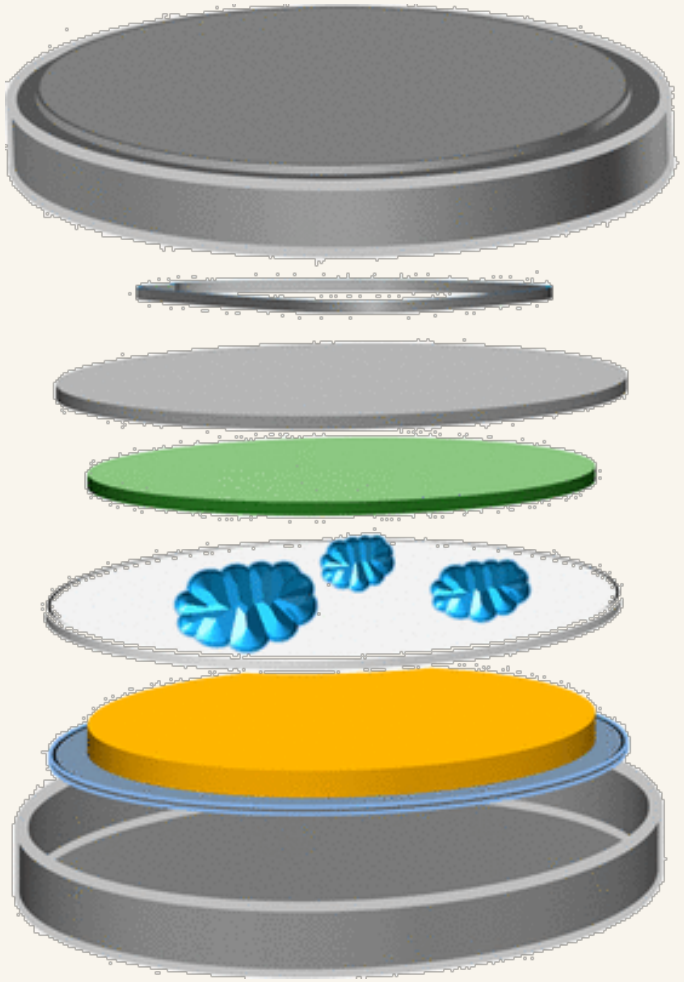
Prismatic Cells

- Advantages:
  - Hard case provides protection
  - No standard size – advantage in design
    - Customizable packaging to meet cell/pack requirements
- Challenges:
  - No standard size – disadvantage in production
  - Harder/more expensive to manufacture
    - Larger cells difficult for automated assembly
    - Often ineffective in high pressure situations
- Applications:
  - Mobile phones, tablets and laptops

M Zschornak et al., *Physical Sciences Reviews,* **2018**, 20170111;
https://www.vpwllc.com/prismatic-cells/

Coin Cells

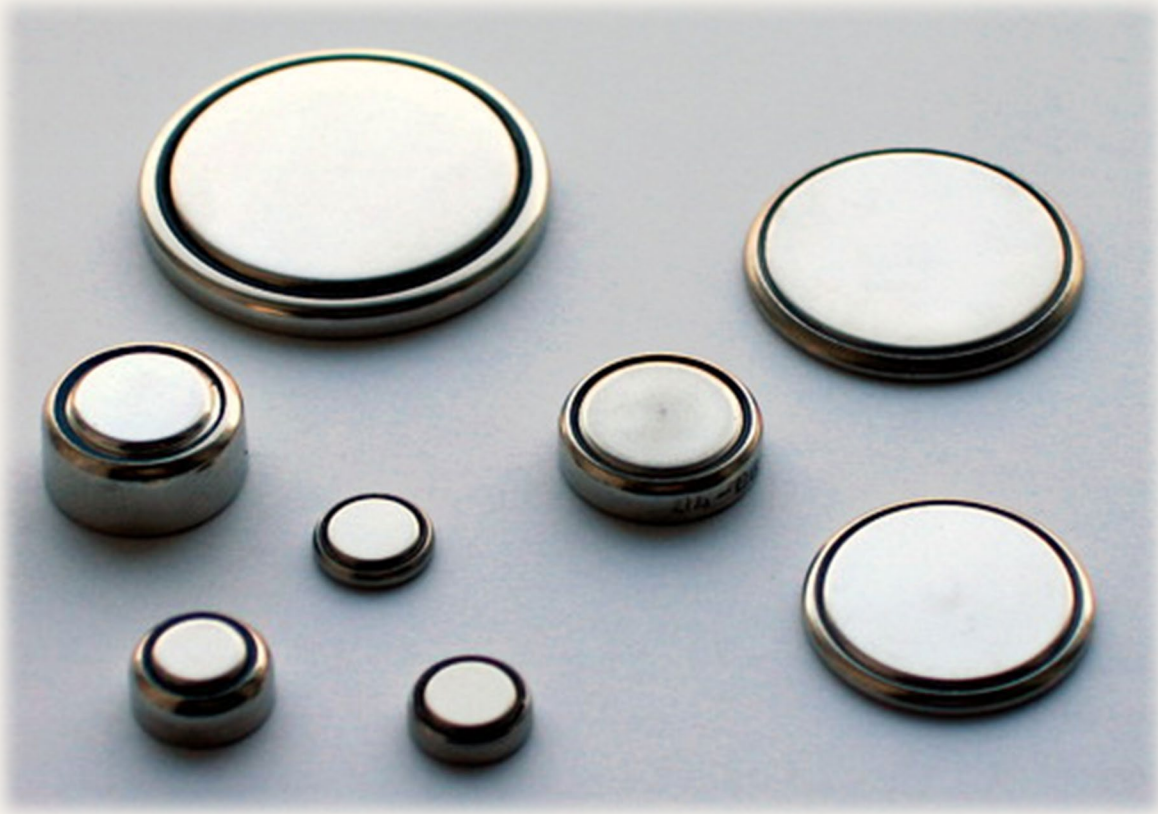
- Definition
  - Miniature battery w/circular cross-section
  - Overall height < diameter
- Typical format for testing materials



C. J. Cleveland et al., Dictionary of Energy, Second Edition;
E Talaie et al., *Chem. Mater.*, **2017**, 29, 1, 90-105

Coin Cells

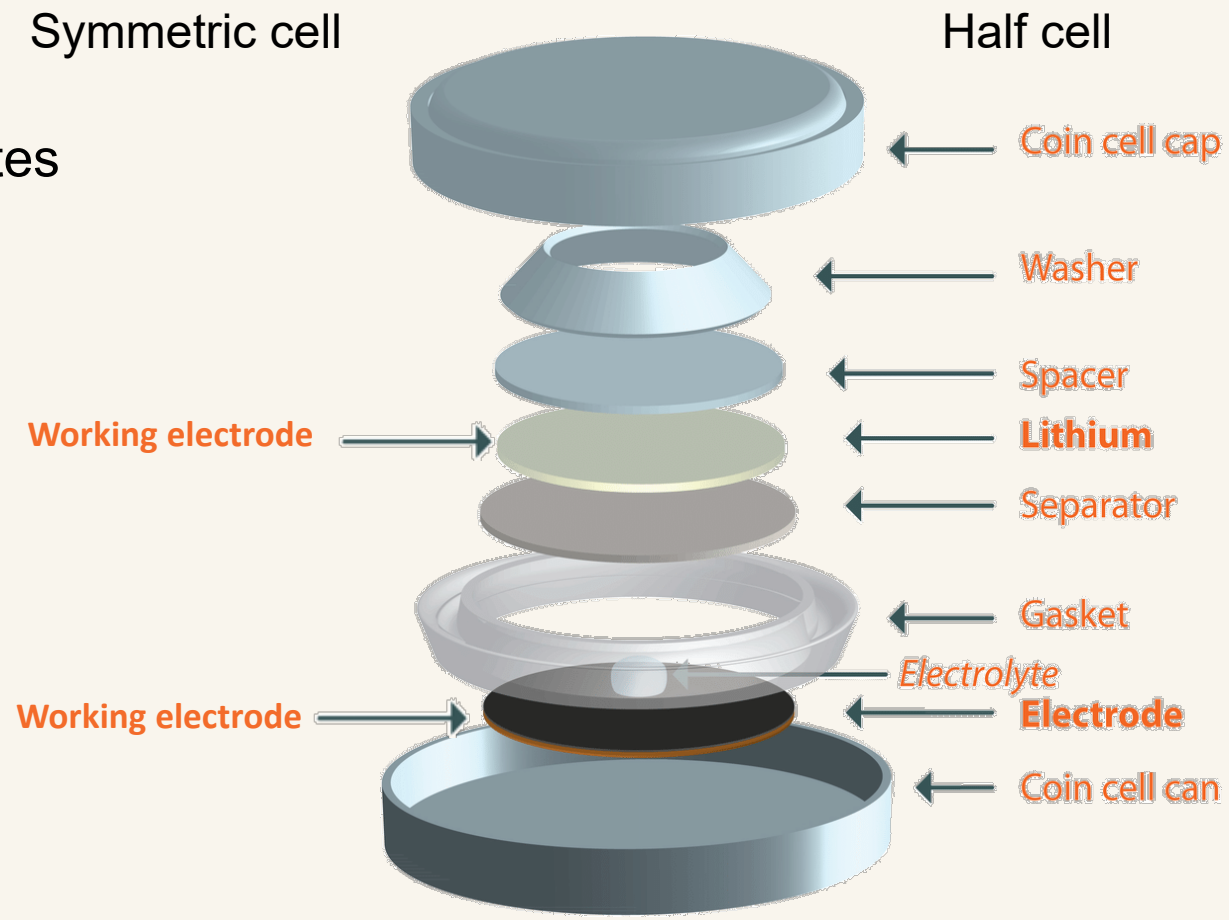
- Advantages:
  - Easy & cheap to manufacture
  - Standardized sizes
- Challenges:
  - Usually single layer – limited capacity
  - Often require slow charge rates
  - Performance not scalable
- Applications:
  - Portable: cordless telephones, medical devices



E Talaie et al., *Chem. Mater.,* **2017**, 29, 1, 90-105
https://en.wikipedia.org/wiki/Button_cell

Coin cells--utility for research

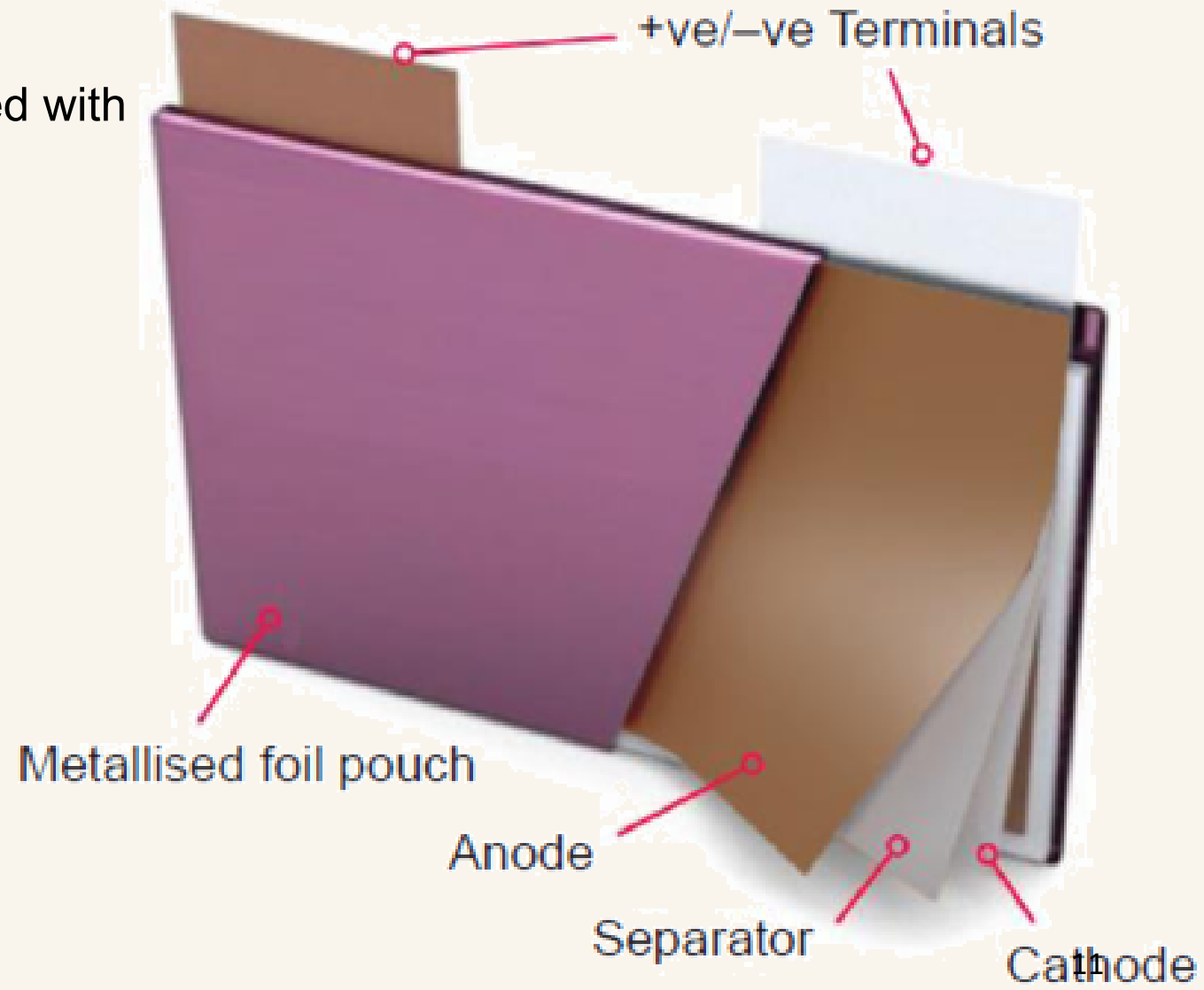
- Symmetric cell
  - Uses 2 identical electrodes
    - One lithiated, the other delithiated
  - Limits Li supply and Li foil reactions w/electrolytes
  - Differs from full cell
    - Only side reactions induced by the range of tested electrode's potential can be observed
- Half cell
  - Using Li foil as reference/counter electrode
  - Easy to make, can provide repeatable data
  - Abundance of Li
    - Unable to observe problems with Li consumption



J. C. Burns et al., *J. Electrochem. Soc.,* **2011**, 158 (12) A1417-A1422;
T. Matsuyama et al., *J. Electrochem. Soc.,* **2019**, 166 (2) A329-A333

Pouch Cells

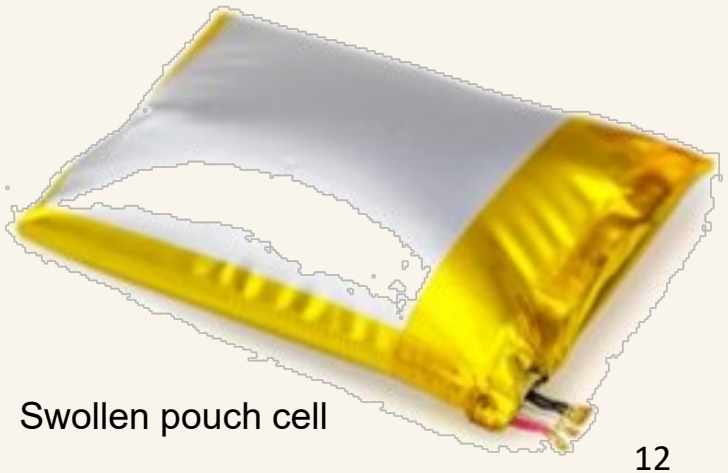
- Definition
  - Prismatic cell with metallic case replaced with
  - flexible, heat-sealable foil package



C. J. Cleveland et al., *Dictionary of Energy*, Second Edition;
M Zschornak et al., *Physical Sciences Reviews,* **2018**, 20170111

Pouch Cells

- Advantages:
  - Lightweight packaging
    - Optimized packing efficiency >95%
  - Easily stackable
- Challenges:
  - No inherent protection against swelling
    - High temperature and humidity shorten cell life
    - Robust cell packaging required at pack level
  - Electrode delamination
    - Works best with pressure on stack

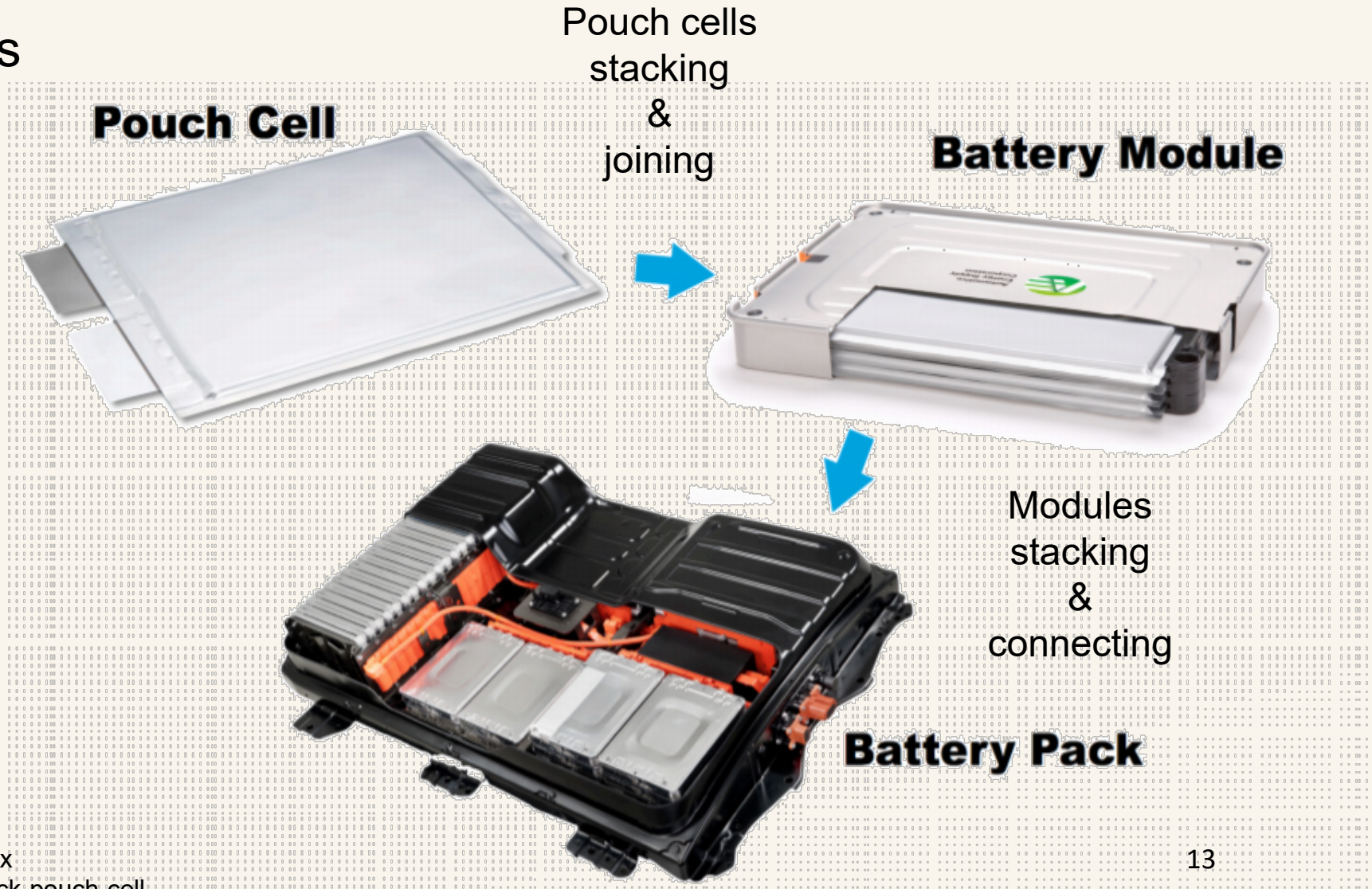


Swollen pouch cell

https://www.vpwllc.com/pouch-cells/
https://www.stockwell.com/blog/designing-battery-pad-for-li-ion-pouch/

Pouch Cells

- Commercial battery packs



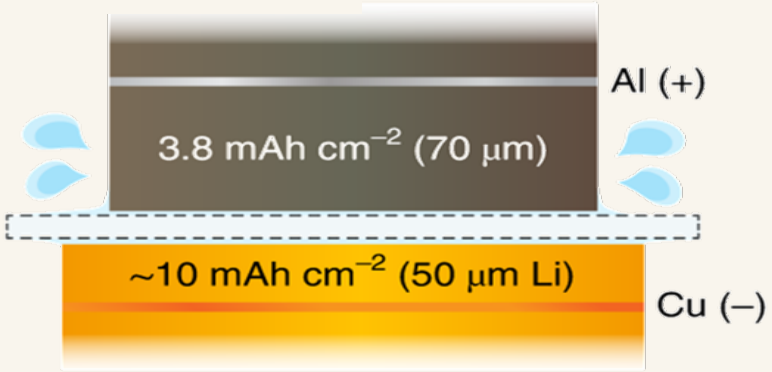
- Applications:
  - Electric bikes, scooters
  - Consumer electronics
  - Electric tools

http://www.talgaresources.com/IRM/content/default.aspx
https://battery-system.com/product/3-7v-lipo-battery-pack-pouch-cell

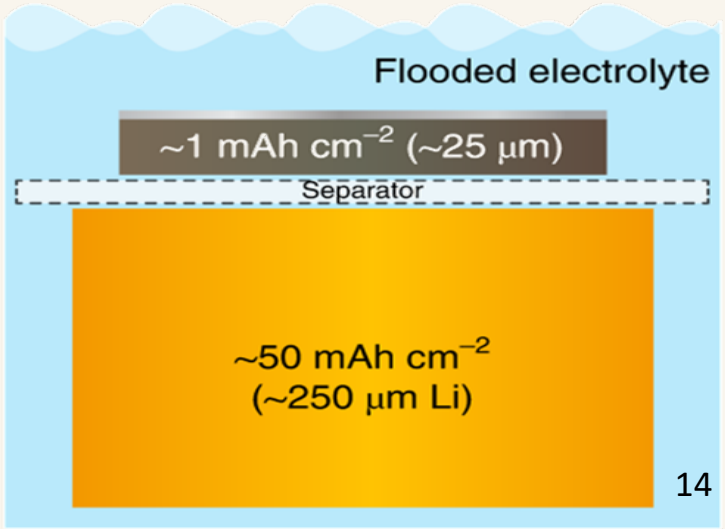
Pouch vs coin cells--utility for research

- Pouch cells:
  - High area capacity cathode (3.8 mAh cm^{-2})
  - Limited Li (N:P ratio of 2.6)
    - Areal capacity of anode to cathode
  - Lean electrolyte (E/C ratio of 3.0 g Ah^{-1})
    - E/C ratio: electrolyte mass to capacity
  - Commercial Li^+ batteries: N/P ~1.1, E/C ~1.3 g Ah^{-1}
- Typical Li metal coin cells (half cell):
  - Low area capacity cathode (~1.0 mAh cm^{-2})
  - large excess Li (N:P ratio of 50)
  - Flooded electrolyte (E/C ratio >75 g Ah^{-1})
  - Inconsistent results with practical batteries

Pouch cell



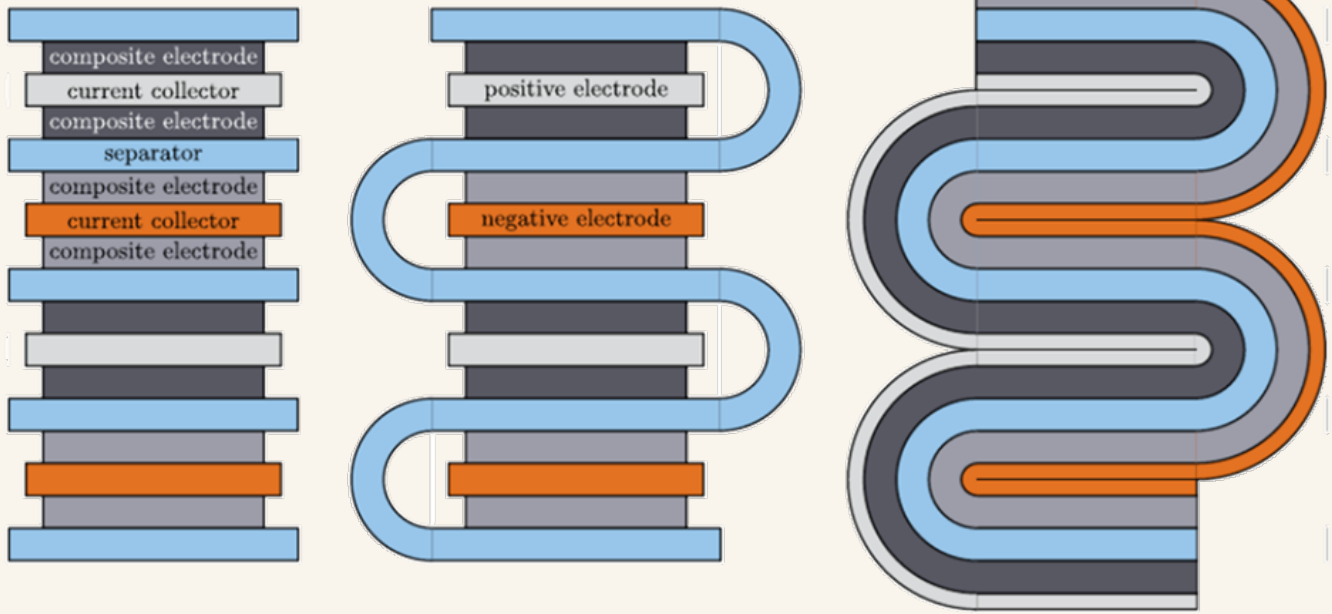
Coin cell

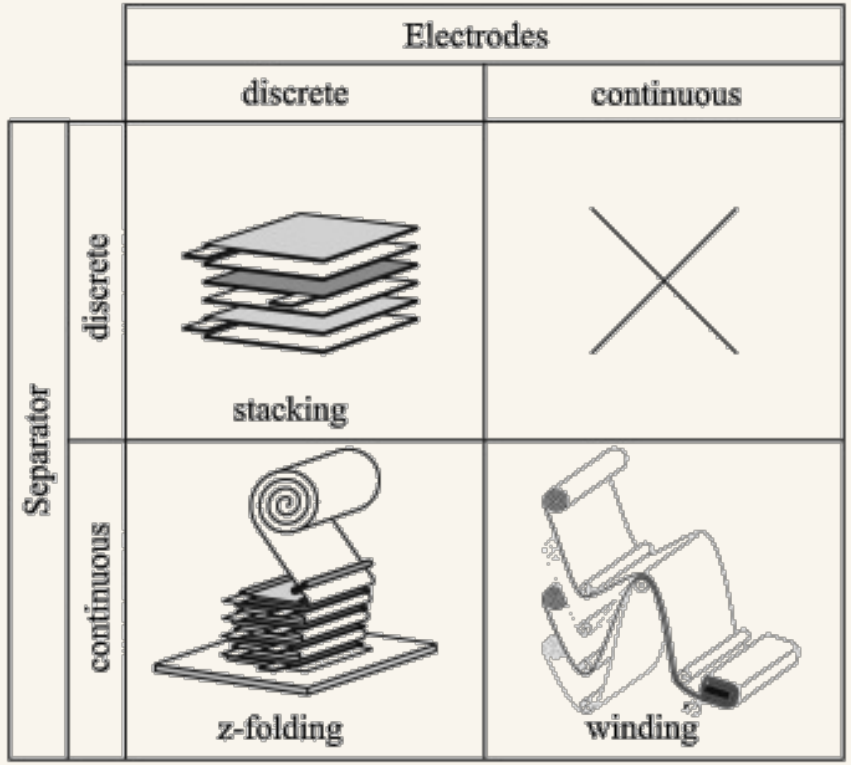


C. J. Niu et al., *Nature Energy*, **2019**, 4, 551–559

Pouch cell processing Z-stacking

- Z-stacking is more commonly used in industry





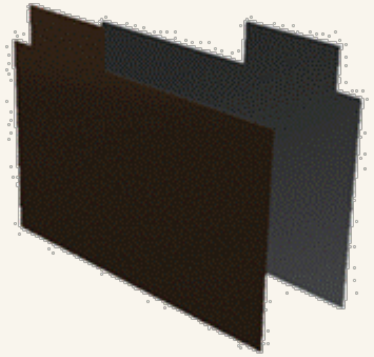
Regular stacking:
Stacked electrodes
&
stacked separators

Z-stacking:
Stacked electrodes
&
Z-folded separators

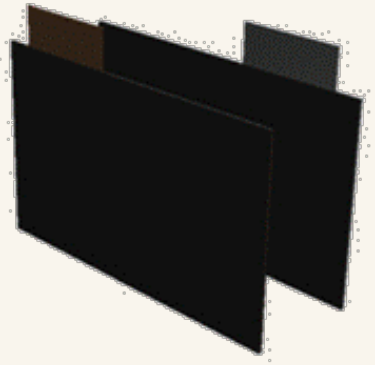
Z-stacking:
Z-folded electrodes
&
Z-folded separators

A. Rheinfeld et al., *J. Electrochem. Soc.*, **2020**, 167, 013511; J. Schmitt et al., *CIRP Ann-Manuf. Tech.*, **2014**, 63, 9–12

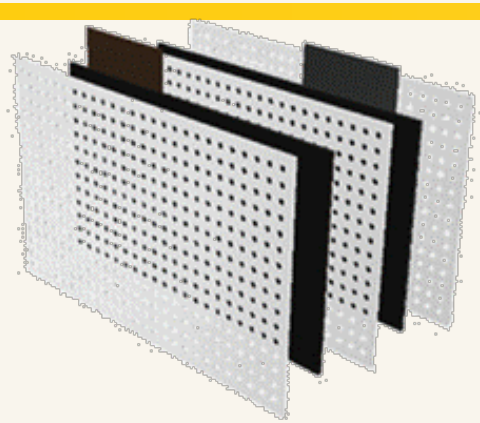
Pouch cell processing regular-stacking



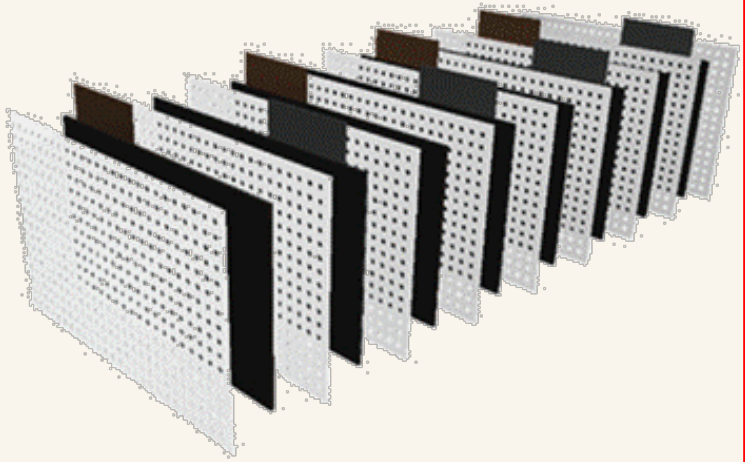
(a) Cu and Al electron collectors



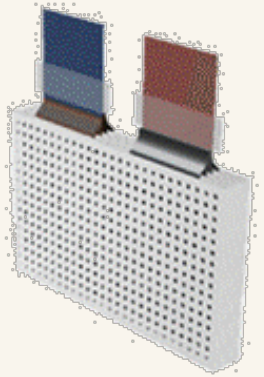
(b) Coat active materials



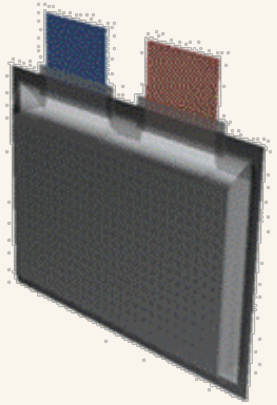
(c) Insert separators



(d) Stacking



(e) Electrode-to-tab joining

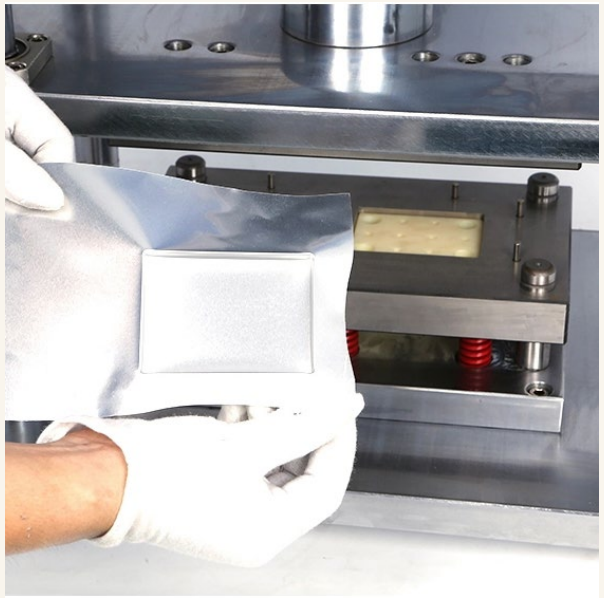


(f) Fill electrolyte and seal

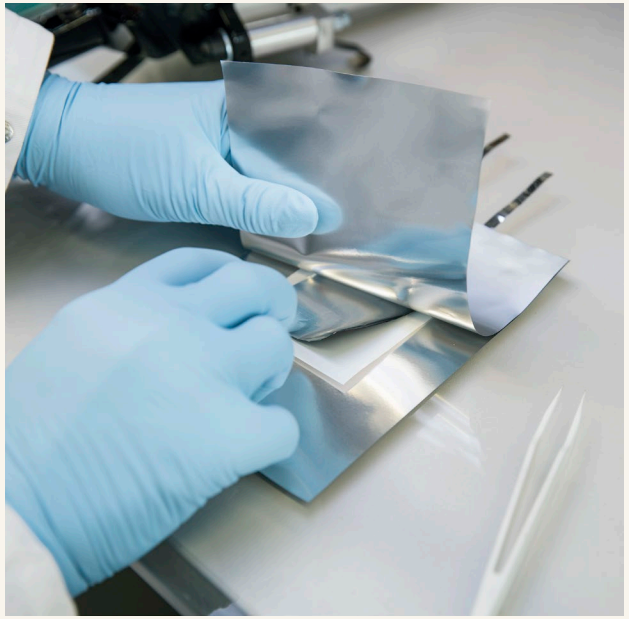
M. S. K. Mutyala et al., *J. Powder Sources*, **2014**, 260 43–49

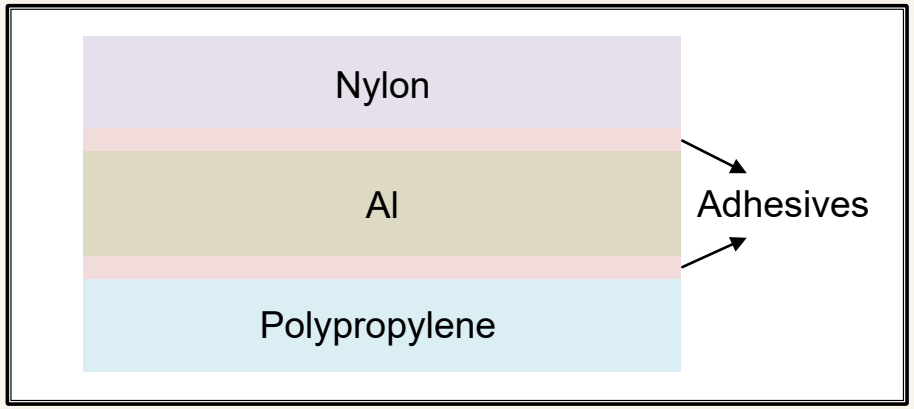
Pouch cell case Al laminated film

Punch



Assembly

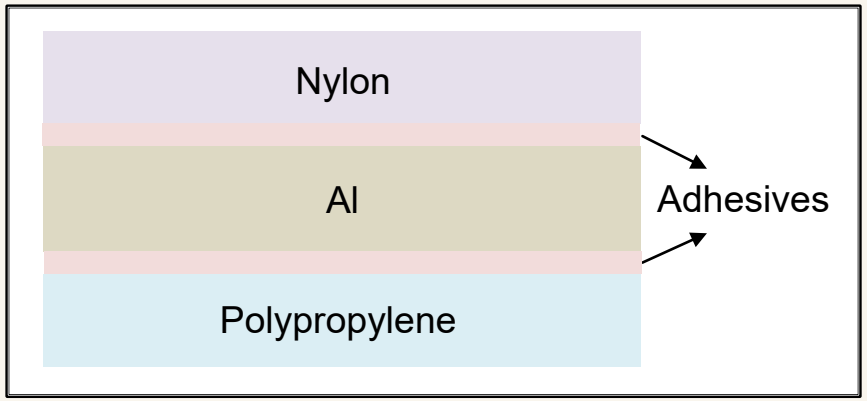




https://www.tvservice.basf.com/portal/basf/en/dt.jsp?setCursor=1_203919_492322&cursorPath=%7C492298%7C481768%7C492296%7C492298&setClientType=Desktop
https://www.mtixtl.com/AluminumLaminatedFilm400mmWx7.5mL-EQ-alf-400-7.5M.aspx
https://www.tmaxcn.com/aluminum-laminated-film-pouch-cell-case-cup-punching-forming-machine-with-optional-die_p910.html

Pouch cell case Al laminated film

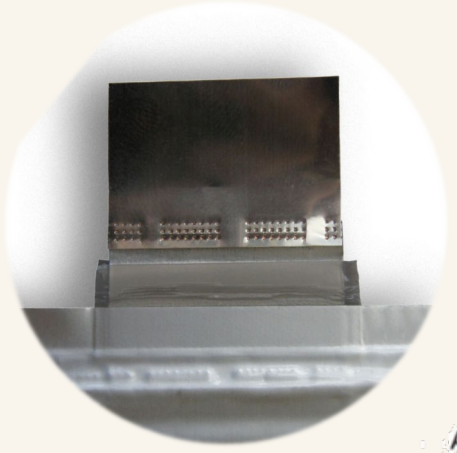
- **Nylon:**
  - Keeps the shape of aluminum laminated film
  - Avoids deformation before manufacture
- **Aluminum:**
  - A layer of metal Al
    - Al reacts with oxygen to form a dense oxide film that prevents water and gas from penetrating
  - Blocks moisture infiltration (Nylon not waterproof)
  - Provides the plasticity for punching
- **Polypropylene:**
  - Heating PP layer causes melting/bonding to seal cells
    - Melting temperature ~ 100°C and PP is viscous
- **Thickness: 71 - 156 μm**
  - Different thickness for each layer in different models

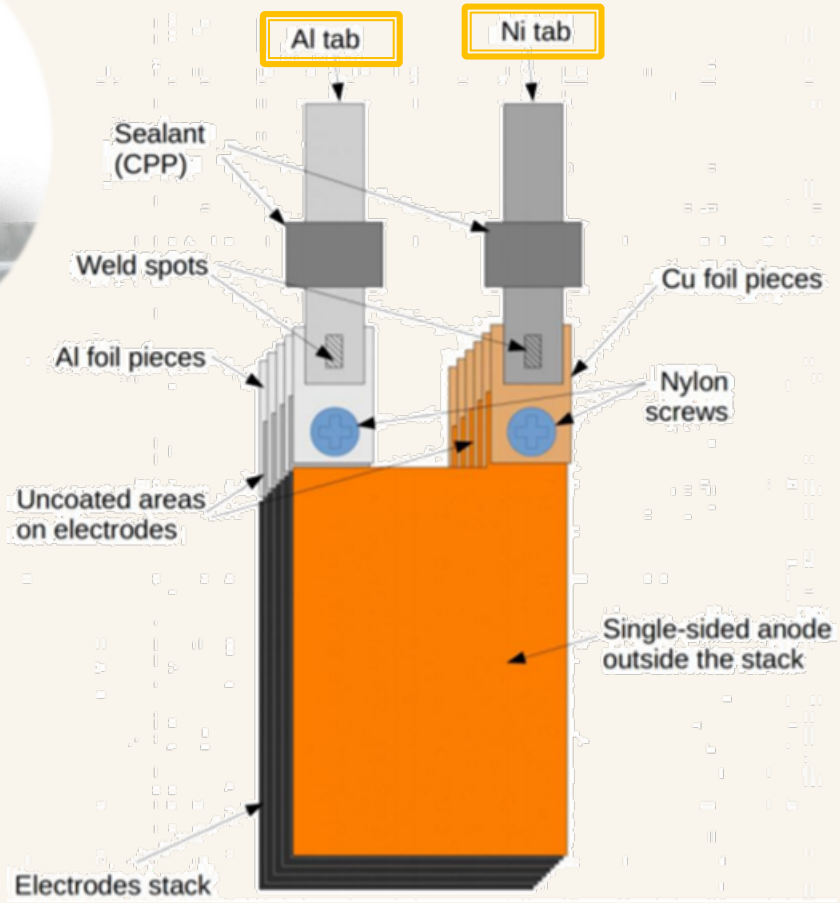


https://www.targray.com/li-ion-battery/packaging-materials/aluminum-laminate-pouch

Pouch cell processing electrode-to-tab joining

- **Tab/terminal:**
  - Cathode: Al
  - Anode: Ni or Cu
- **Sealant:**
  - Usually contains PP
  - Bond with cell case (Al laminated film) under heating
- **Electrode-to-tab weld:**
  - Gather all the current collectors inside a cell
  - Join all current collectors to a tab which exits casing
  - Allow energy to be transferred to external sources

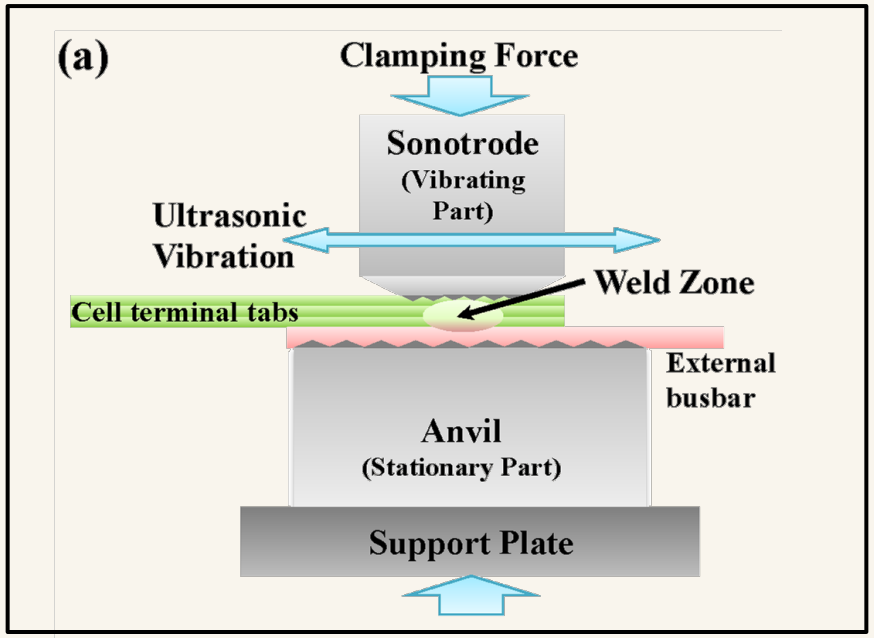




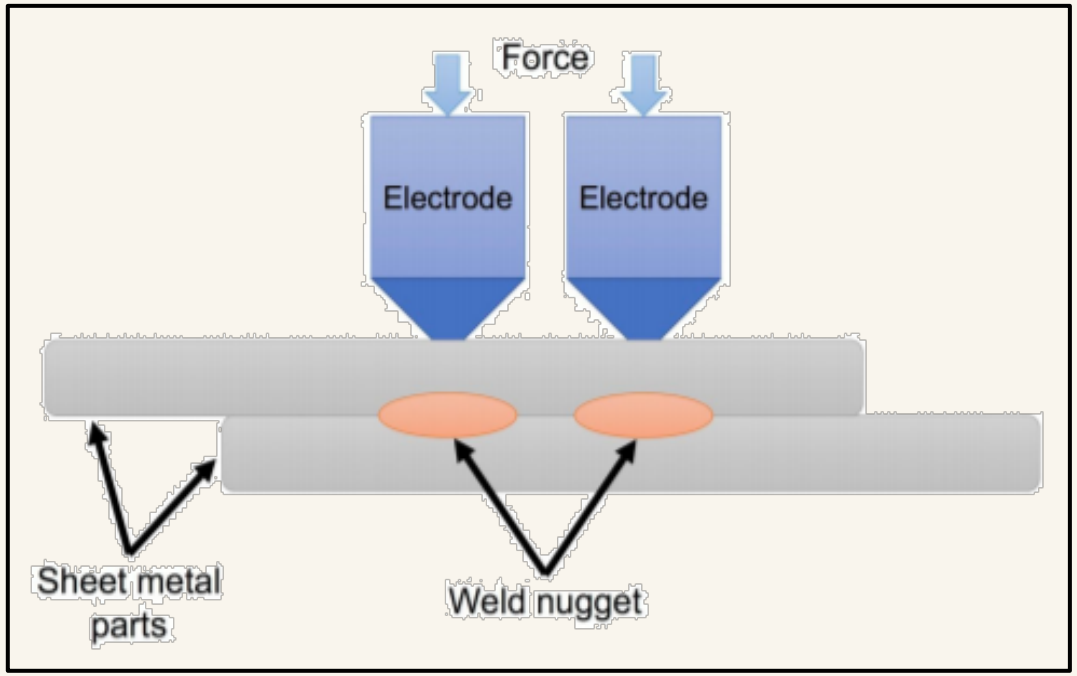
http://www.soteriabig.com
https://www.targray.com/li-ion-battery/packaging-materials/tabs
http://www.aga88.com/products-services/ultrasonic-welding/applications/batteries/

Electrode-to-tab joining welding

- Commonly used welding methods
  - Ultrasonic friction welding (UMW)
    - Join substrate materials by high frequency ultrasonic vibration (>20 kHz) to under a clamping pressure
  - Resistance spot welding (RSW)
    - Metal sheets welded together by electrical current and pressure between two electrodes
  - Laser Beam Welding (LBW)
    - Materials fused together by concentrated heat generated by a laser beam



Working principles of
← UMW
RSW →



J. Coignard et al., *World Electr. Veh. J.* **2018**, *9*(2), 22
https://www.telsonic.com/en/metal-welding/battery-foil-sheet-cylinder-welding/; https://www.teknat.uu.se/student

Seal--temporary seal

- **Temporary seal:**
  - Cell is completely sealed with an air receiver/air bag
  - Electrolyte wets/saturates electrodes
- **Formation:**
  - Cyclic charge/discharge, form SEI
  - Air receiver collects produced gas

← Formation towers

https://www.mtixtl.com/8mmWidthNickelTabasNegativeTerminalforPolymerLi-ionBattery50pcs.aspx
http://www.youfil.com/lead-acid-storage-battery-production-equipment/Battery-formation-line.html

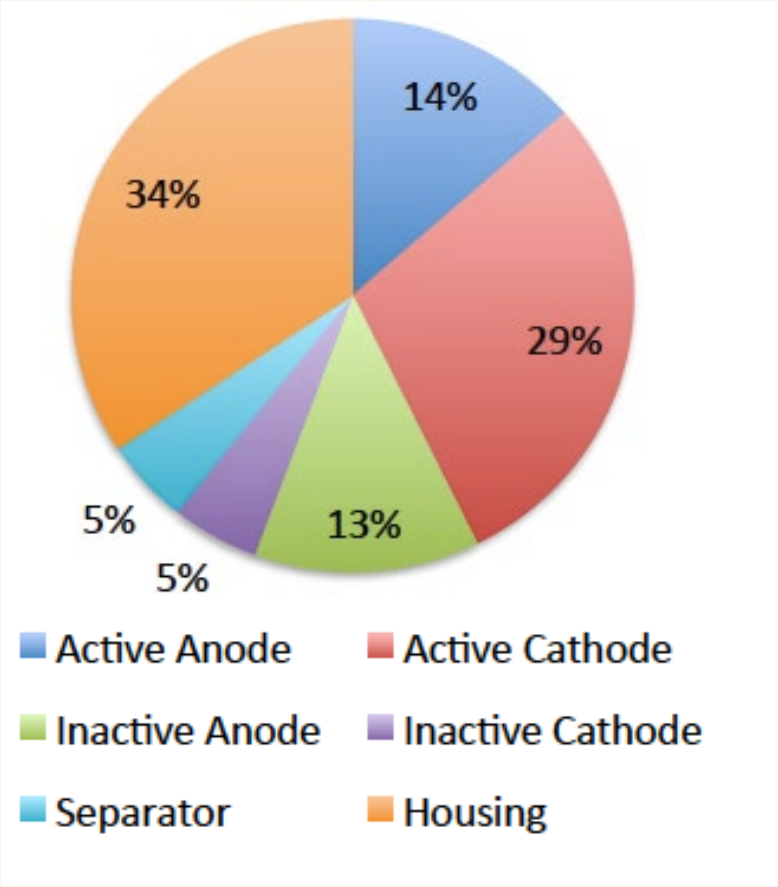
Seal--final seal

- **Warm-pressing:**
  - Improve uniformity of cell flatness and thickness
  - Drive air out into receiver
  - Closely press separators and electrodes together
  - Shorten Li^+ diffusion distance to reduce internal resistance
- **Final seal:**
  - Degas
    - Air receiver punctured 1st under vacuum to remove residual gases
  - Cell vacuum-seal
    - An important step
  - Remove air receiver
    - Last step in assembly
  - Preferably limit time between formation and degassing

https://www.mtixtl.com/8mmWidthNickelTabasNegativeTerminalforPolymerLi-ionBattery50pcs.aspx

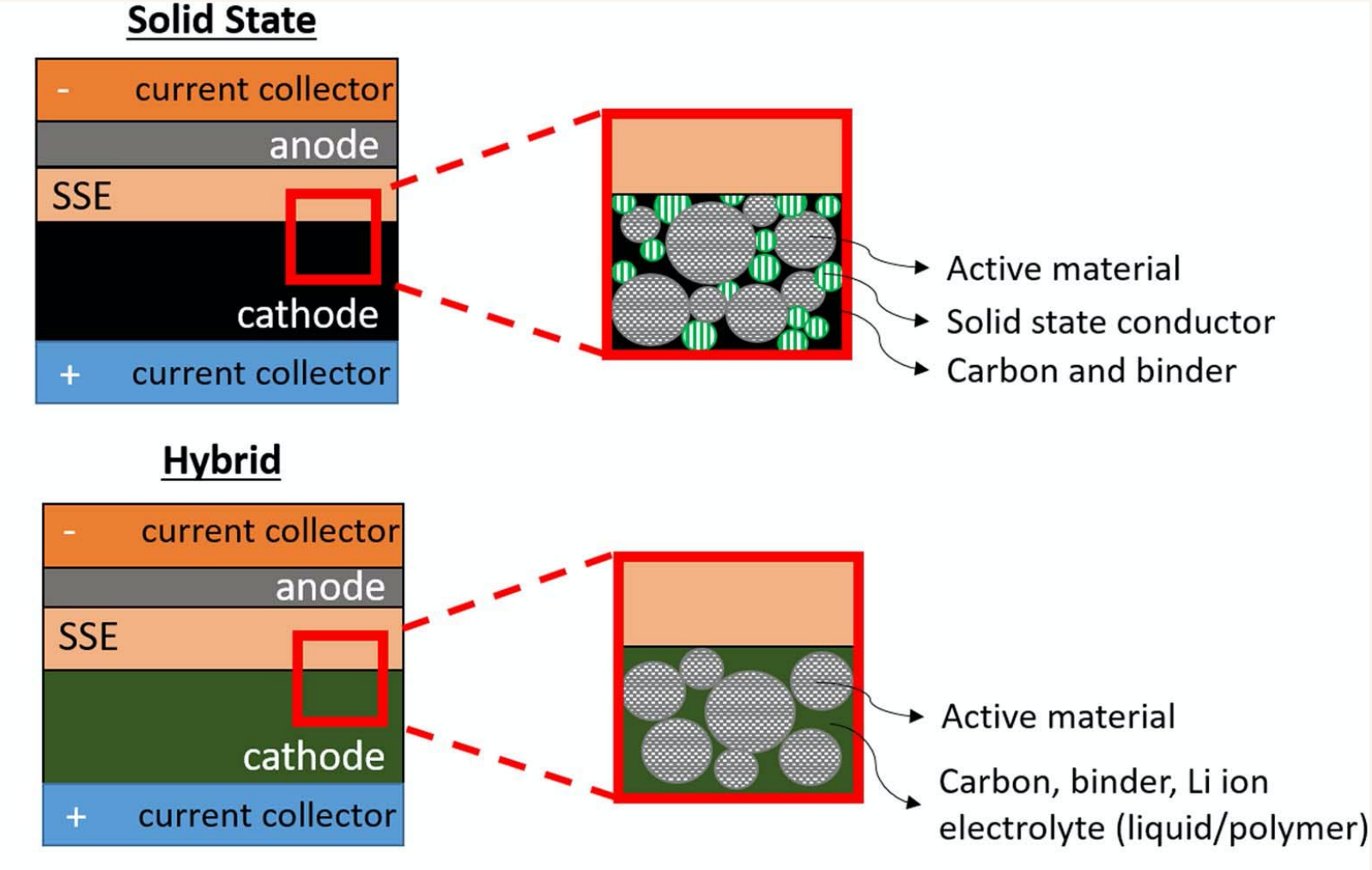
Challenges of Li^+ battery architecture

- Volume changes & structural degradation due to Li insertion/deinsertion
- Liquid electrolyte leakage
- Current collector corrosion
- High peripheral mass & housing package size
  Decreases the energy density



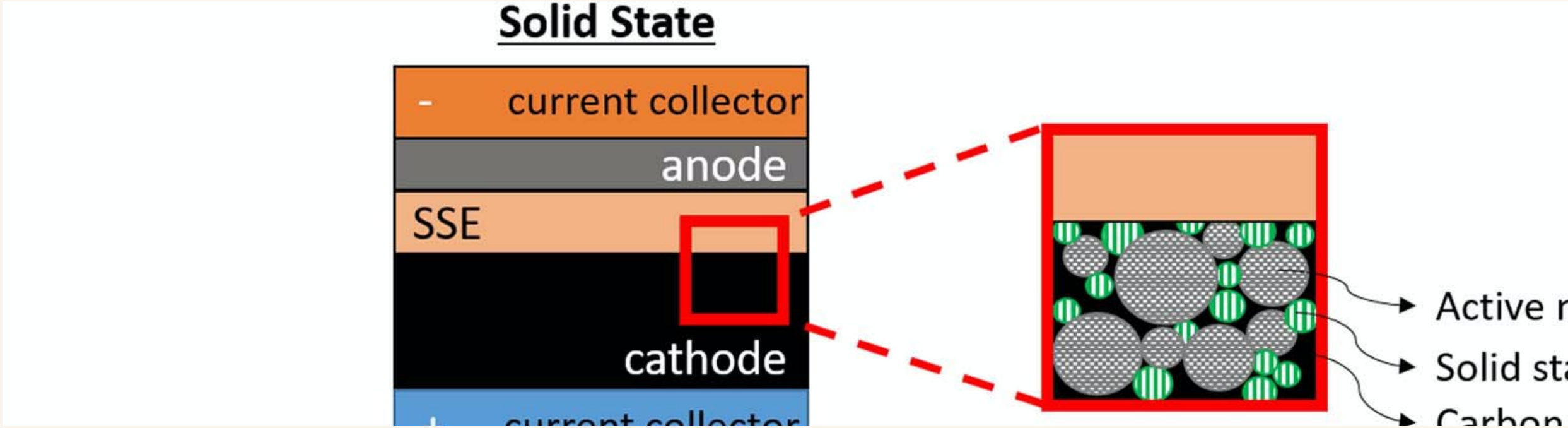
- Development of SSBs could overcome these challenges

Solid state batteries architecture



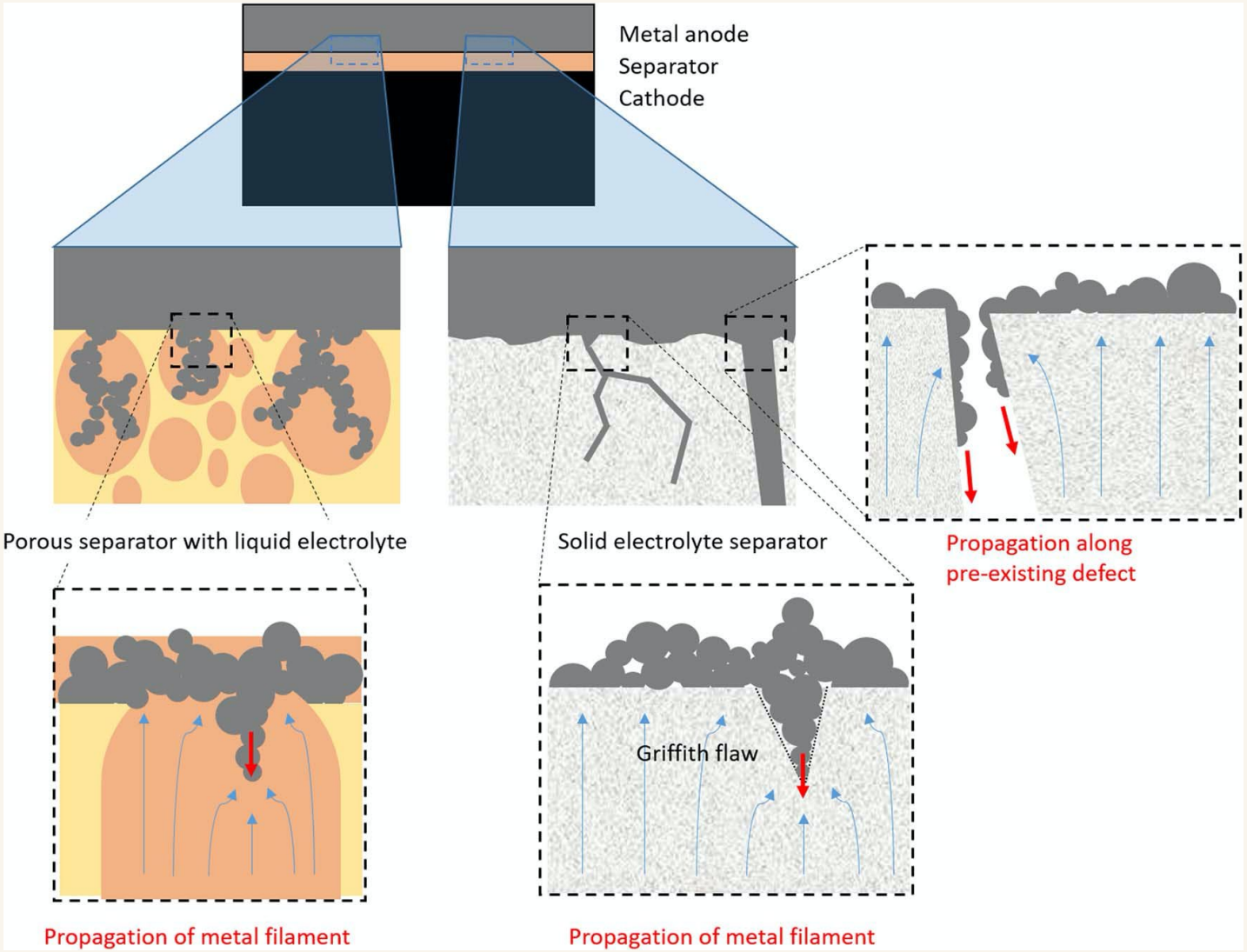
Kerman, Kian, et al. *Journal of The Electrochemical Society* 164.7 (2017): A1731.

Anode free- solid state batteries



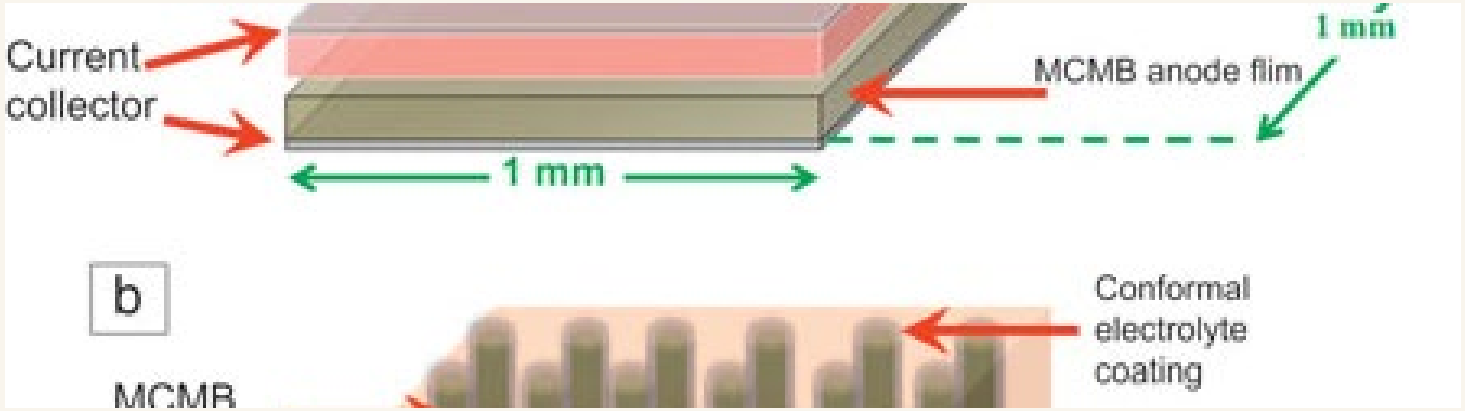
Kerman, Kian, et al. *Journal of The Electrochemical Society* 164.7 (2017): A1731.

Porous separator vs. solid electrolyte separators



2-D battery configuration

- 2D battery design compromise between energy density and power density because of the limitation in footprint area.
- Limited areal capacity 0.5 – 5 $mAhcm^{-2}$
- Making electrodes thicker in order to store more energy is not a viable approach
  - The mechanical integrity of the film decreases due to expansion and contraction of the active materials during cycling
  - Thicker films reduce the power density of the device

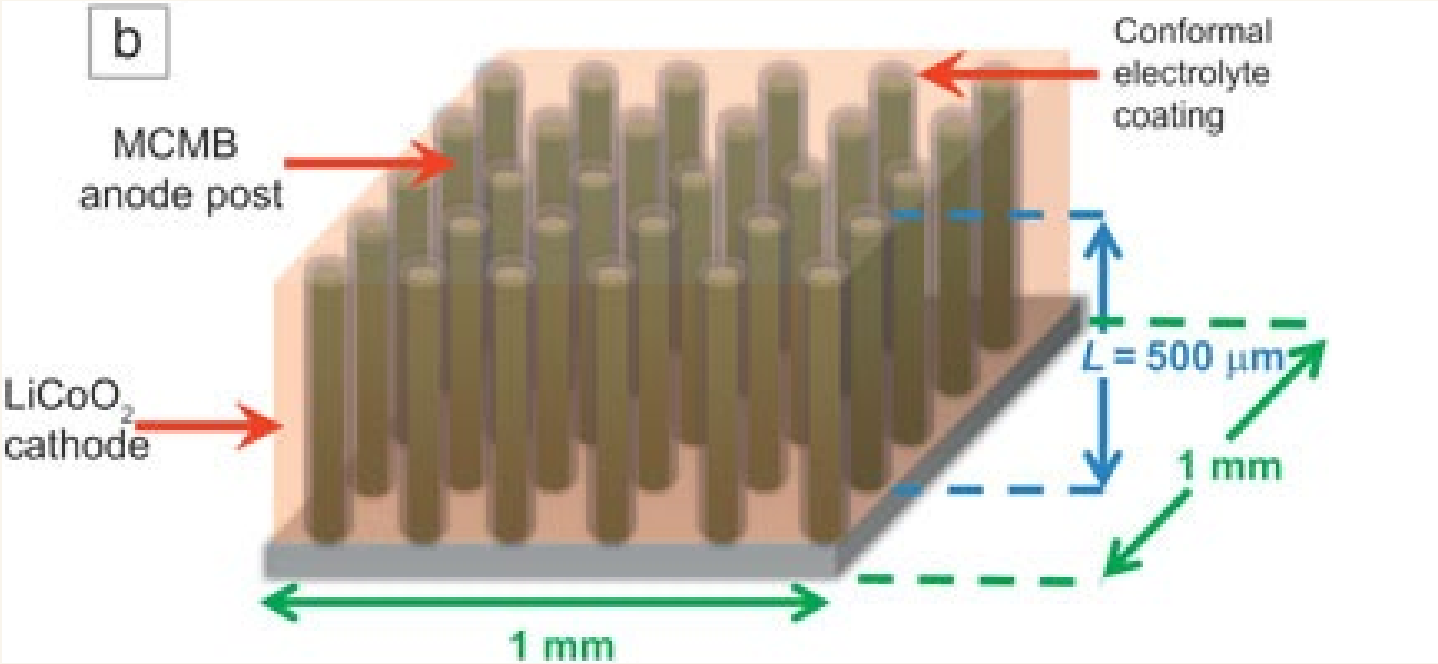


MCMB, mesocarbon microbeads.

Arthur, Timothy S., et al. "Three-dimensional electrodes and battery architectures," *MRS Bulletin* **2011** *36*, 523-531.

3-D battery configuration

- 3D battery architectures takes advantage of the third dimension, height,
  - The amount of electrode material within a given footprint area is high
  - Areal capacity ~ 10 $mAhcm^{-2}$
  - Energy density and power density are effectively decoupled
  - Anode and cathode arrangements are unaffected by the additional thickness



Arthur, Timothy S., et al. "Three-dimensional electrodes and battery architectures." *MRS Bulletin* **2011** *36*, 523-531.

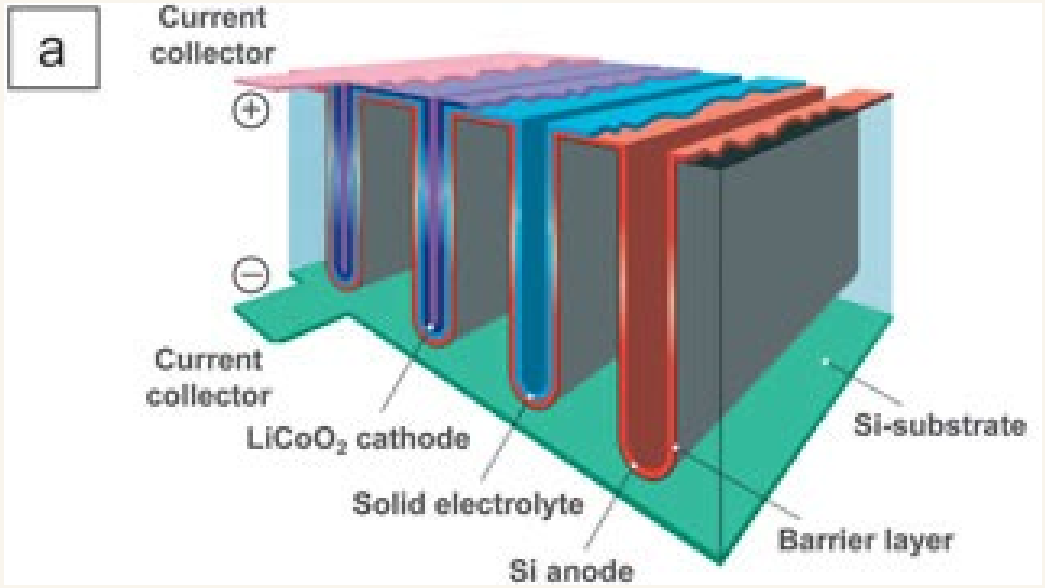
Solid state batteries--micro batteries

3D micro batteries for MEMS devices

- Powering autonomous systems for applications e.g. medical implants, communications, & sensing
- 3D micro batteries use nanostructures to increase areal capacity; high surface area enables fast charging and discharging
    - Thin films deposited in trenches, pores, nanowires, or other structures to increase effective area within the same footprint.

Arthur, Timothy S., et al. "Three-dimensional electrodes and battery architectures." *MRS Bulletin* **2011** *36*, 523-531.

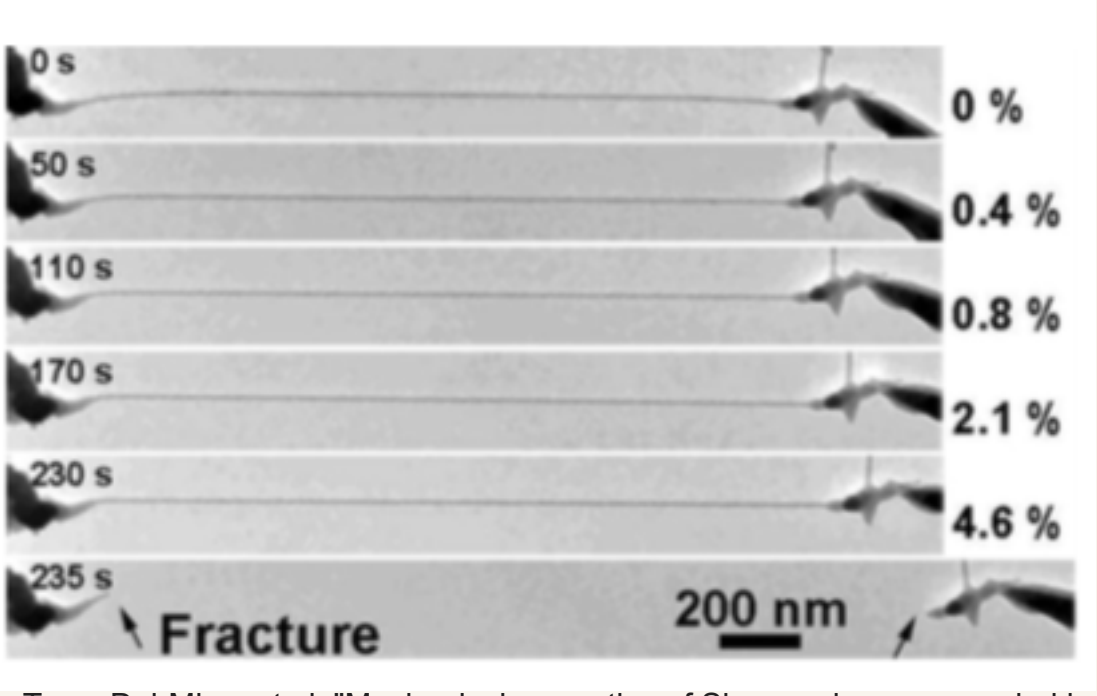
Examples of 3-D battery configuration



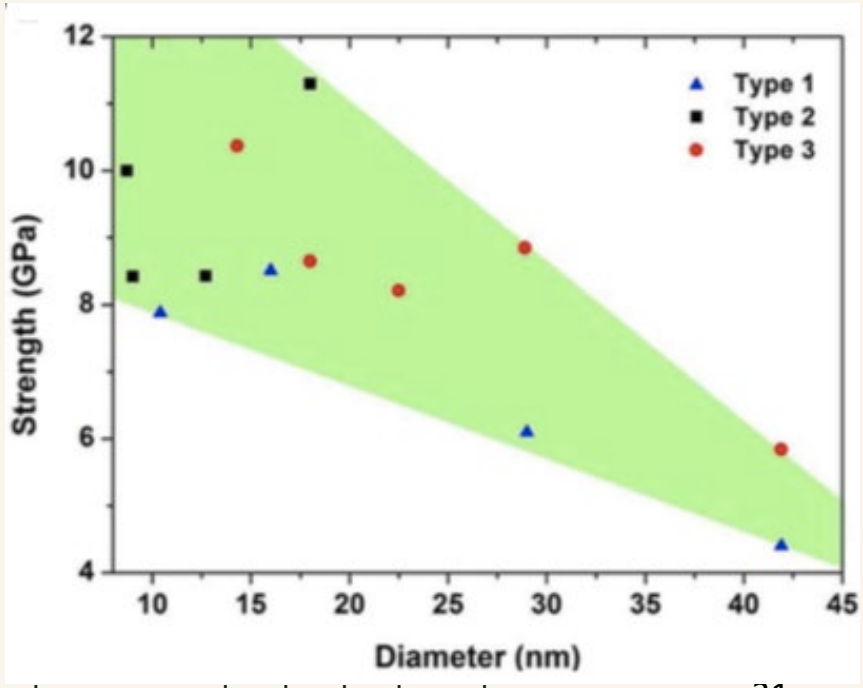
Arthur, Timothy S., et al. "Three-dimensional electrodes and battery architectures." *MRS Bulletin* **2011** *36*, 523-531.

Geometries to overcome material limitations

- Material properties at the nanoscale can differ from bulk properties
  - Nano and microscale geometry can result in different apparent properties
- Significantly higher surface to volume ratio - fast charge/discharge



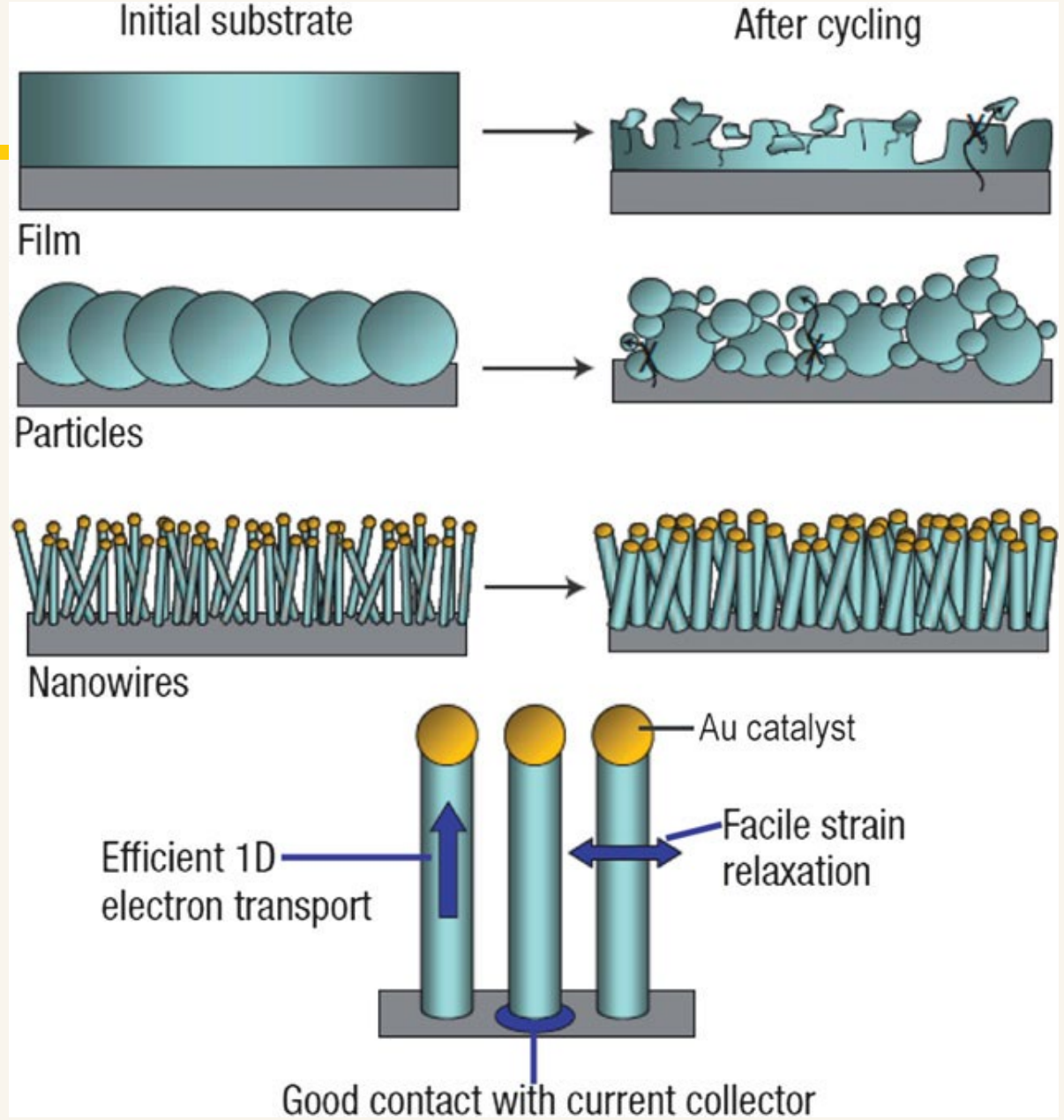
In situ TEM tensile testing of Si nanowires



Tang, Dai-Ming, et al. "Mechanical properties of Si nanowires as revealed by in situ transmission electron microscopy and molecular dynamics simulations." *Nano letters* 12.4 (2012): 1898-1904.

Si Nanowire Anodes

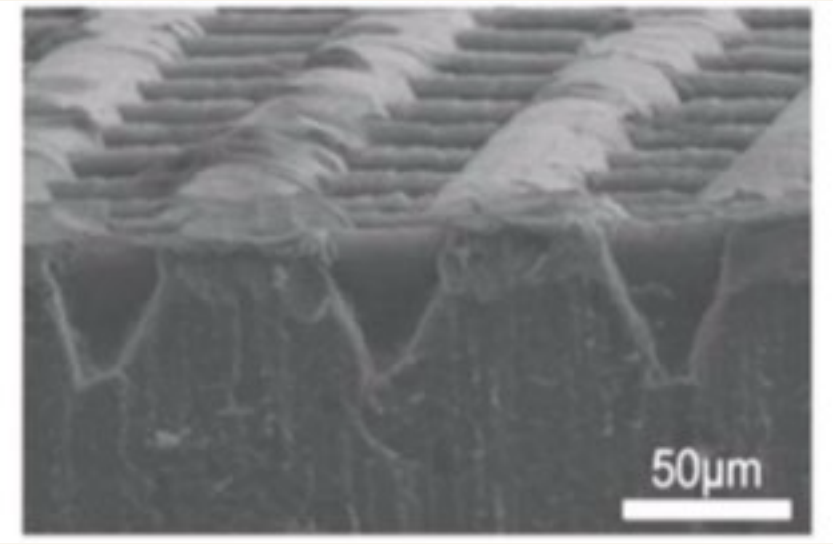
- Si volume changes drastically (400%) during Li insertion and removal
  - structural damage
  - Loss of electronic contact
- Nanowire morphology:
  - Leaves open space for expansion
  - Size dependent material properties
  - Direct electrical contact with current collector

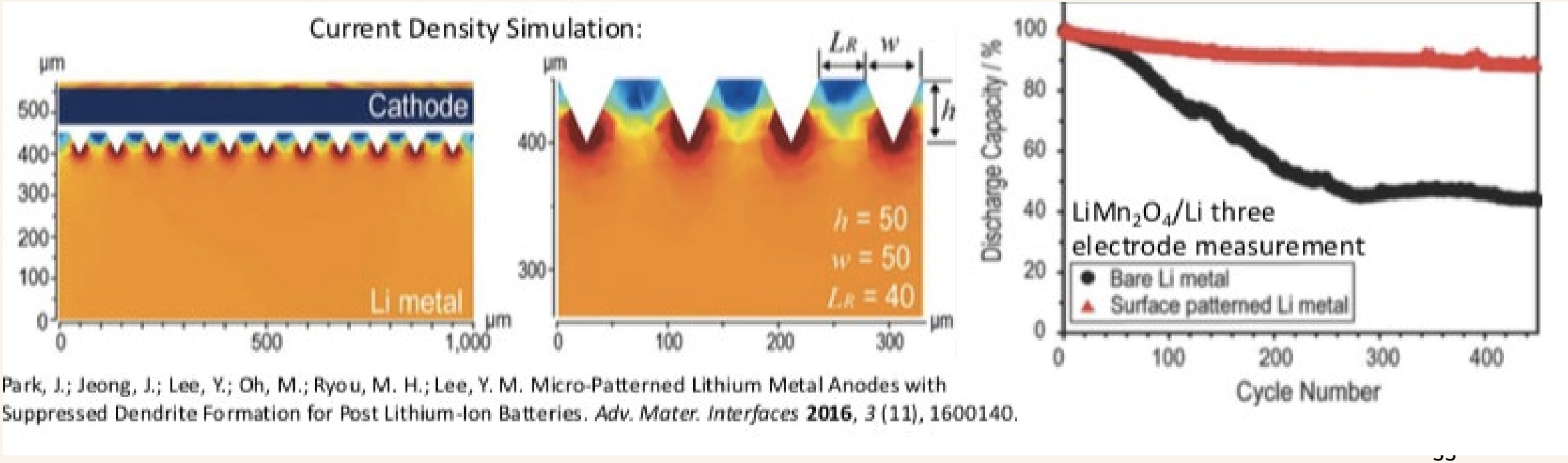


Arthur, Timothy S., et al. "Three-dimensional electrodes and battery architectures." *MRS Bulletin* **2011** *36*, 523-531.

Li plating: Textures Li Surface

- Mechanically stamped Li electrode
- Li plates in pits (where there is higher current density)
- Suppresses uncontrolled Li dendrite growth

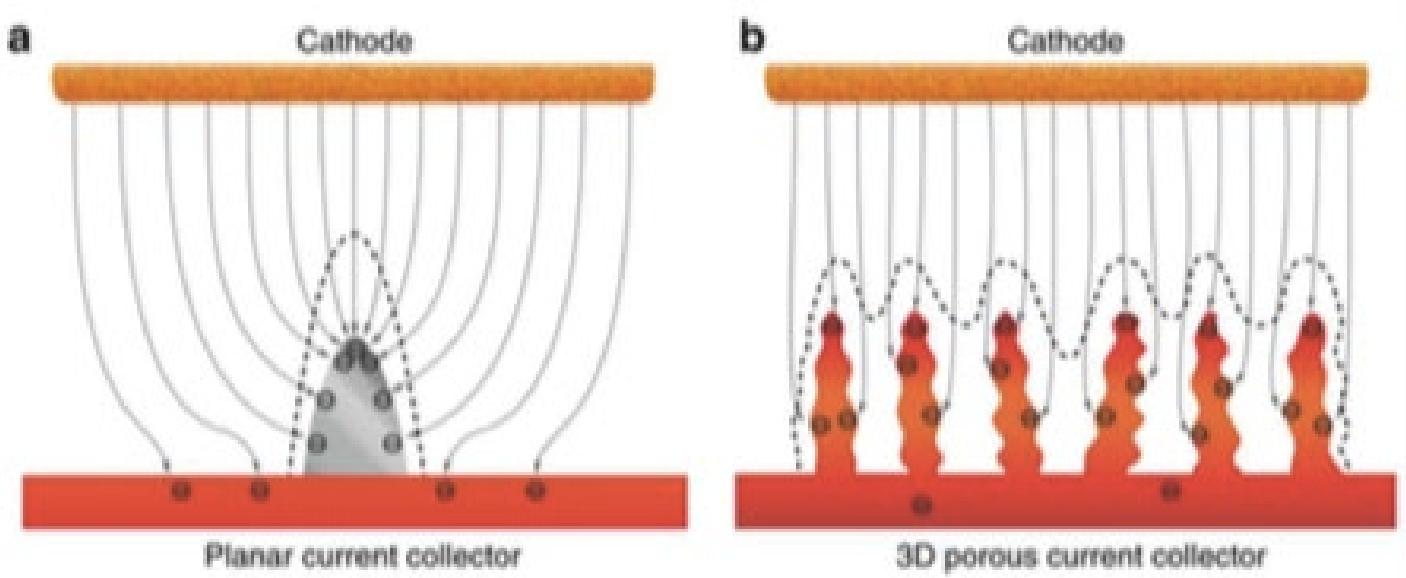




Park, J.; Jeong, J.; Lee, Y.; Oh, M.; Ryou, M. H.; Lee, Y. M. Micro-Patterned Lithium Metal Anodes with Suppressed Dendrite Formation for Post Lithium-Ion Batteries. *Adv. Mater. Interfaces* **2016**, *3* (11), 1600140.

Nano - Cu current collectors

- Inhomogeneities occur plating Li onto planar current collectors
  - Nucleation creates hotspots that grow into dendrites



Yang, C. P.; Yin, Y. X.; Zhang, S. F.; Li, N. W.; Guo, Y. G. Accommodating Lithium into 3D Current Collectors with a Submicron Skeleton towards Long-Life Lithium Metal Anodes. *Nat. Commun.* **2015**, *6* (1), 8058.

- Microporous Cu current collectors
  - More uniform current density
  - Higher surface area - lower local current density
  - Li fills in the pores and dendrites are suppressed
- Scale and pore size matters
  - <5um pores performed significantly better than ~170um pores

Challenges for implementing 3D geometries

- SEI formation on high surface areas can be particularly detrimental
- SSBs require thin, conformal pinhole free films
    - Continued development of solid-state electrolytes
- In many cases, nano & micro-structures slow and costly to produce
    - Production scalability
    - Competitive market pricing
- Many approaches require further rigorous testing under a variety of conditions
    - Depth of charge/discharge
    - Rate of charge/discharge

COLLEGE OF ENGINEERING
NEXUS
UNIVERSITY OF MICHIGAN

Battery component design
Lecture 3

Taylor Brandt, Mengjie Yu, Richard M. Laine, Eleni Temeche, and Xinyu Zhang,

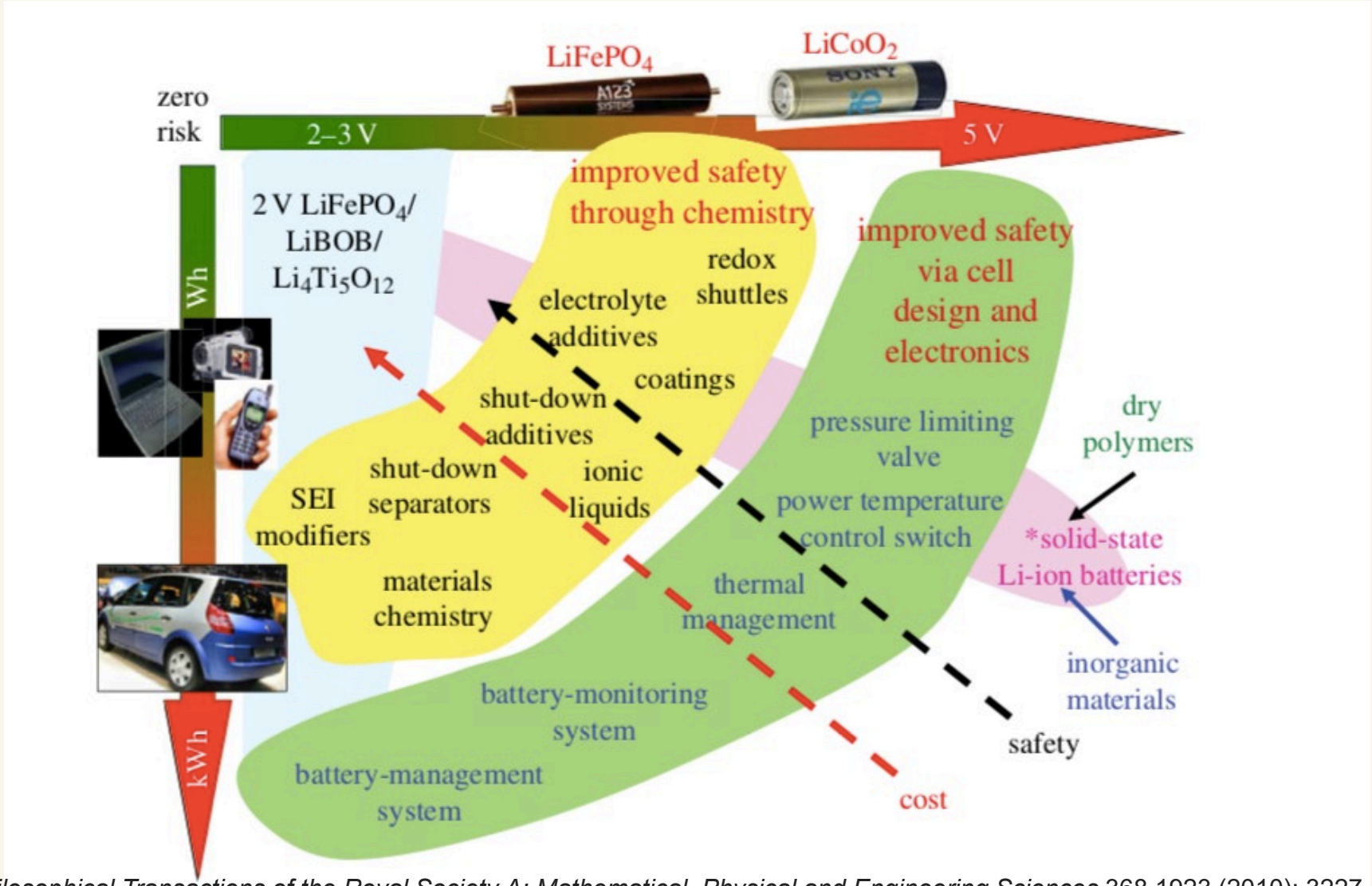
Depts of Materials Sci. & Eng. And Macromolecular Sci. & Eng.

University of Michigan

Content

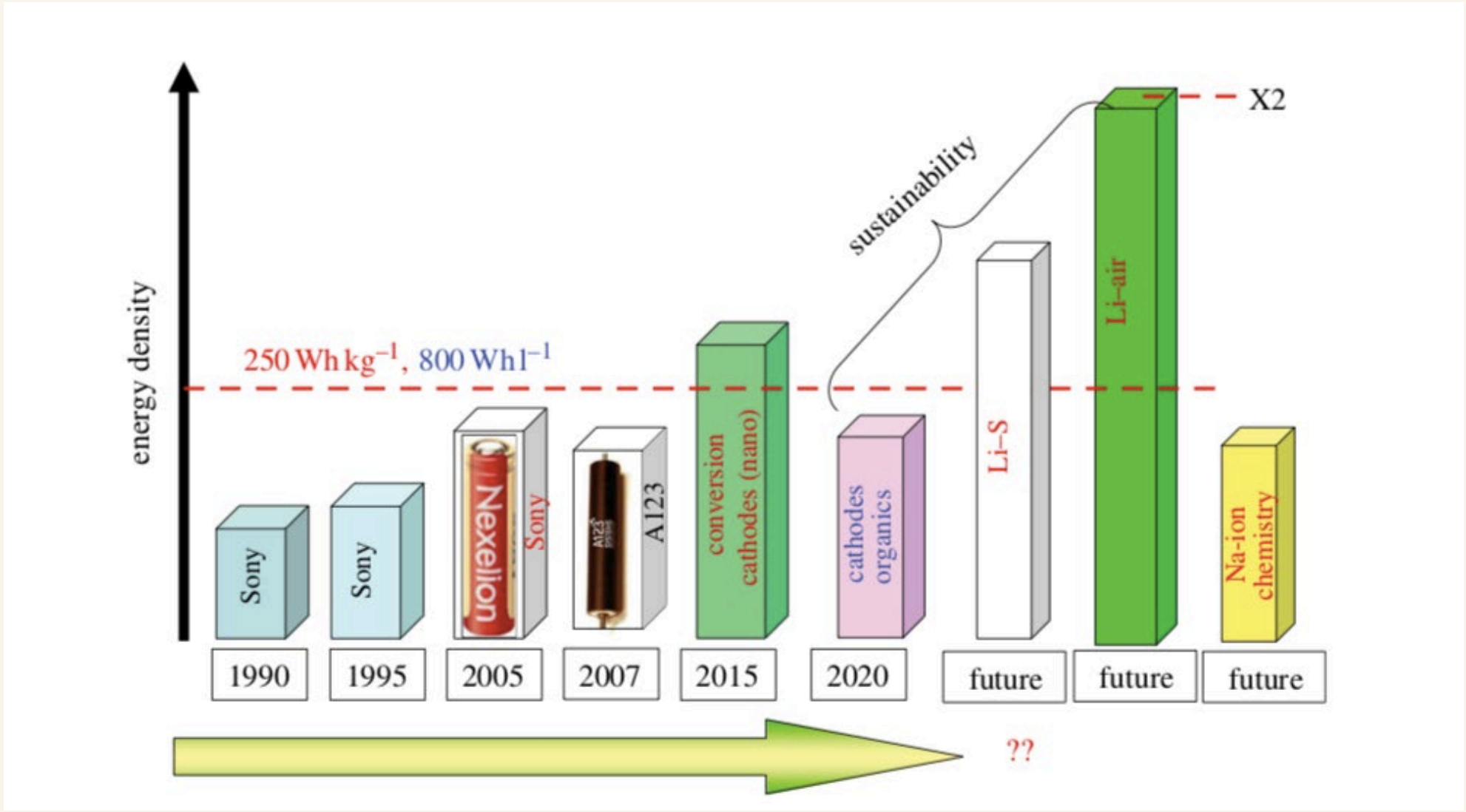
- Battery component design
  - Electrode
  - Electrolyte
  - Current collector
  - Binder

Battery management systems



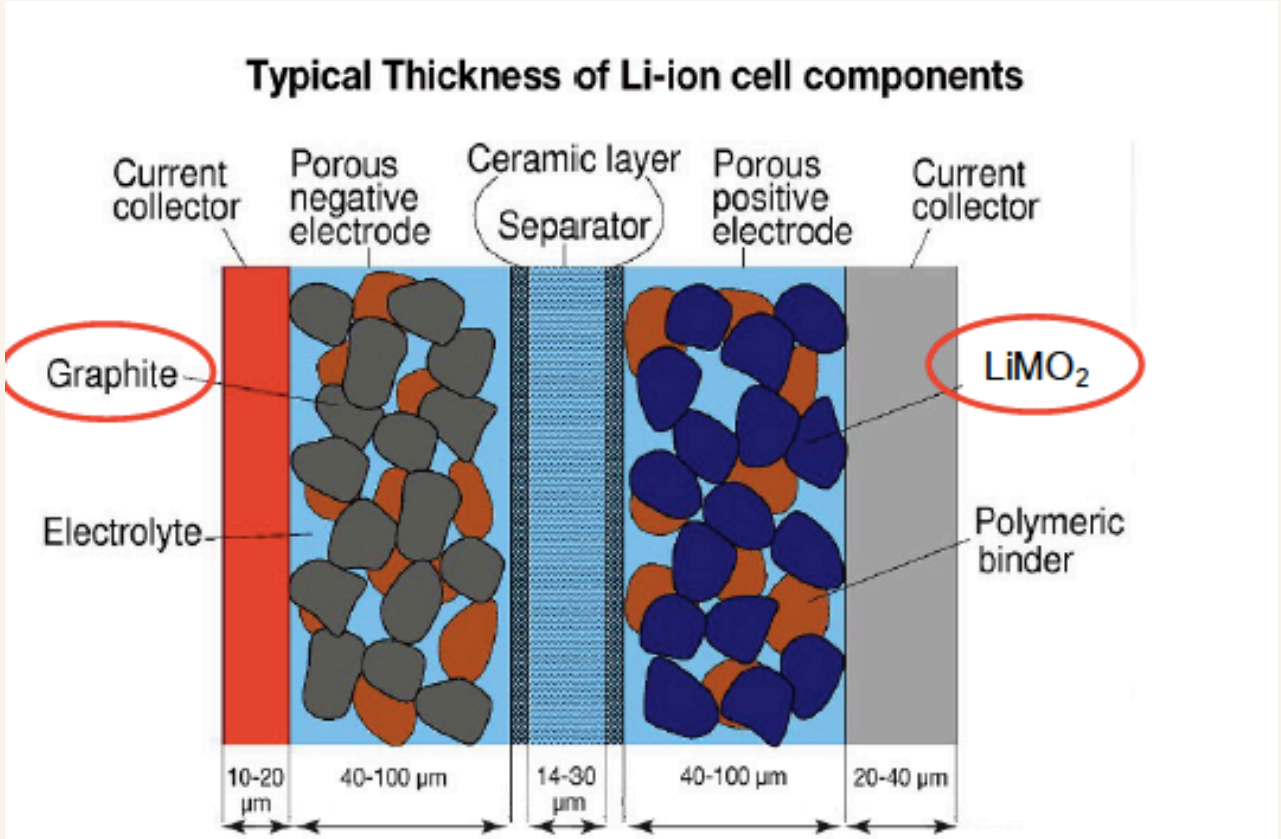
Tarascon, J-M. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 368.1923 (2010): 3227-3241.

Battery chemistries vs. energy density



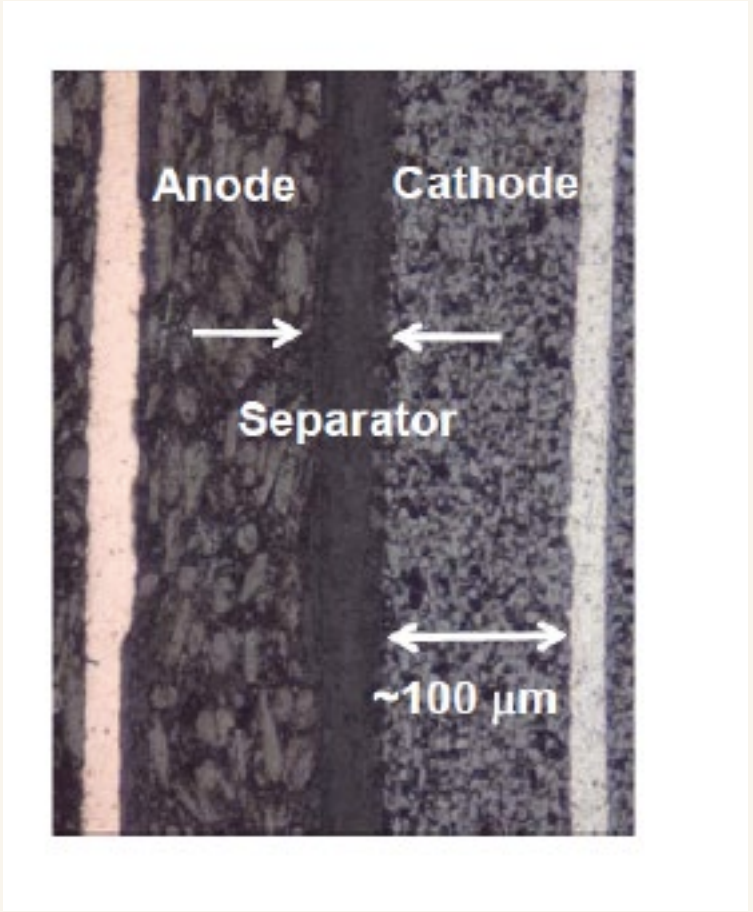
Tarascon, J-M. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 368.1923 (2010): 3227-3241.

Battery components



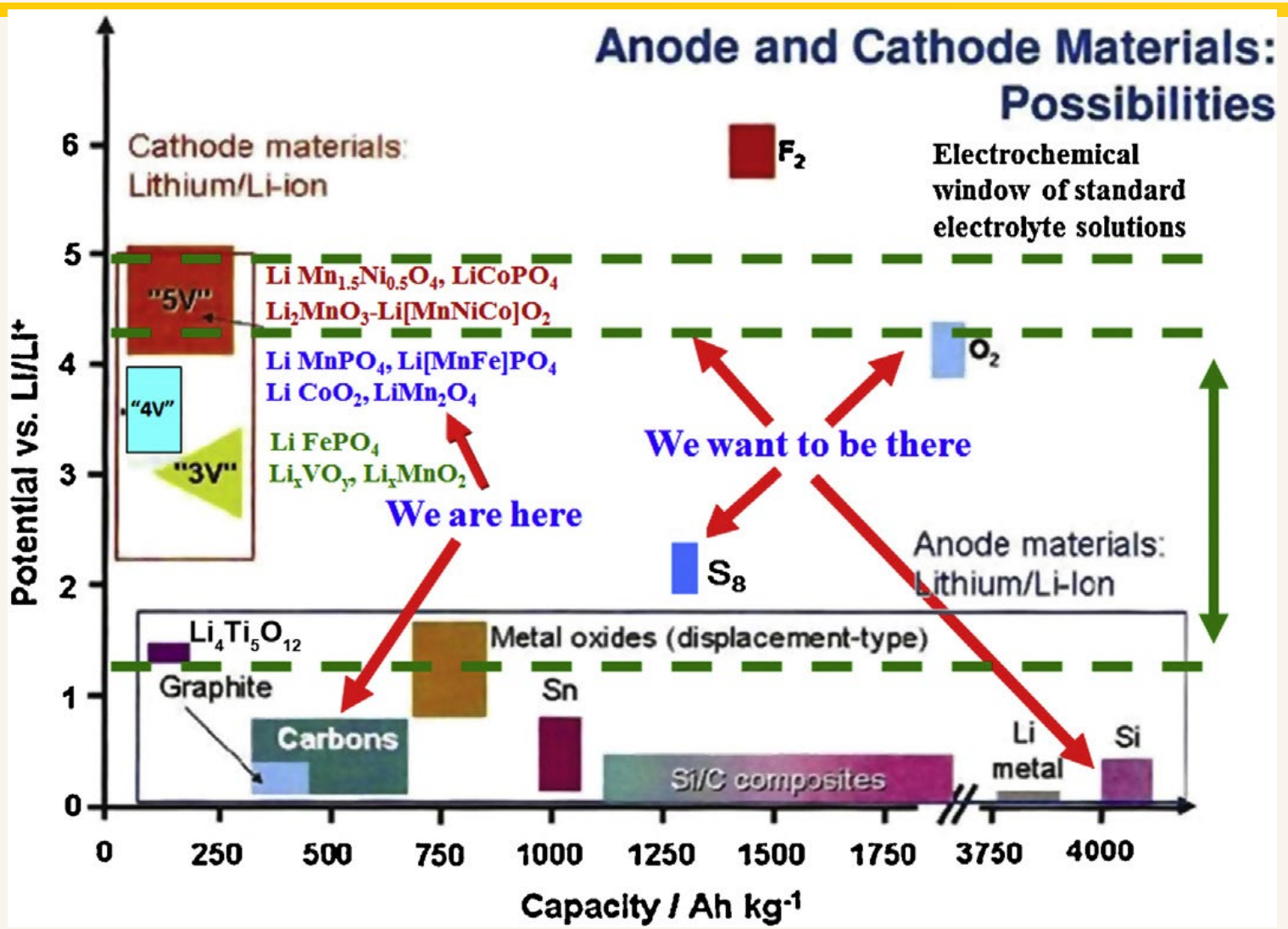
Ponticel. P, 2012. Society of Automotive Engineers: Vehicle Electrification: 6-28.

Electrode capacity: how much Li/mass (mAh/g)



Q. C. Horn and K. C. White. ECS meeting, 2007

Electrode design



H. D. Yoo et al., *Materials Today*, **2014**, 17, 3, 110-121

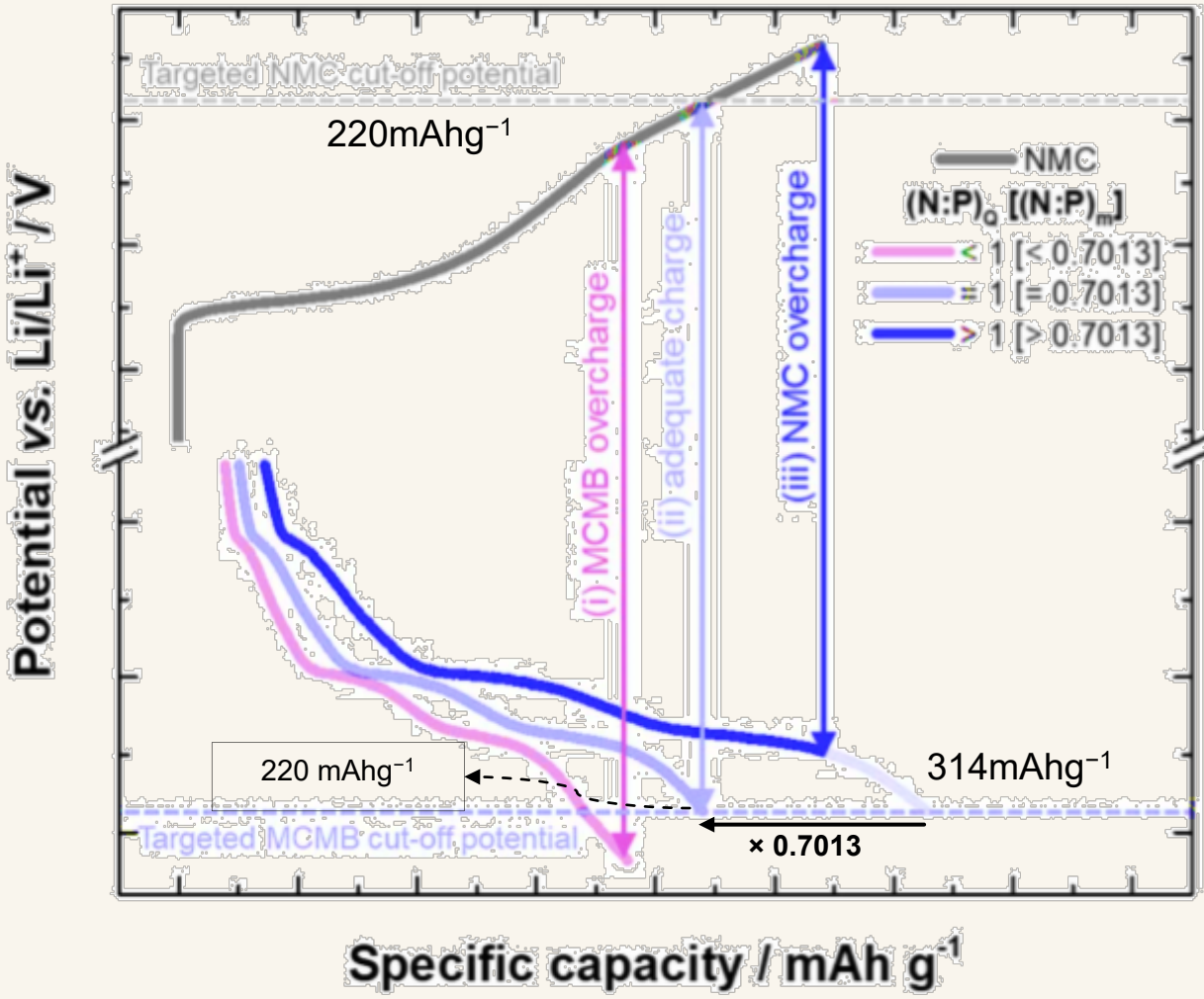
Material loading to prepare electrodes

- Active Material (AM) content
  - Ideally maximizes AM content
  - Common cathode formulation - 94:3:3 (AM : Conductive Carbon : Binder)
  - Common anode formulation - 95:5 (AM : Binder)
- High cell specific energy (Wh/kg) requires highest areal capacity
  - Focus on ↑ AM wt.% and ↓ current collector mass
  - Drawbacks:
    - ↑ loading electrode ↓ power performance
    - Manufacture difficulties

Electrode Design

- N:P Ratio
  - Areal capacity [mAh cm^{-2}] of anode: cathode
  - Important to avoid overcharge
  - Capacity balancing: slight oversizing of anode capacity to avoid Li metal plating
    - Commercial N/P ratio ≈ 1.1–1.2 : 1
    - Decrease in specific energy w/increase in unused material mass and volume

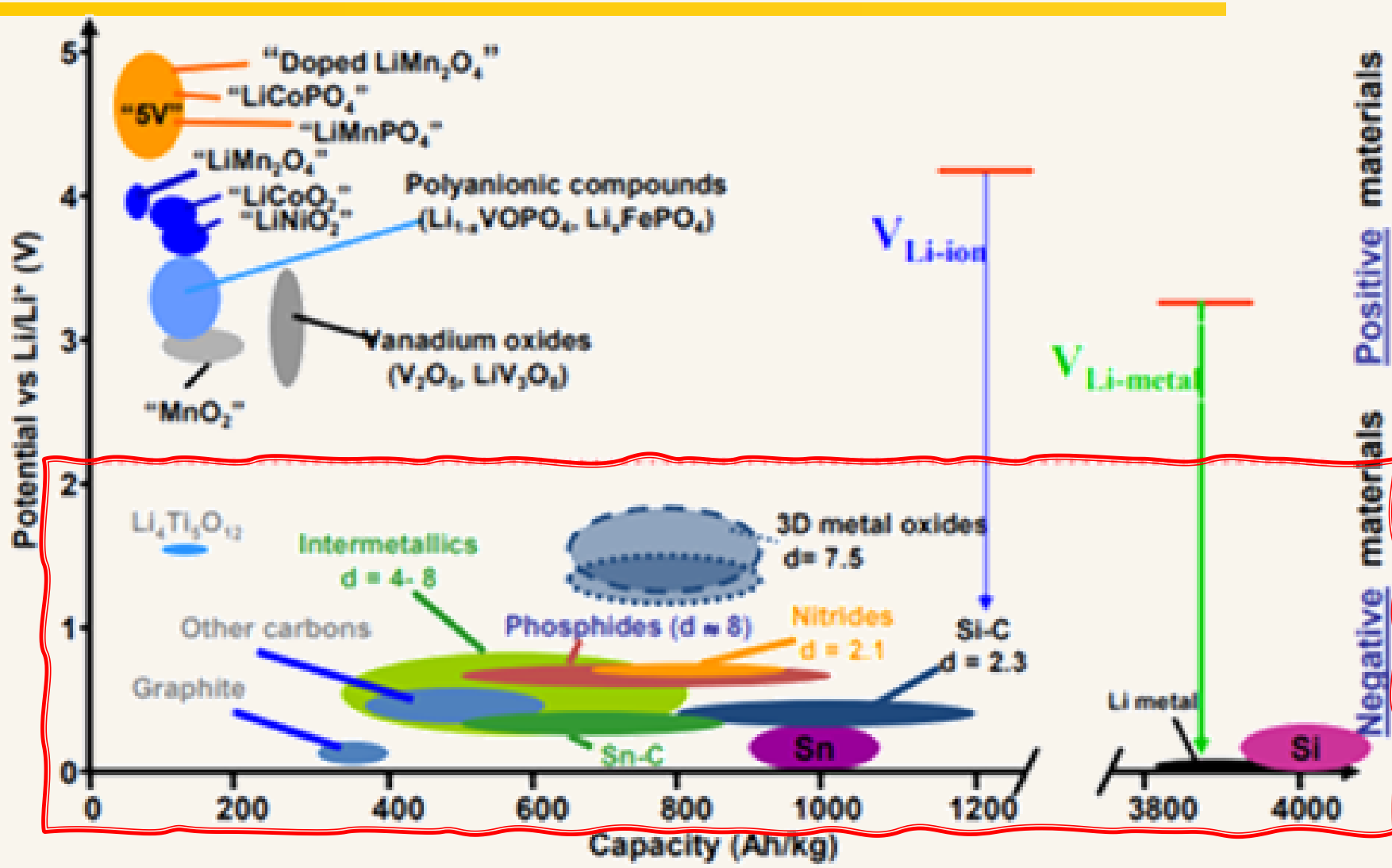
Graphite anode (MCMB, 314 $mAhg^{-1}$) & NMC (220 $mAhg^{-1}$) cathode potential profiles for different N/P ratios → (N:P)Q - capacity used by active materials mass (N:P)m – capacity by active mass



J Kasnatscheew et al., *J. Electrochem. Soc.*, **2017**, 164 (12) A2479-A2486

Anodes

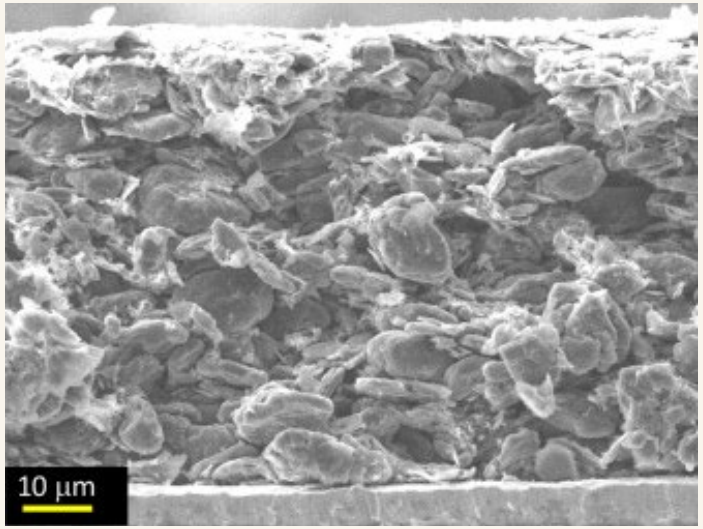
- Graphite
- Metals
- Alloys
- Oxides
- Silicon-based



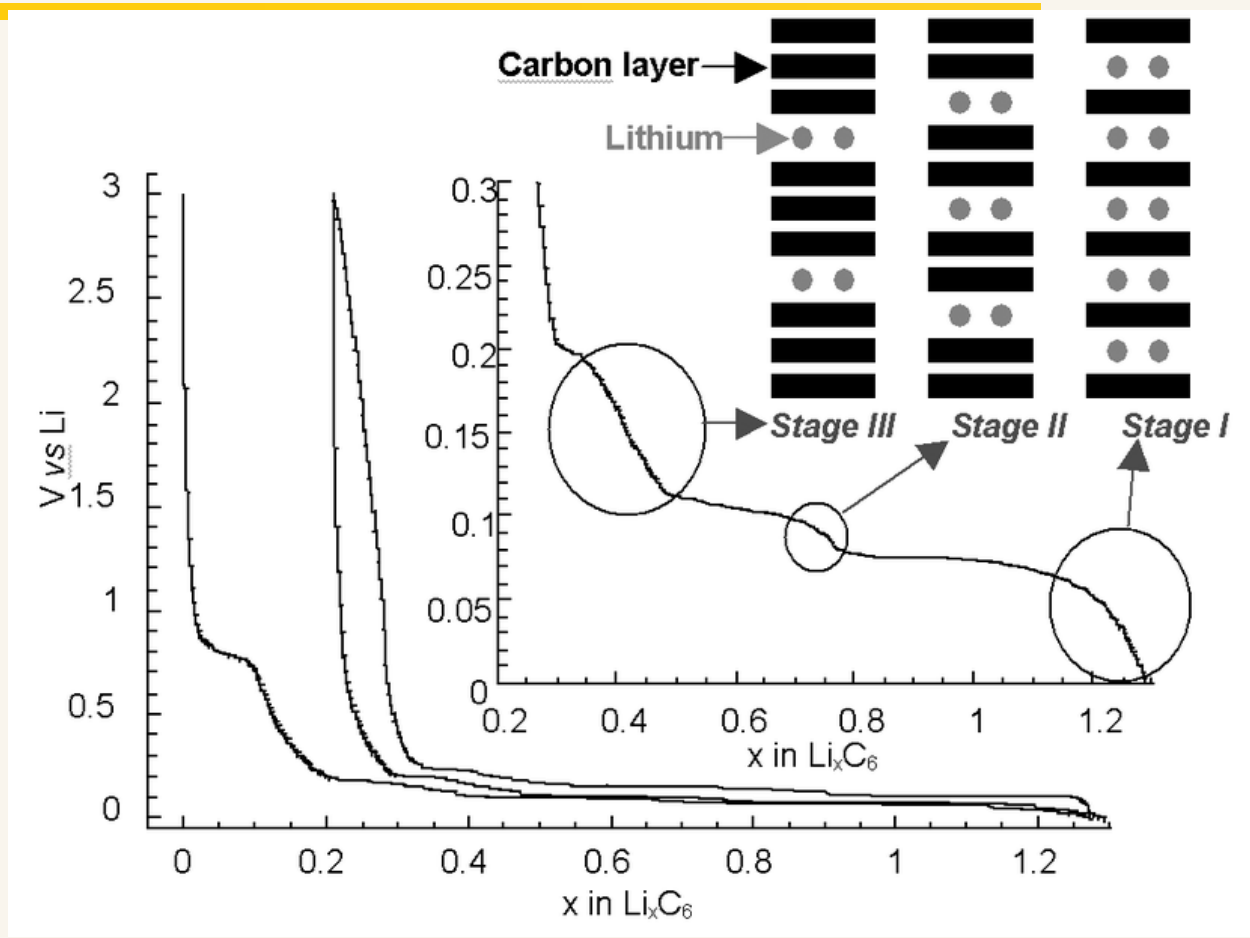
http://www.eai.in/blog/2018/12/research-status-of-anode/cathode-material.html

Anodes--graphite

- Industry standard
- Long cycle life
- Limited energy density
  - Theoretical capacity ≈ 372 mAh/g
- Layered structure
  - Intercalate/deintercalate Li to LiC_6
  - Rüdorff model
    - Stage III: LiC_{36}
    - Stage II: LiC_{12}
    - Stage I: LiC_6



← Cross section of a graphite anode

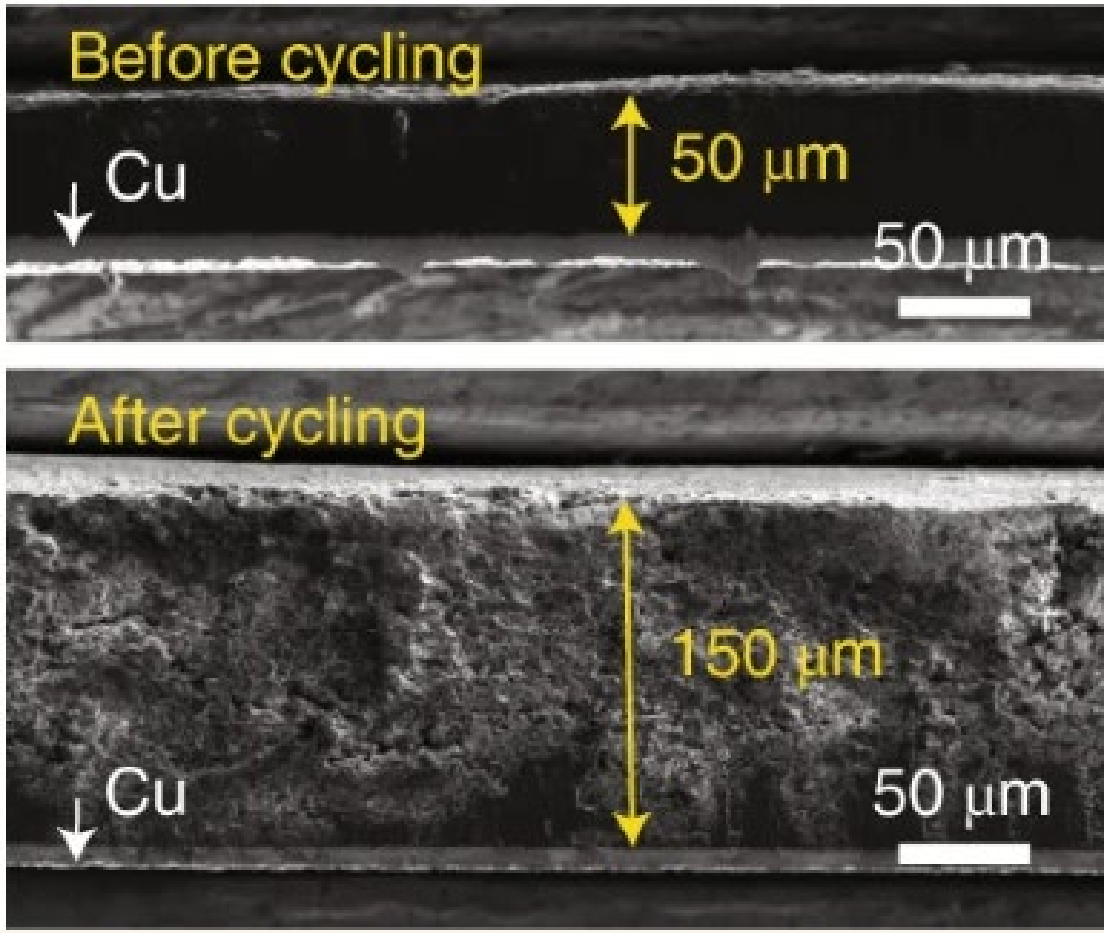


↑ Galvanostatic intercalation/deintercalation of lithium in graphite anode

S.E Trask et al., *J. Power Sources*, **2014**, 259, 233-244
Beguin, Francois et al., "Surface properties, porosity, chemical and electrochemical applications.", **2019**, 677, 495-549

Anodes--metals

- Ideal, have highest theoretical energy density
  - Lithium: 3860 mAh/g
  - Sodium: 1166 mAh/g
  - Magnesium: 3833 mAh/g
- Thickness varies
  - For some large-scale Li is 40 um
  - For coin cells 750 um is common
- Volume change
- No stable/metastable SEI forms on Li surface

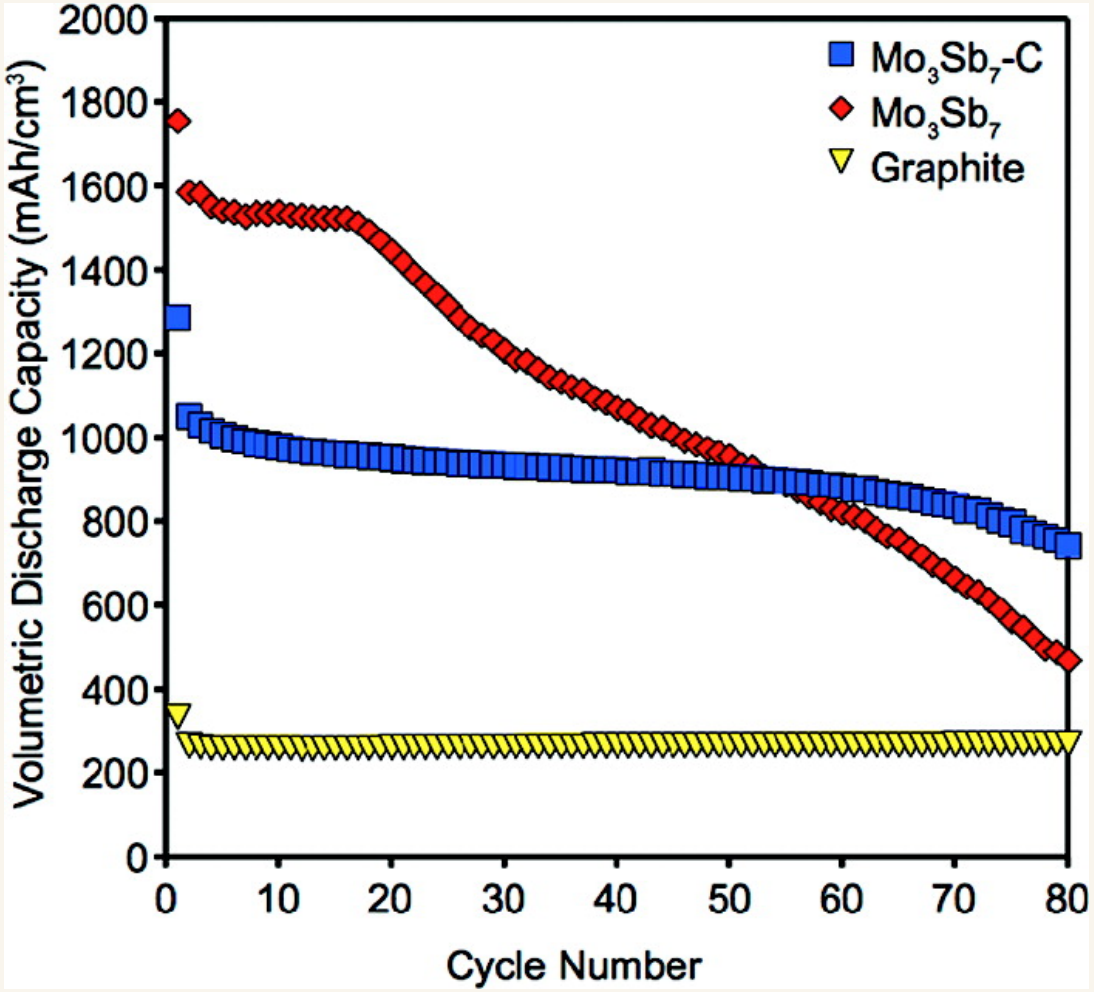


↑ Thickness change of Li metal anode

J. Liu et al., *Nature Energy*, **2019**, 4, 180–186

Anodes--alloys

- Improved stability
  - Lower reactivity, less dendrite formation
- Theoretical capacity > graphite
  - $Li_{3.75}Si$ (3578 mAh/g);
  - $Li_{3.75}Ge$ (1385 mAh/g);
  - $Li_{4.4}Sn$ (993 mAh/g);
  - Li_3Sb (660 mAh/g)
- Lower cost
- Volume change & particle agglomeration
- Example: Mo_3Sb_7 –C
  - Discharge capacity (518 mAh/g and 907 mAh/cm^3)
  - Exhibit capacity fade at ≈ 70 cycles

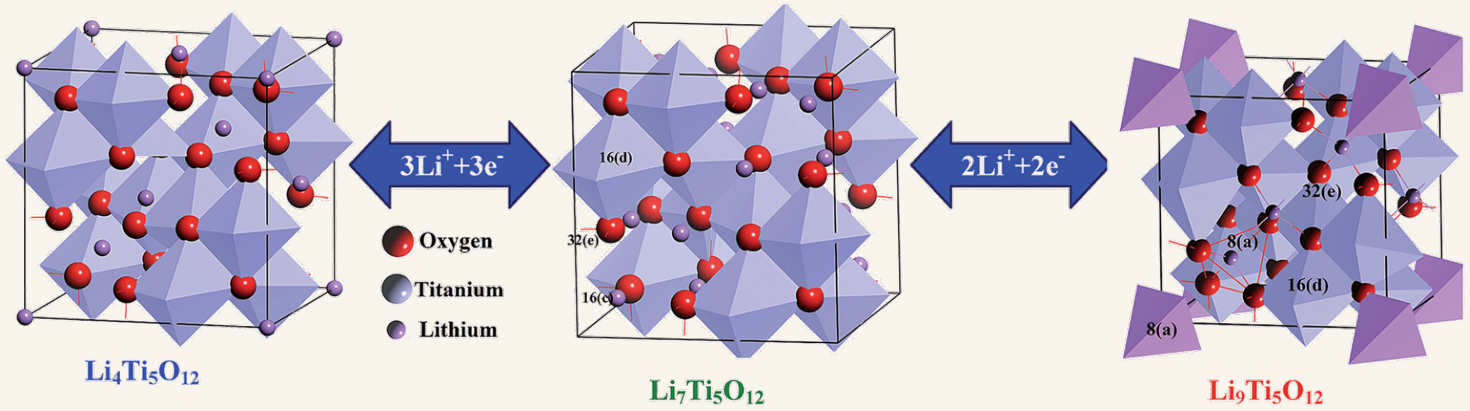


↑ Comparison of cyclability of Mo_3Sb_7, Mo_3Sb_7–C, & graphite (0–2 V vs Li/Li$^+$, current 100 mA/g AM)

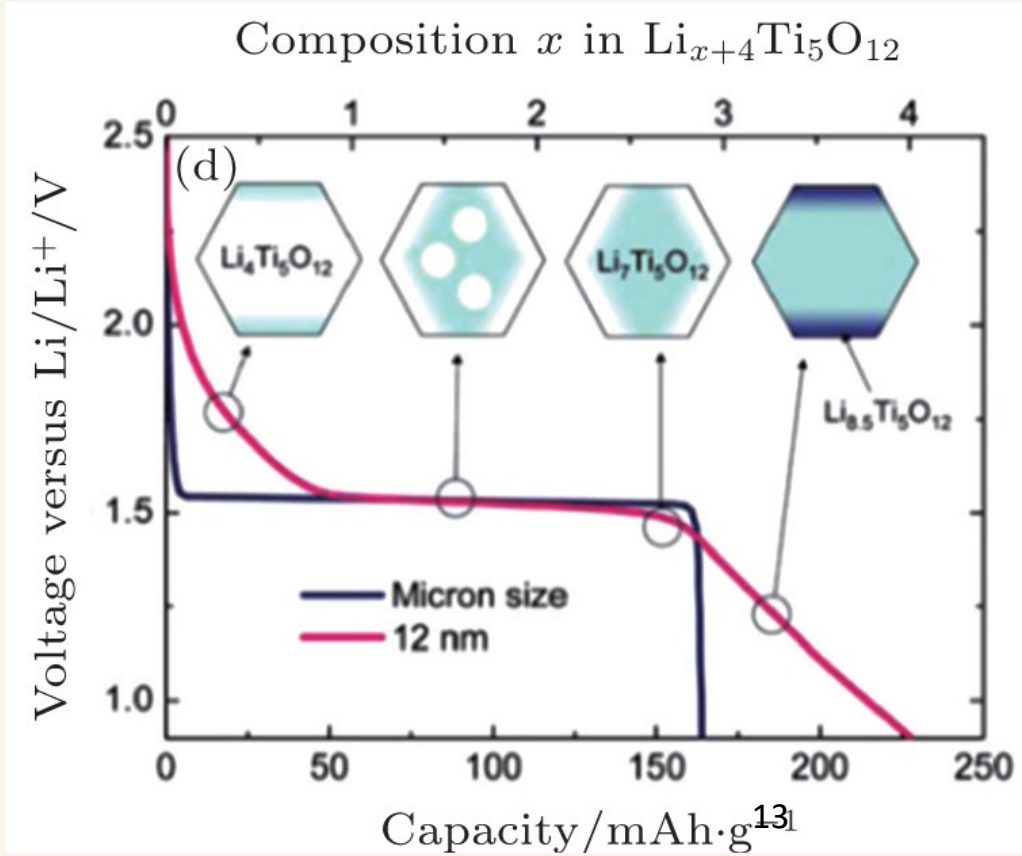
D. Applestone et al., *J. Phys. Chem. C* **2011,** 115, 18909-18915

Anodes--oxides

- Transition metal oxides
- 2D layer or 3D network structure
  - Reversibly intercalate Li into lattice without destroying xtal structure
- Example: lithium titanate (LTO) $Li_4Ti_5O_{12}$



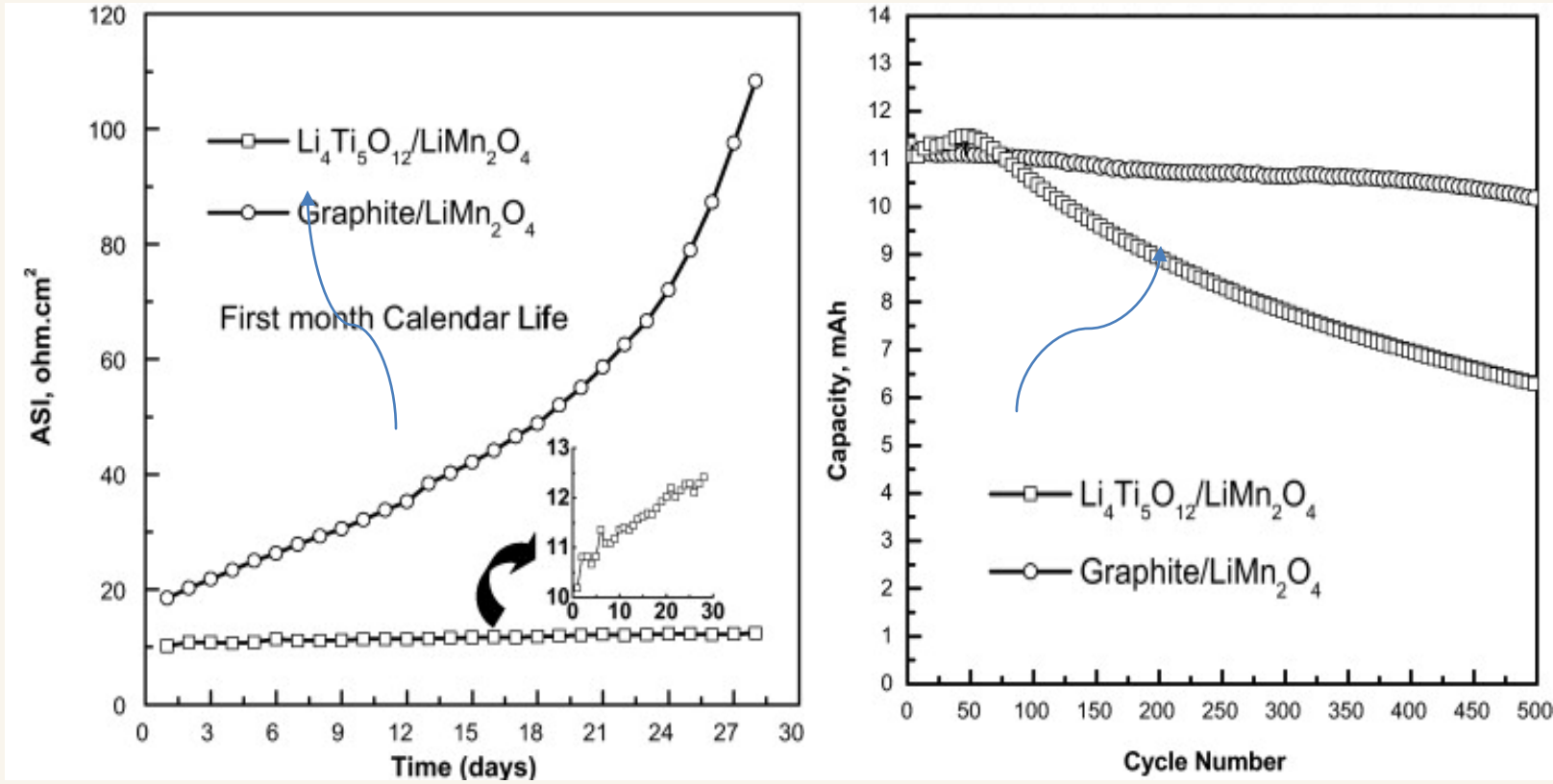
Discharge process of $Li_{x+4}Ti_5O_{12}$ →



G. Jian et al., *Chinese Physics B*, **2016**, 25(1), 018210
T. F. Yi et al., *J. Mater. Chem. A*, **2015**, 3, 5750

Anodes--oxides

- Example: lithium titanate (LTO)
  - Theoretical capacity: 175 mAh g^{-1}
  - Negligible volume change
  - Compared to graphite:
    - Improved cycle life and calendar life
    - Improved pulsing impedance

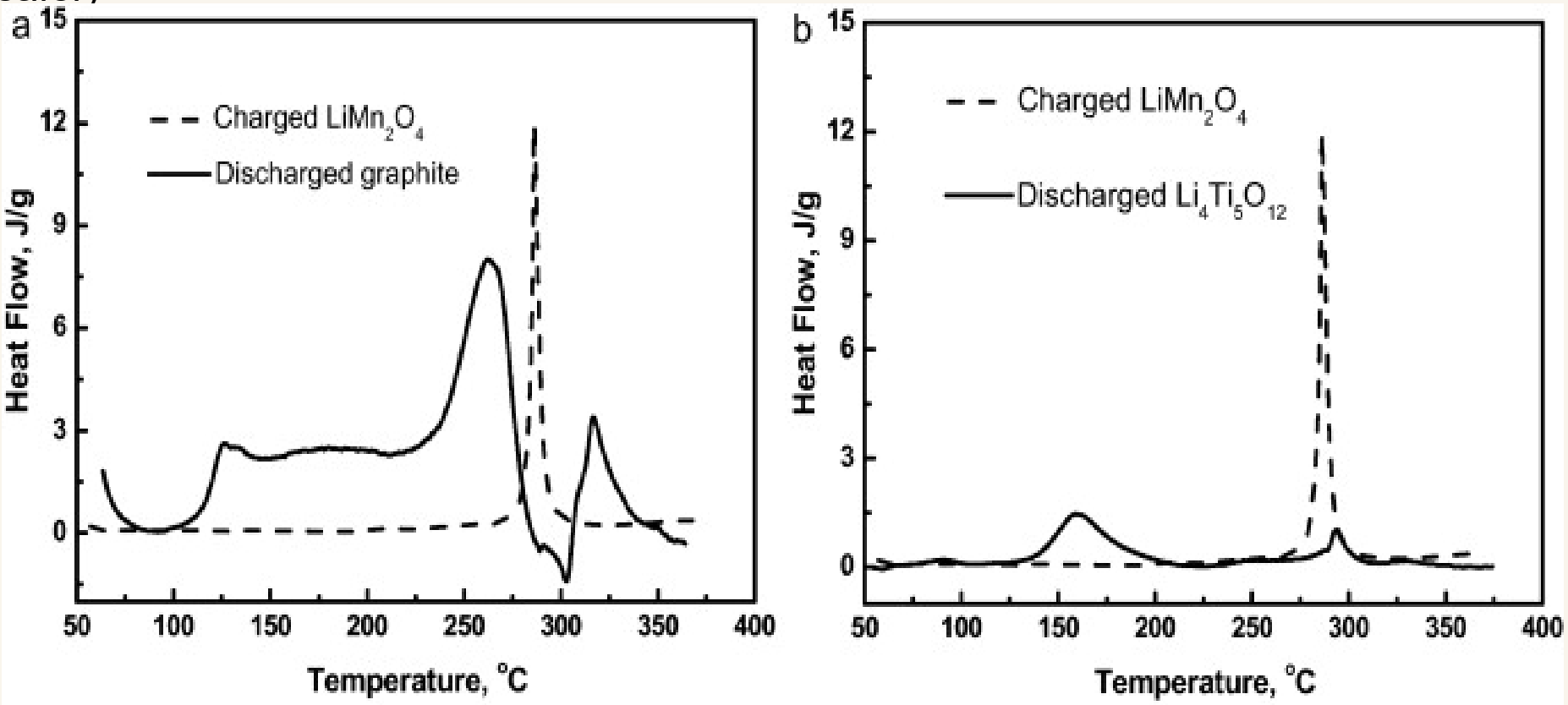


LTO/LMO and G/LMO pouch cells
Area specific impedance measurements (55 °C, 28 d) (left)
Cell discharge capacity (6C, 55 °C) (right)

L. Belharouak et al., *J. Power Sources*, **2011**, 196, 10344–10350

Anodes--oxides

- Example: LTO vs graphite
  - Lower heat generation (safer)

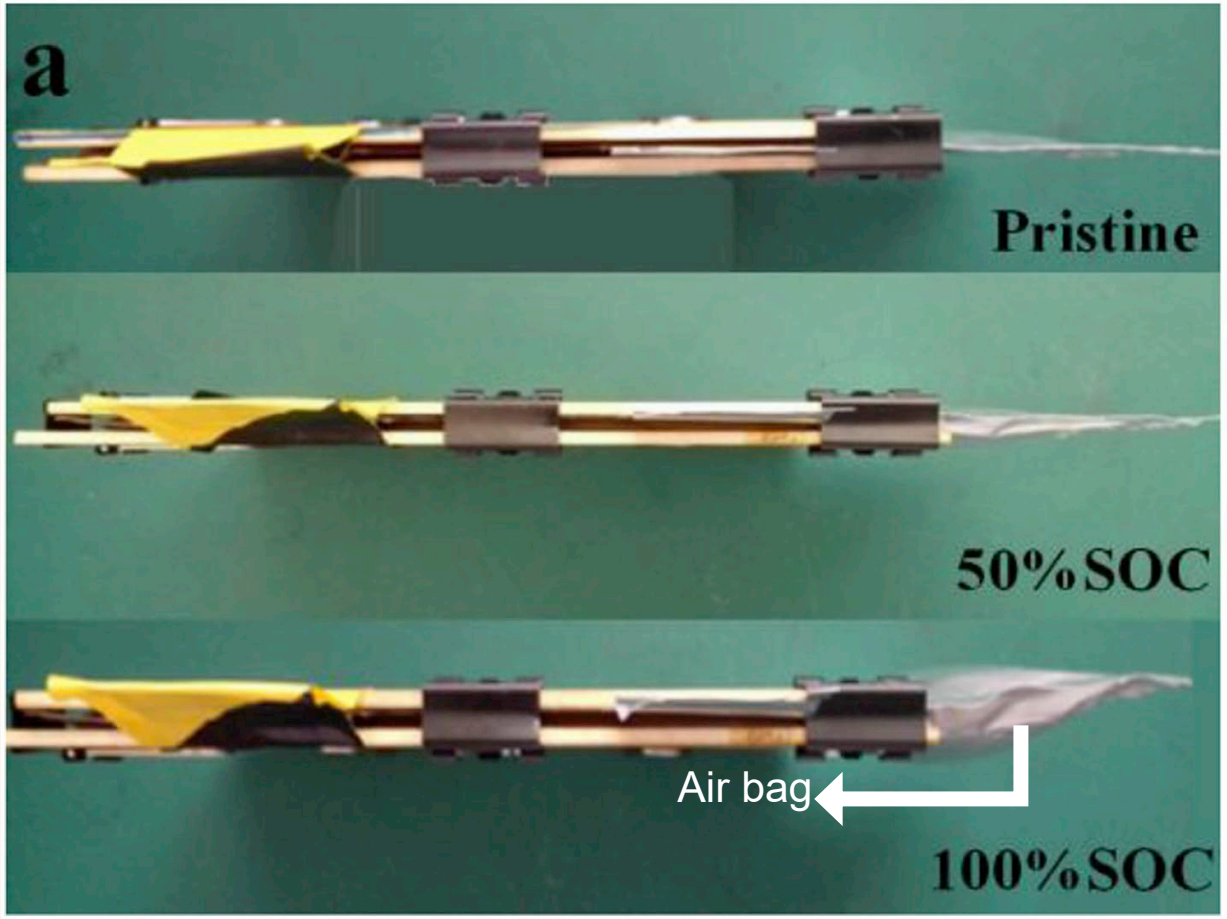


DSC of fully charged Graphite/LMO (left) LTO/LMO (right) pouch cells

M. Pfanzelt et al., *J. Power Sources*, **2011**, 196, 6815–6821

Anodes--oxides

- Example: LTO
  - Compatibility with electrolytes
    - Avoids electrolyte deduction & SEI formation
  - Elevated temperature tolerance
  - Gas swelling
  - Applied in high-power-density fields
    - E.g. vehicles



Air bag volume changes in LTO/NCM pouch cells after ageing at 55 °C

W. Liu et al., *J. Power Sources*, **2017**, 369, 103-110

Anodes--Silicon

- High theoretical energy density
  - Crystalline Si: 3579 mAh/g
- Drawback:
  - High volumetric expansion on lithiation (up to 400%)
    - Breaks electrode during cycling - mechanically unstable
    - Engineering of Si particle sizes to reduce expansion effects
  - High cost
  - Low coulombic efficiency (50–80%)
  - Most likely be used as a composite with carbon
    - Improves electrical conductivity and mechanical properties

S. Chae et al., *Joule*, **2017**, 1, 47–60

Anodes--Silicon

- Example: nano graphene–nano Si
  - Si largely amorphous after 1st charge
  - Particles expand >2x after the 1st charge & crack after 1st discharge

→

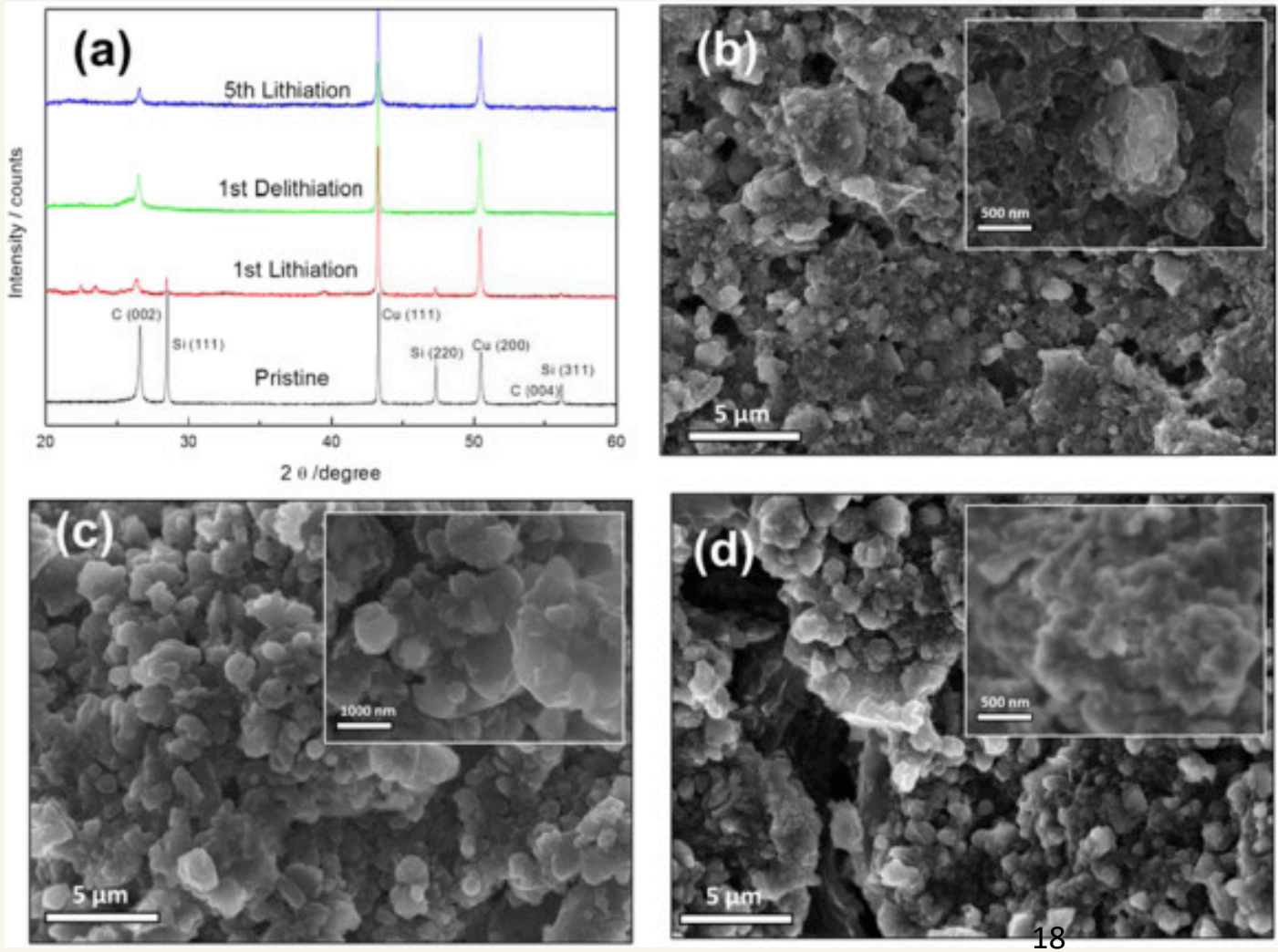
a. XRDs & SEM surface morphologies of

b. Si-graphene electrode

c. before/after 1st lithiation,

d. before/after 1st delithiation

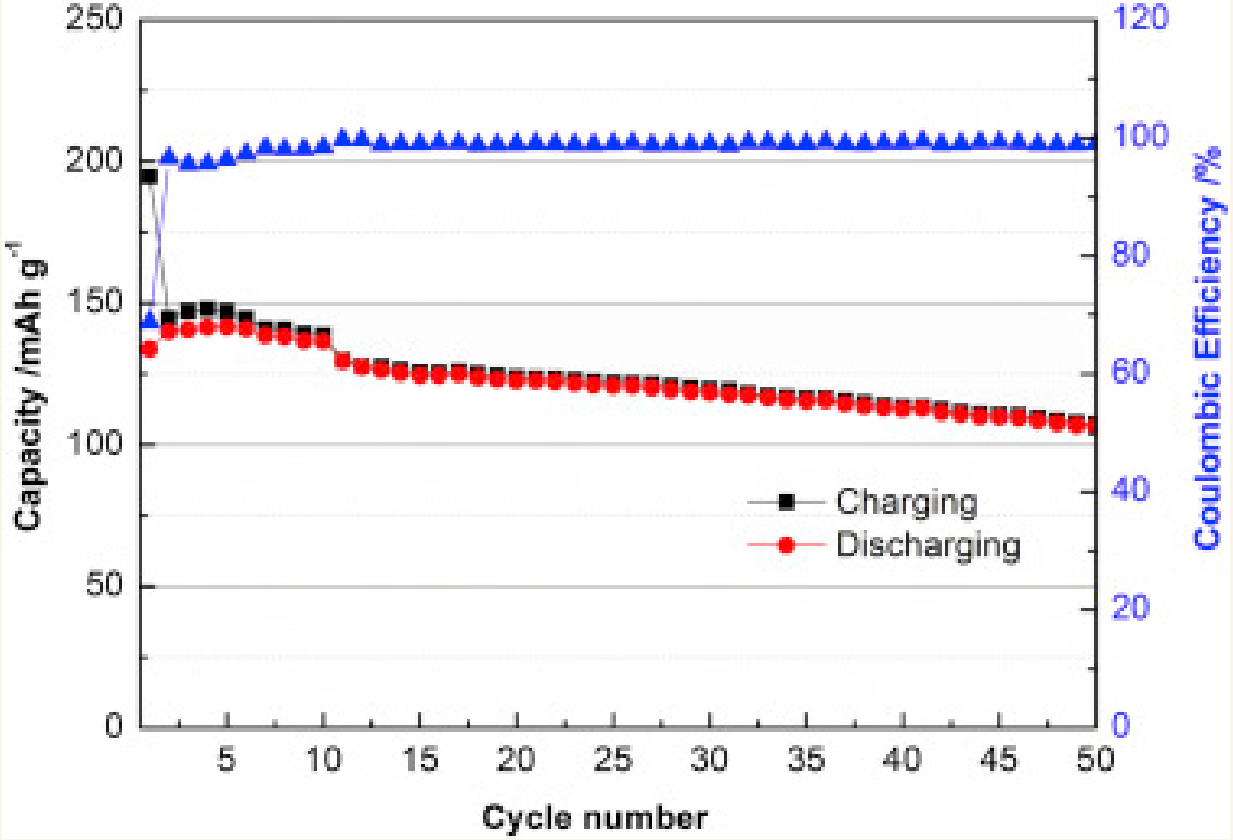
in full cell test (cathode: NCA)



KS. Eom et al., *J. Power Sources*, **2014**, 249, 118-124

Anodes--Silicon

- Example: nano graphene–nano Si
  - Continuous capacity decrease
    - Continuous SEI formation & Si pulverization - cell performance affected significantly by anode

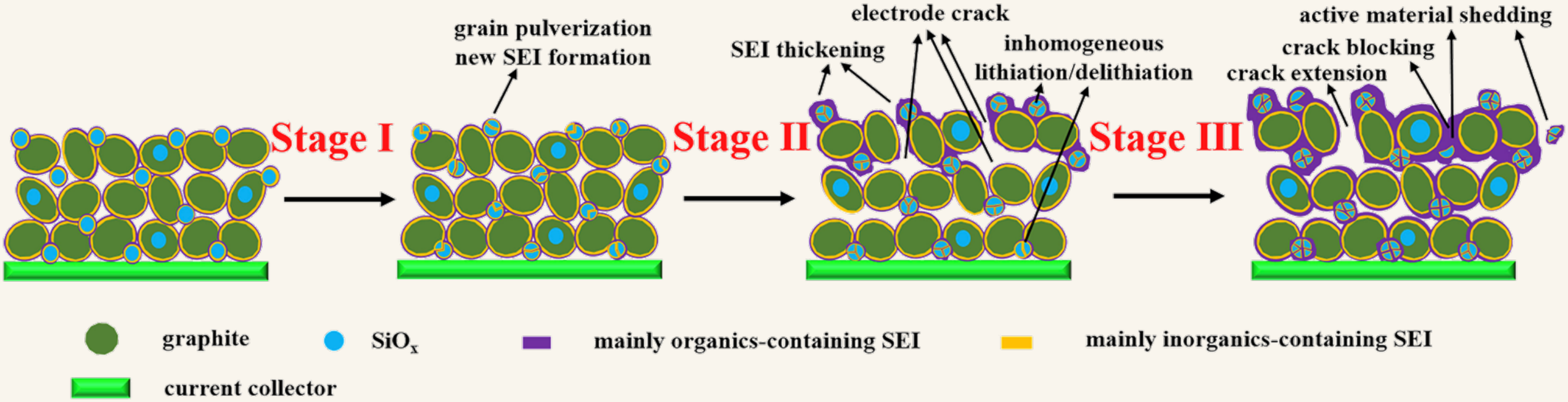


← Capacity fade
(C/15 in 1st-5th, C/5 in 5th -10th, C/2 in 10th-50th)
(cathode: NCA, electrolyte: $LiPF_6$)

KS. Eom et al., *J. Power Sources*, **2014**, 249, 118-124

Anodes--Silicon

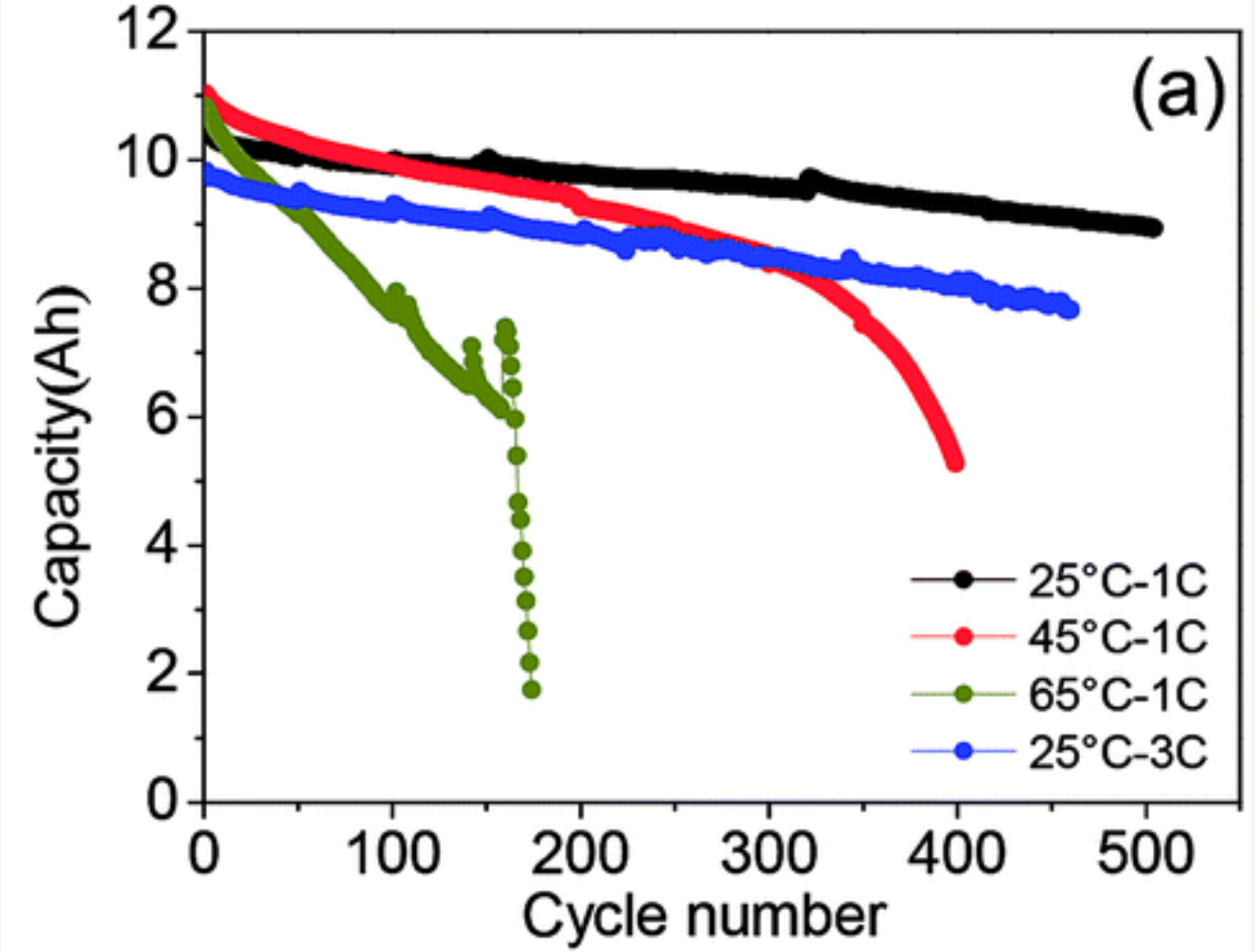
- Example: graphite–SiO_x
  - Li alkyl carbonates (e.g. Li_2CO_3, $ROCO_2Li$) form on anode surface at temps > 40 °C
  - Graphite–SiO_x electrodes failure mechanism



L. Wang et al., *Electrochimica Acta*, **2018**, 286, 219-230;

Anodes--Silicon

- Example: graphite–SiO_x
  - Capacity drops
    - Anode deterioration main cell degradation factor

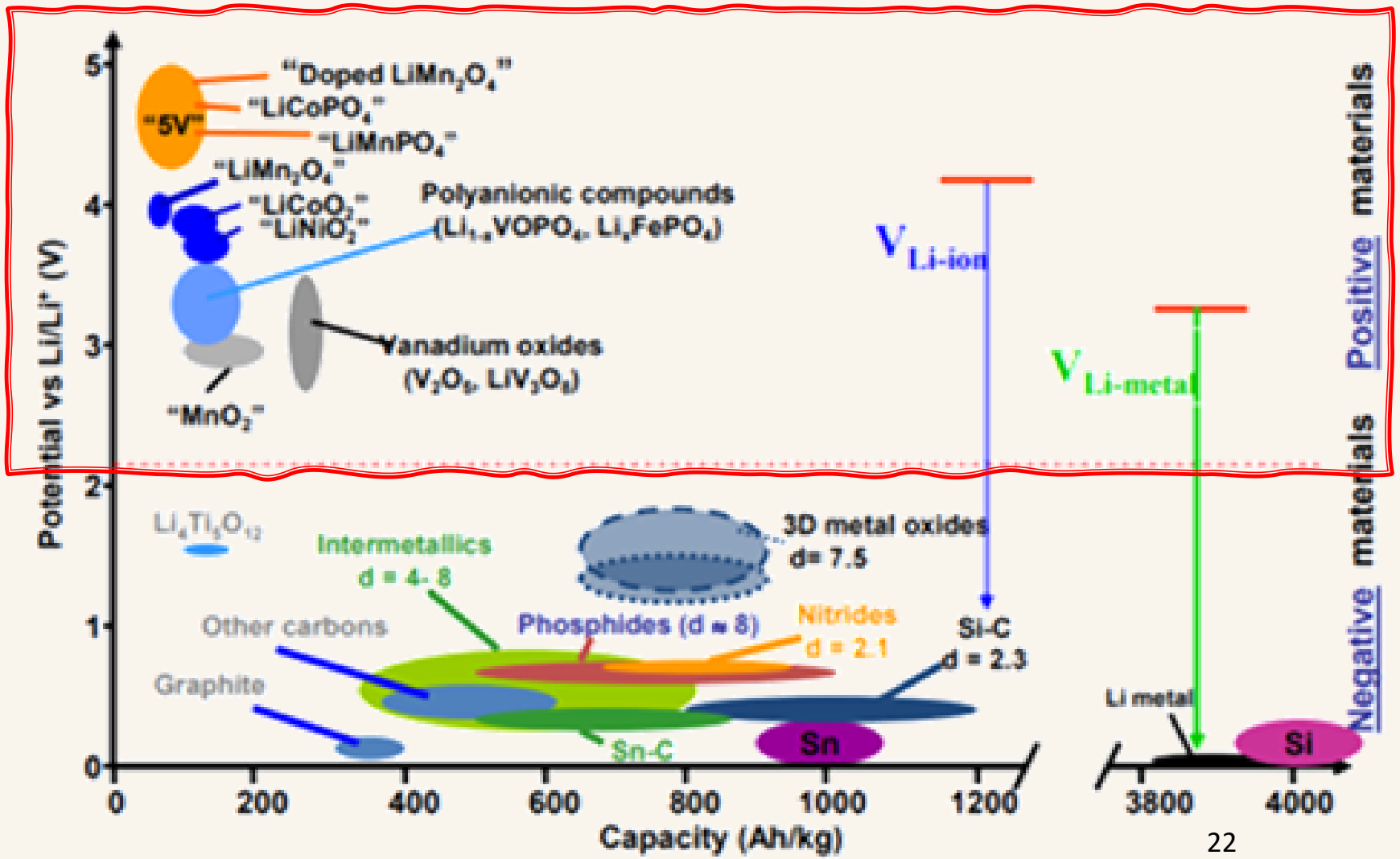


Cycle performance of NCA/graphite–SiO_x pouch cell

C. Liu et al., *J. Mater. Chem. A*, **2018**, 6, 65-72

Cathodes

- Oxides
  - Commercial
  - Near-future
  - Future
- Non-oxides



http://www.eai.in/blog/2018/12/research-status-of-anode/cathode-material.html

Cathode - Oxides

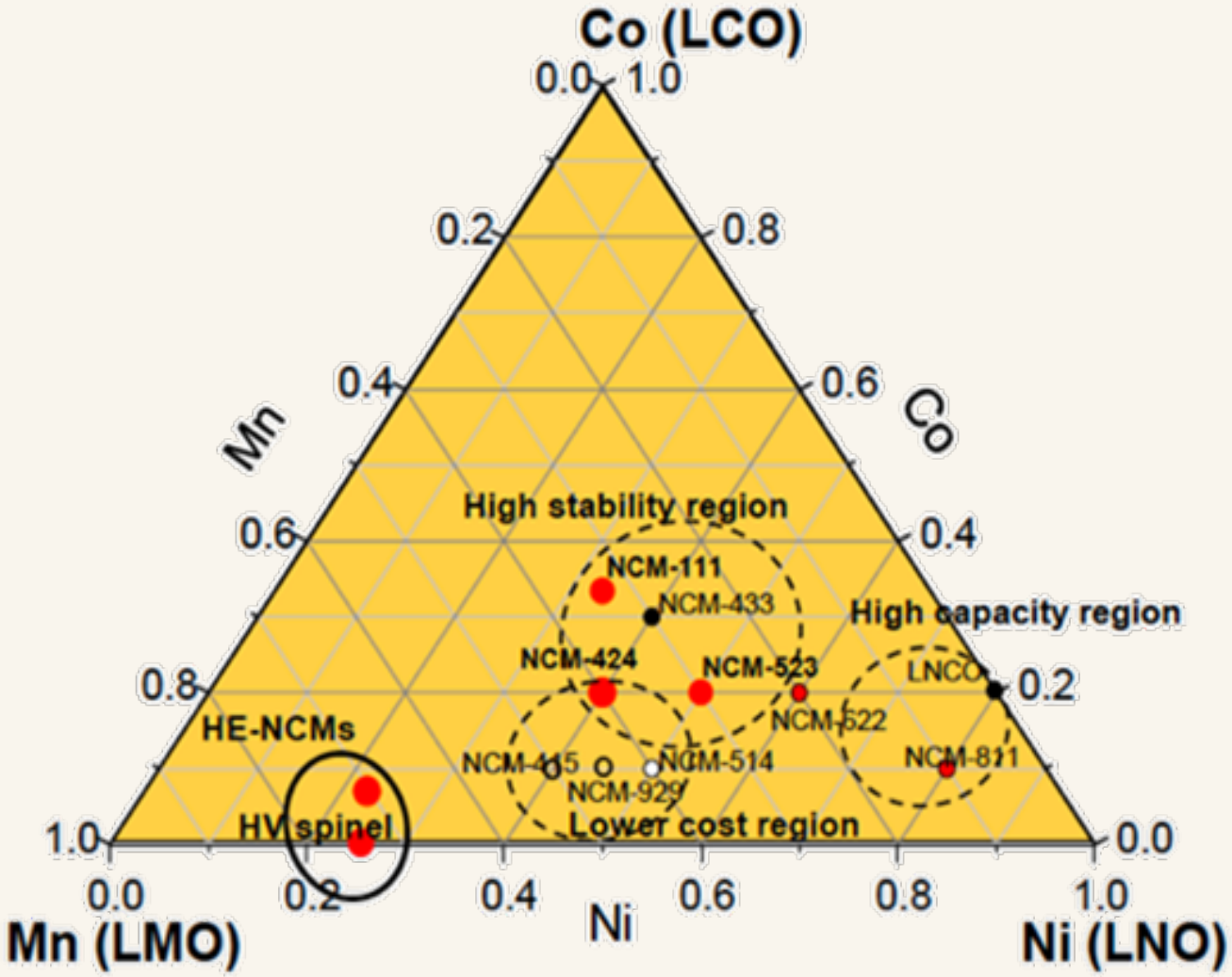
- General characteristics of commercial oxides for Li^+ battery cathode

Material	Structure	Potential versus Li/Li^+, average V	Specific capacity, mAh/g	Specific energy, Wh/kg
$LiCoO_2$	Layered	3.9	140	546
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	Layered	3.8	180–200	680–760
$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC)	Layered	3.8	160–170	610–650
$LiMn_2O_4$ and variants (LMO)	Spinel	4.1	100–120	410–492
$LiFePO_4$ (LFP)	Olivine	3.45	150–170	518–587

R.J. Brodd (ed.), *Batteries for Sustainability: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, **2013**

Cathode - Oxides

- Commercial oxides
  - Nickel cobalt manganese oxide (NCM)
    - High capacity & operating voltage
    - Slow reaction with electrolytes
    - Moderate safety (oxygen release)
    - High cost of Ni and Co
    - Available in different stoichiometries

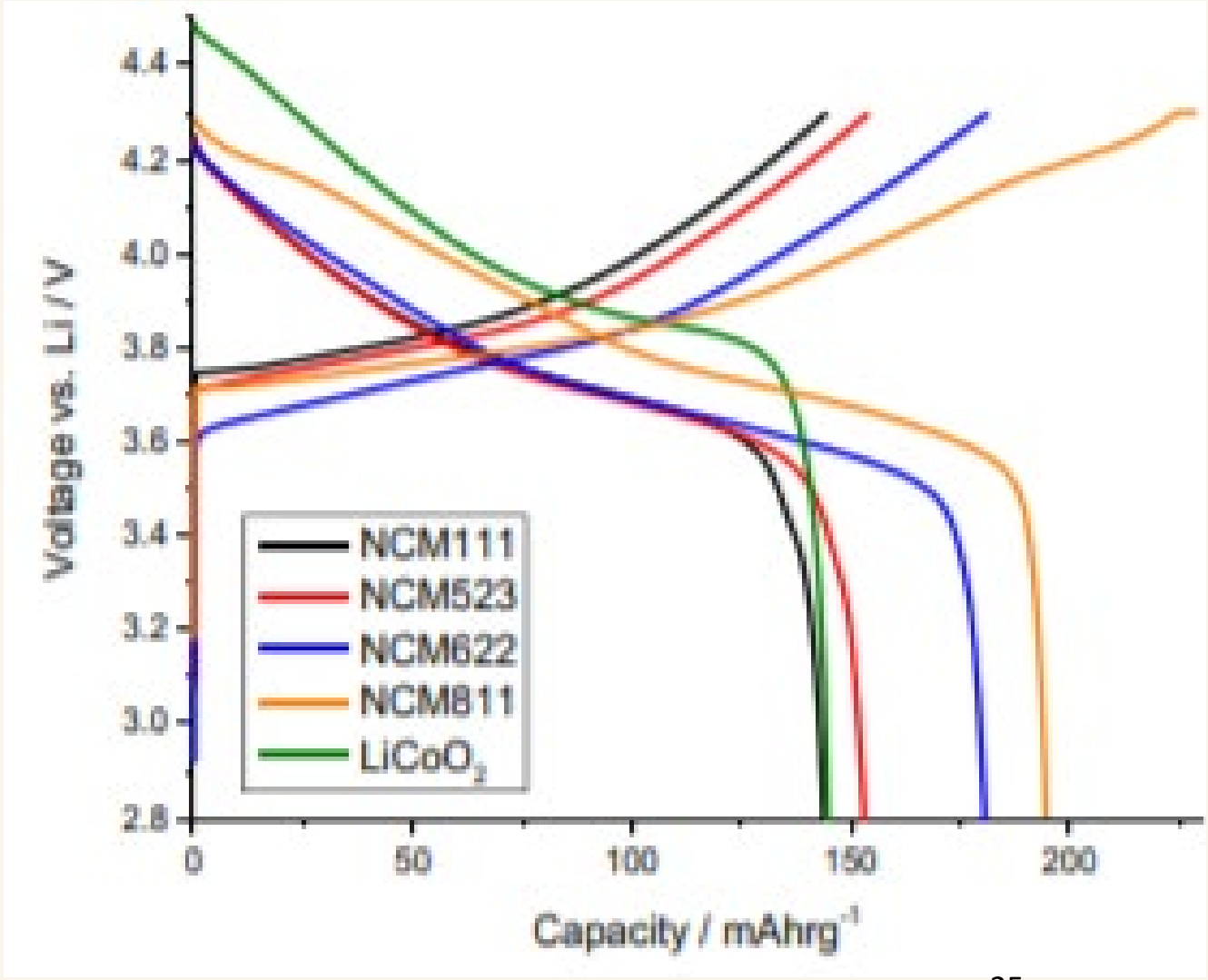


NCM composition diagram

E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274

Cathode - Oxides

- Nickel cobalt manganese oxide (NCM)
  - Available in different stoichiometries
    - $Ni_xCo_yMn_z$, X+Y+Z =1
    - Common XYZ (increasing Ni%):
      - 111 (154 mAh/g)
      - 532 (164 mAh/g)
      - 622 (175 mAh/g),
      - 811 (>185 mAh/g)

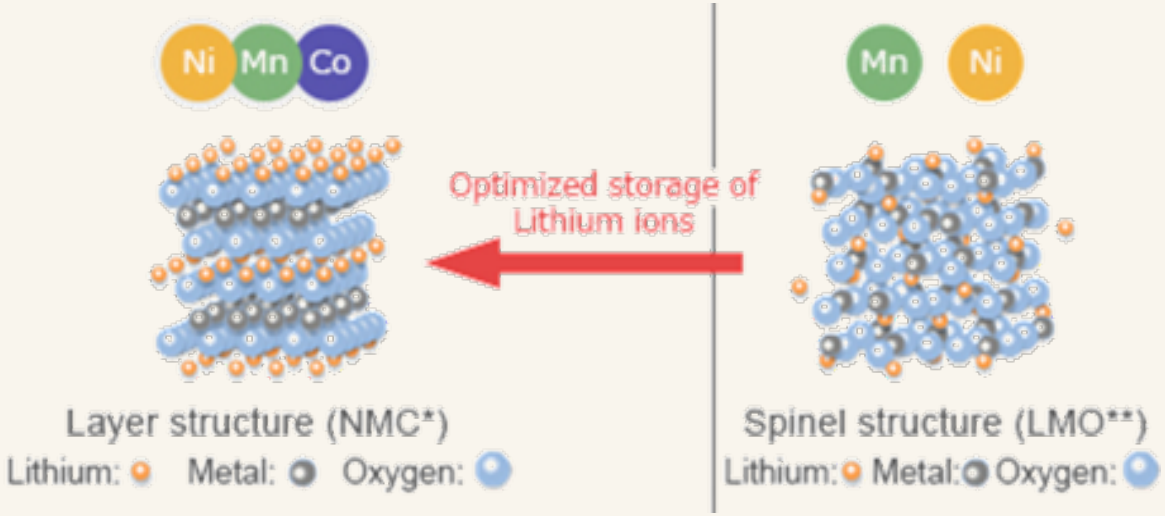


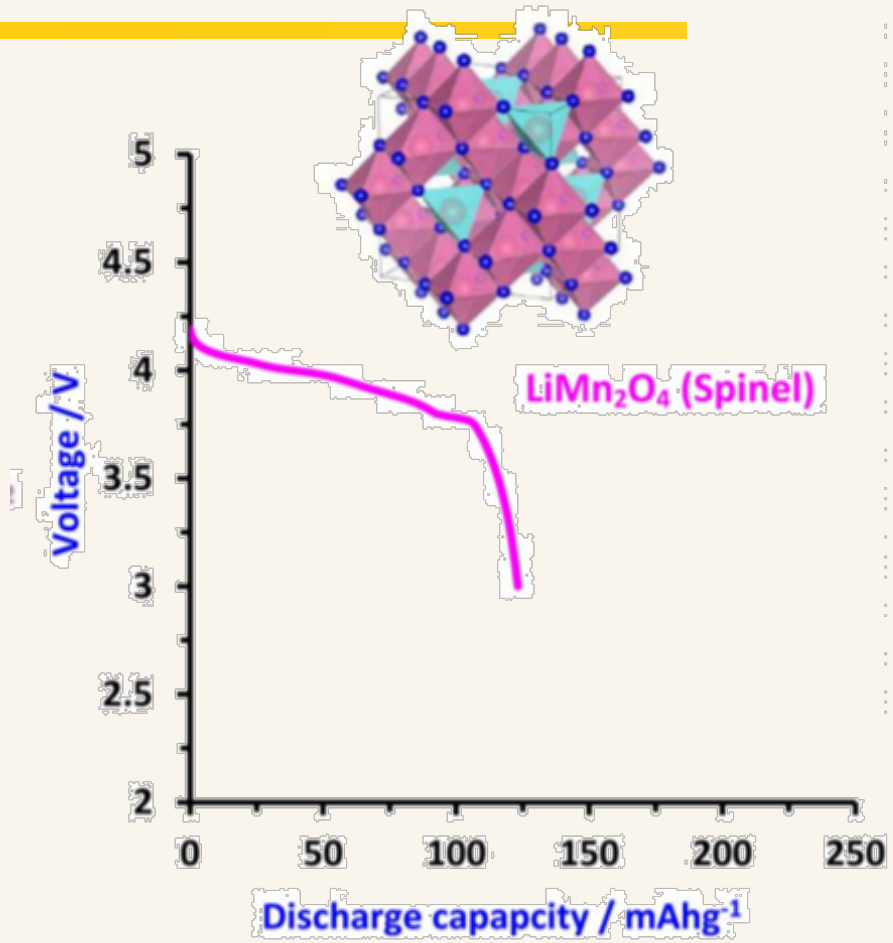
Voltage profiles of NCM and $LiCoO_2$

E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274

Cathode - Oxides

- Lithium manganese oxide (LMO)
  - Low cost
  - Excellent high rate performance
  - High operating voltage
  - Mn dissolution issue, low capacity
    - Now blended with NMC as cathode to suppress Mn dissolution





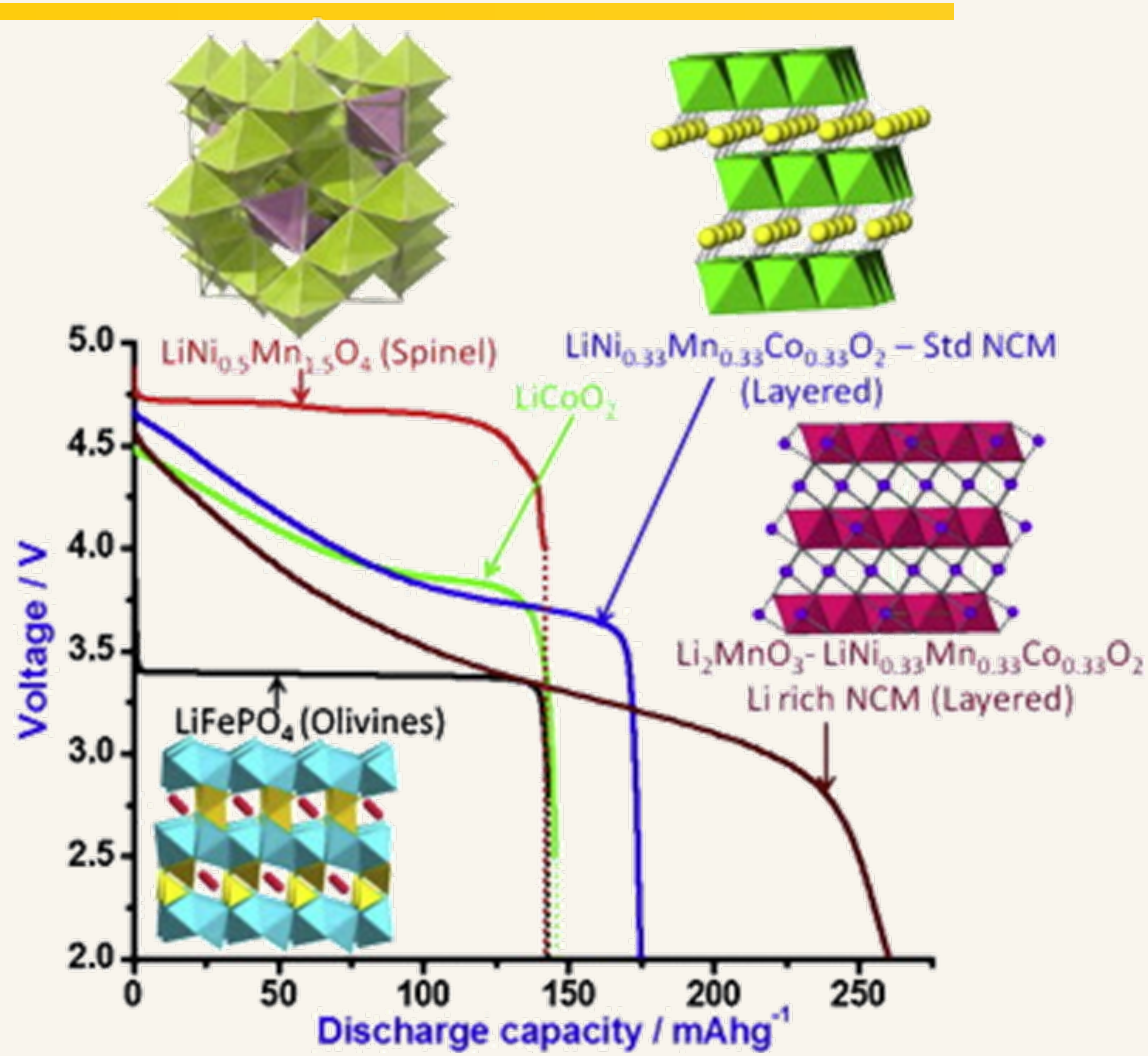
↑ Voltage profile of LMO

← Layered NCM structure stores more Li^+ (applied by NISSAN)

E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274
https://www.nissan-global.com/EN/TECHNOLOGY/OVERVIEW/li_ion_ev.html

Cathode - Oxides

- Lithium Iron Phosphate (LFP) Li_xFePO_4
  - Slow reaction with electrolyte
  - Safe
    - No oxygen release
  - No resource limitations
    - Moderate cost
  - Low operating voltage
  - Low capacity

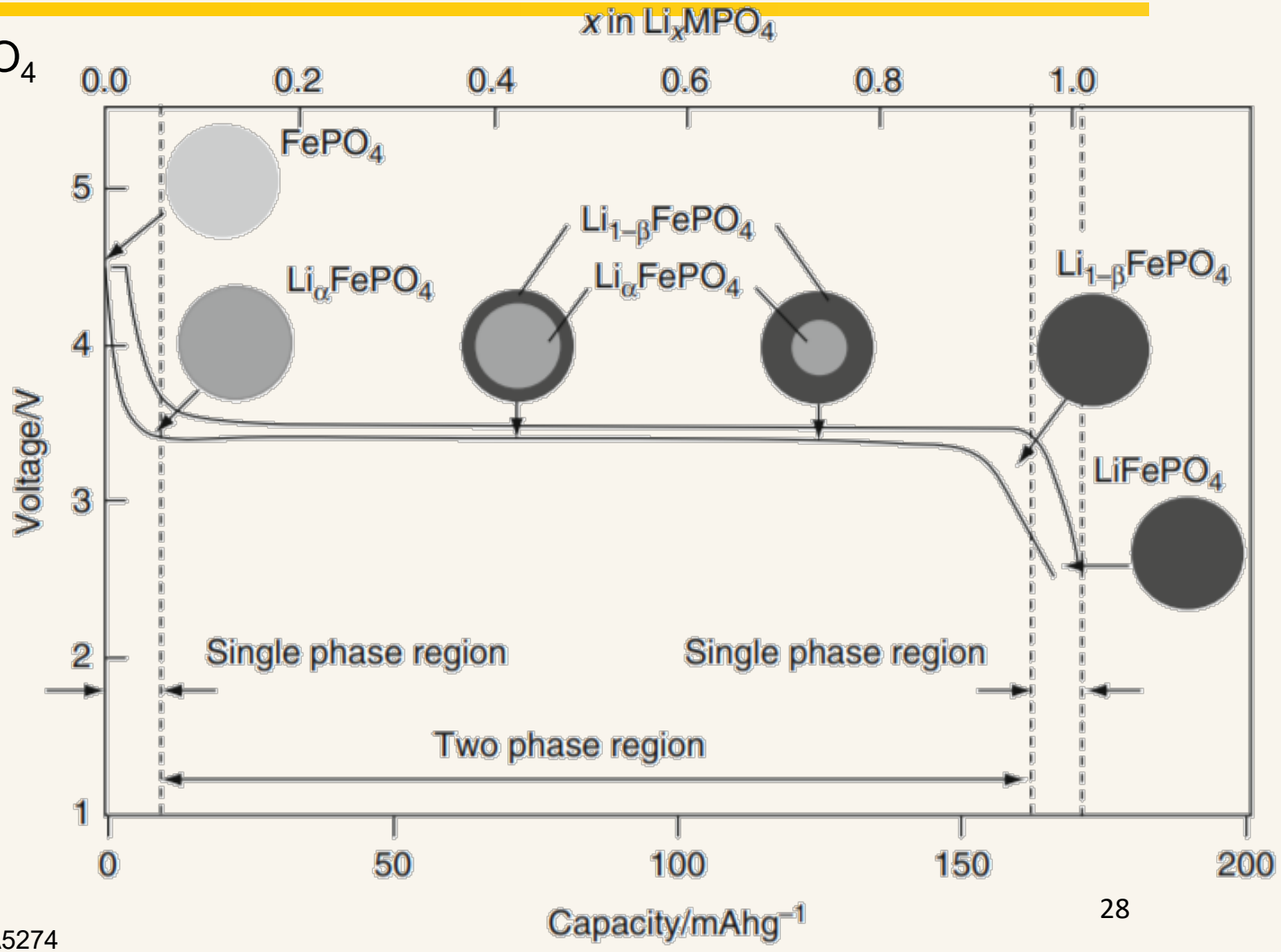


Voltage profiles (versus Li) of LFP compared with $LiCoO_2$ and NCM →

E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274
R.J. Brodd (ed.), *Batteries for Sustainability: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, **2013**

Cathode - Oxides

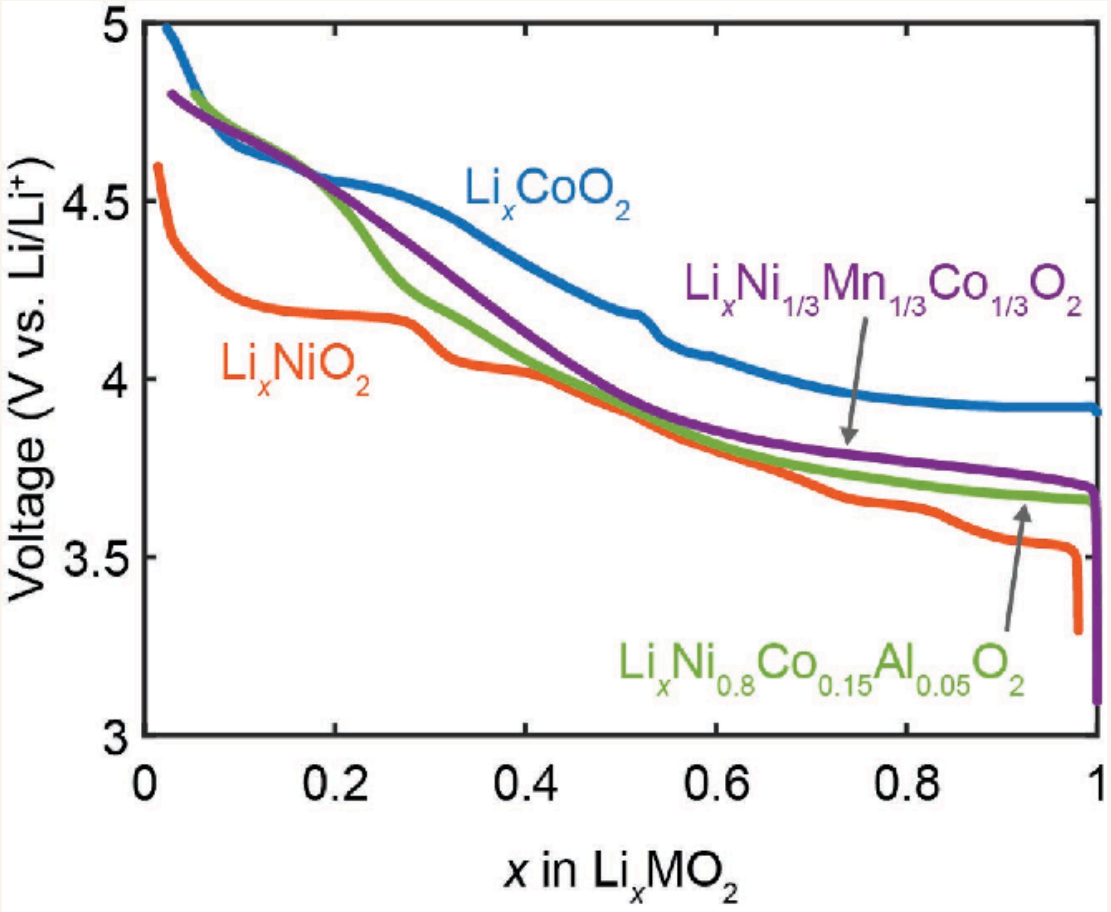
- Lithium Iron Phosphate (LFP) Li_xFePO_4
  - Li_xFePO_4 discharge processes



E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274

Cathode - Oxides

- Lithium cobalt oxide (LCO)
  - Energy density: 180 Wt/kg, capacity = 274 mAh/g
  - Low self-discharge, high discharge voltage ≤ 4.45 V
  - Good cycling performance
  - Used in small electronics
- Nickel cobalt aluminum oxide (NCA)
  - Al in NCA improves thermal & electrochemical properties
  - High capacity
  - High operating voltage
  - Excellent high rate performance
  - Slow reaction with electrolytes
  - Potential resource limitations (high Ni & Co costs)



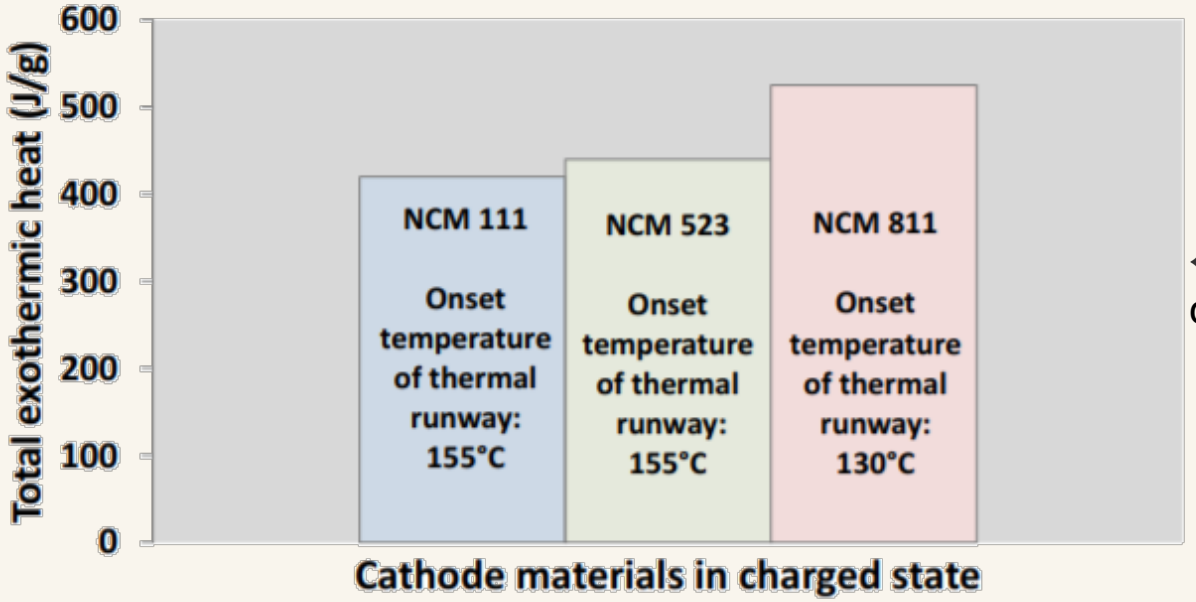
↑ Voltage profiles of first charging of LCO, NCA and NMC

H. D. Yoo et al., *Materials Today*, **2014**, 17, 3, 110-121;
E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274;
R.J. Brodd (ed.), *Batteries for Sustainability: Selected Entries from the Encyclopedia of Sustainability Science and Technology*, **2013**

Cathode - Oxides

Most oxides suffer from **thermal runaway**

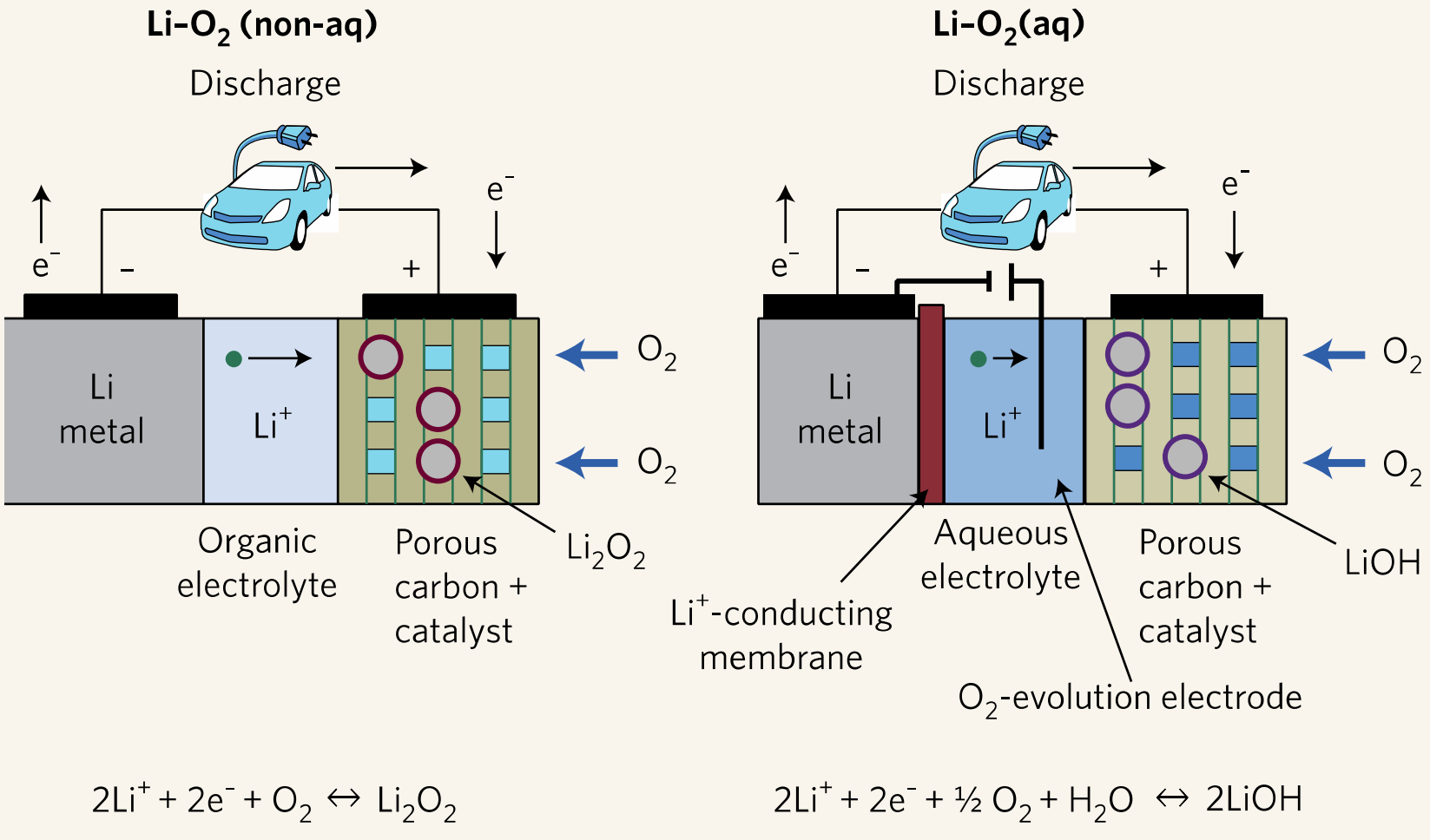
- **Thermal runaway**: occurs when as cell reaches temperature where becomes self-sustaining as it creates O_2 (explosive and flammable)
- Especially severe when fully charged
- Usually, the higher the energy density, the worse safety performance
  - High nickel materials especially susceptible
  - Cathode and electrolyte are main factors for safety issues in a cell/pack argument for solid state electrolytes



← Thermal response of multi-layer pouch cells containing NCM, graphite and $LiPF_6$

E. Markevich et al., *J. Electrochem. Soc.*, **2019**, 166 (3) A5265-A5274; John T. Warner, *Lithium-Ion Battery Chemistries*, **2019**

Li-Air configurations-Future cathode



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

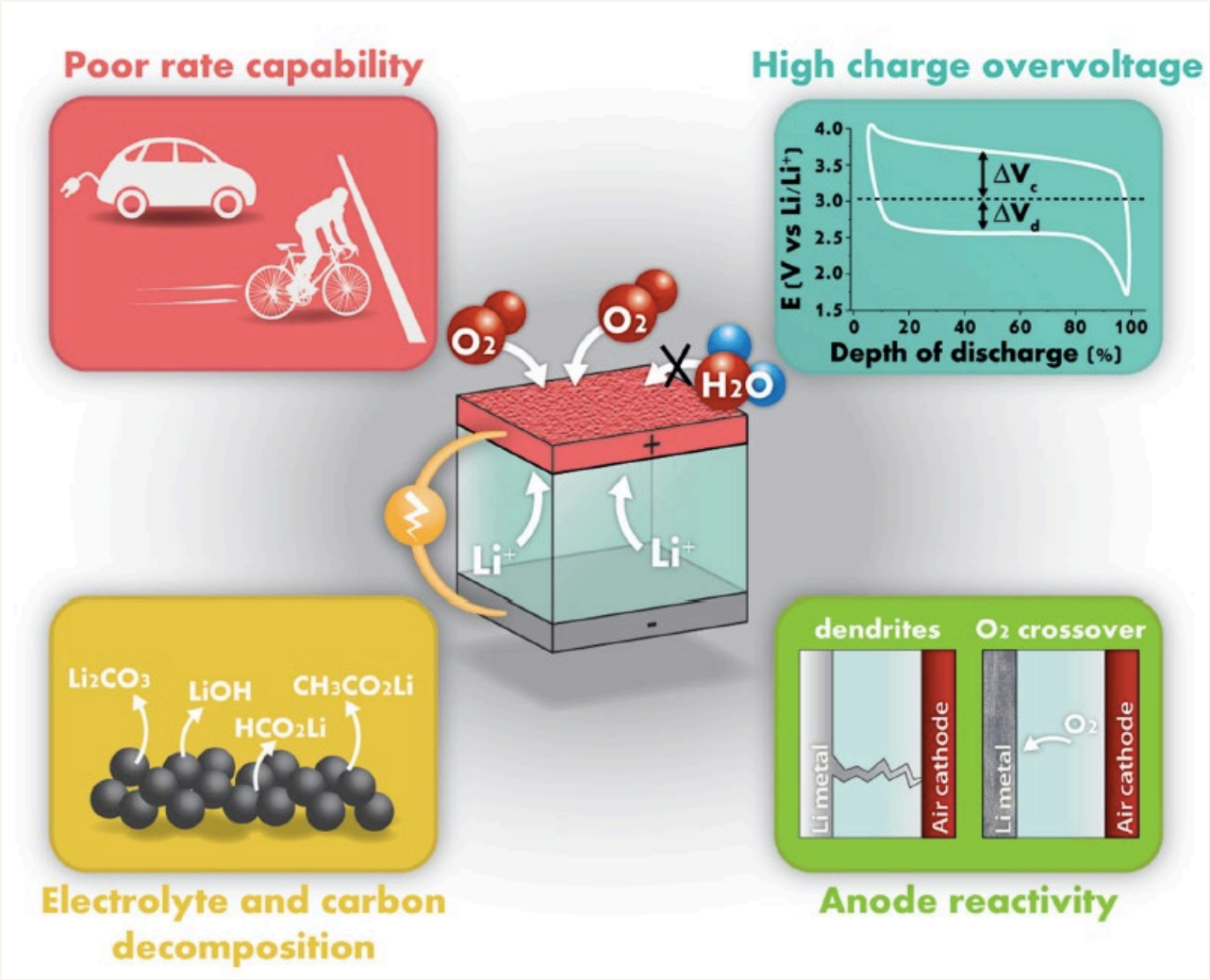
$2Li^+ + 2e^- + ½\ O_2 + H_2O \leftrightarrow 2LiOH$

P. G. Bruce et al, Li–O_2 and Li–S batteries with high energy storage," *Nat. Mater.* 2012, *11*, 19-29.

Li-Air-batteries

Advantages:
- High specific energy density
- Air is everywhere

Disadvantages:
- Existing issues with Li- metal batteries
- Decomposition of active materials
- Poor rate capacity/power output
- High charging overpotential



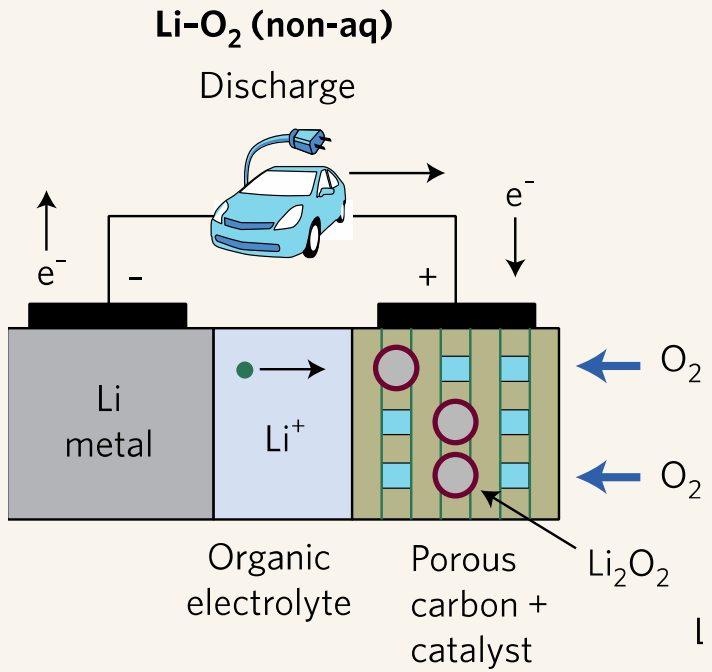
Grande, L.; Paillard, E.; Hassoun, J.; Park, J. B.; Lee, Y. J.; Sun, Y. K.; Passerini, S.; Scrosati, B. *Adv. Mater.***2015**, *27*(5), 784–800.

High charging overpotential

- Voltages (vs. Li/Li^+)
  - Discharging: ~2.7 V
  - Chagrining: 4-4.5 V

Can this over potenital be mitigated with photocatalysis?

Routes for photon-assisted charging
- Mediated
- Unmediated

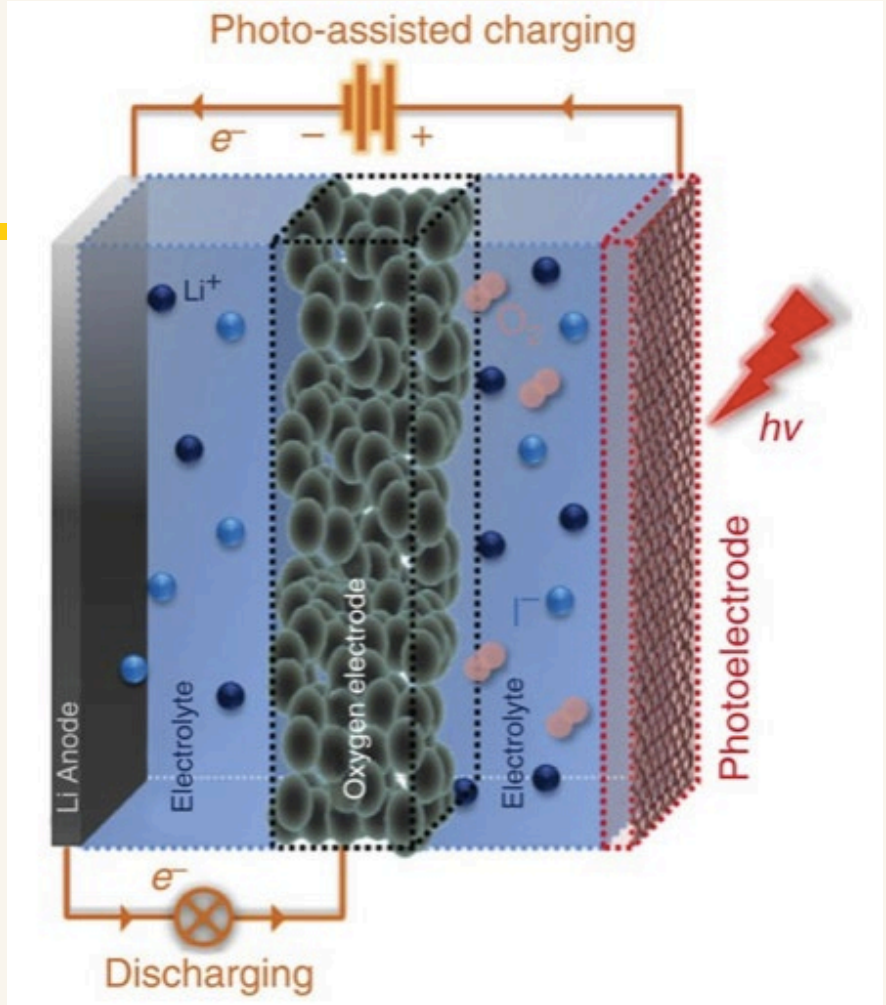


$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$

P. G. Bruce et al, Li–O_2 and Li–S batteries with high energy storage," *Nat. Mater.* 2012, *11*, 19-29.

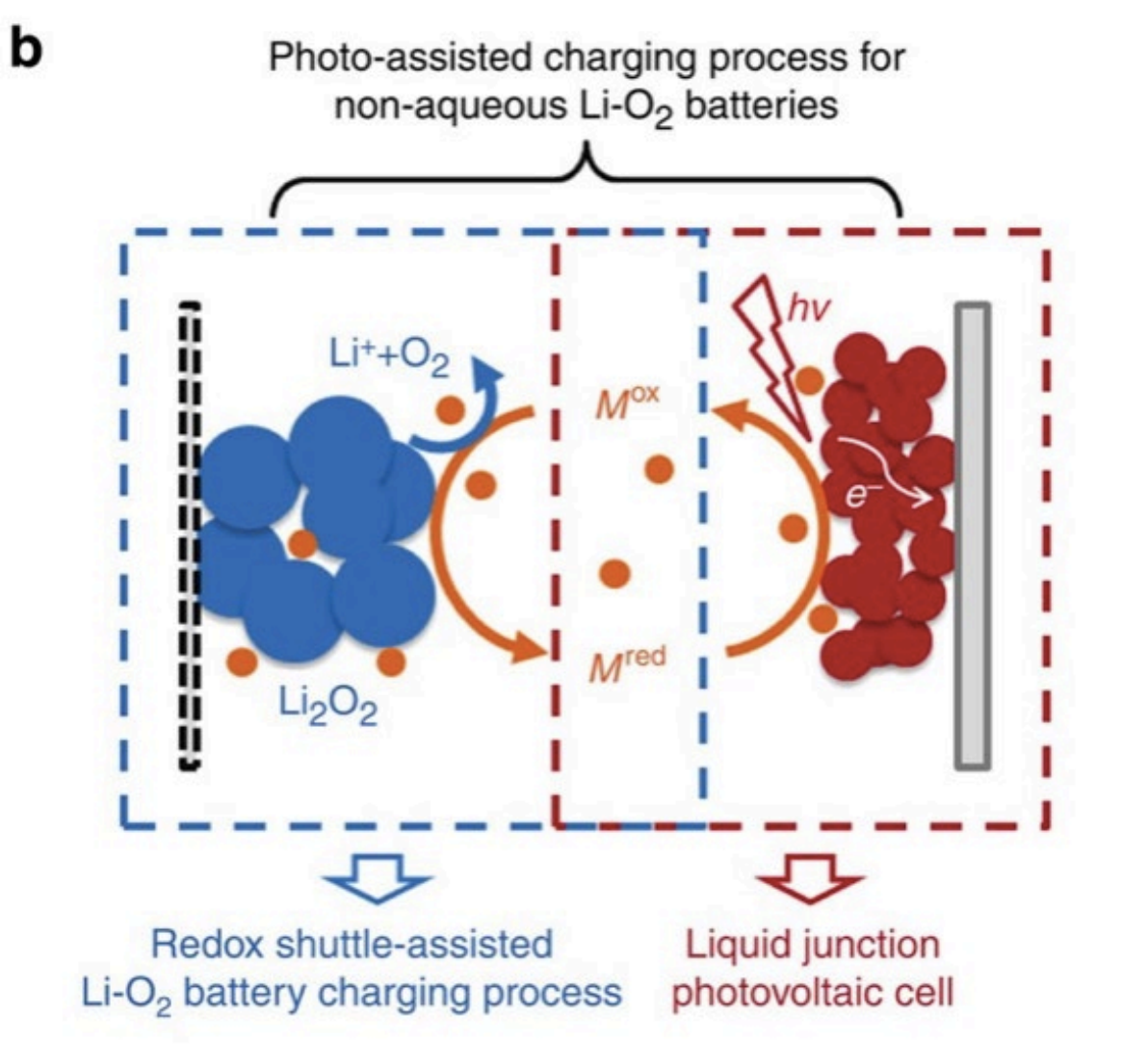
Mediated charging

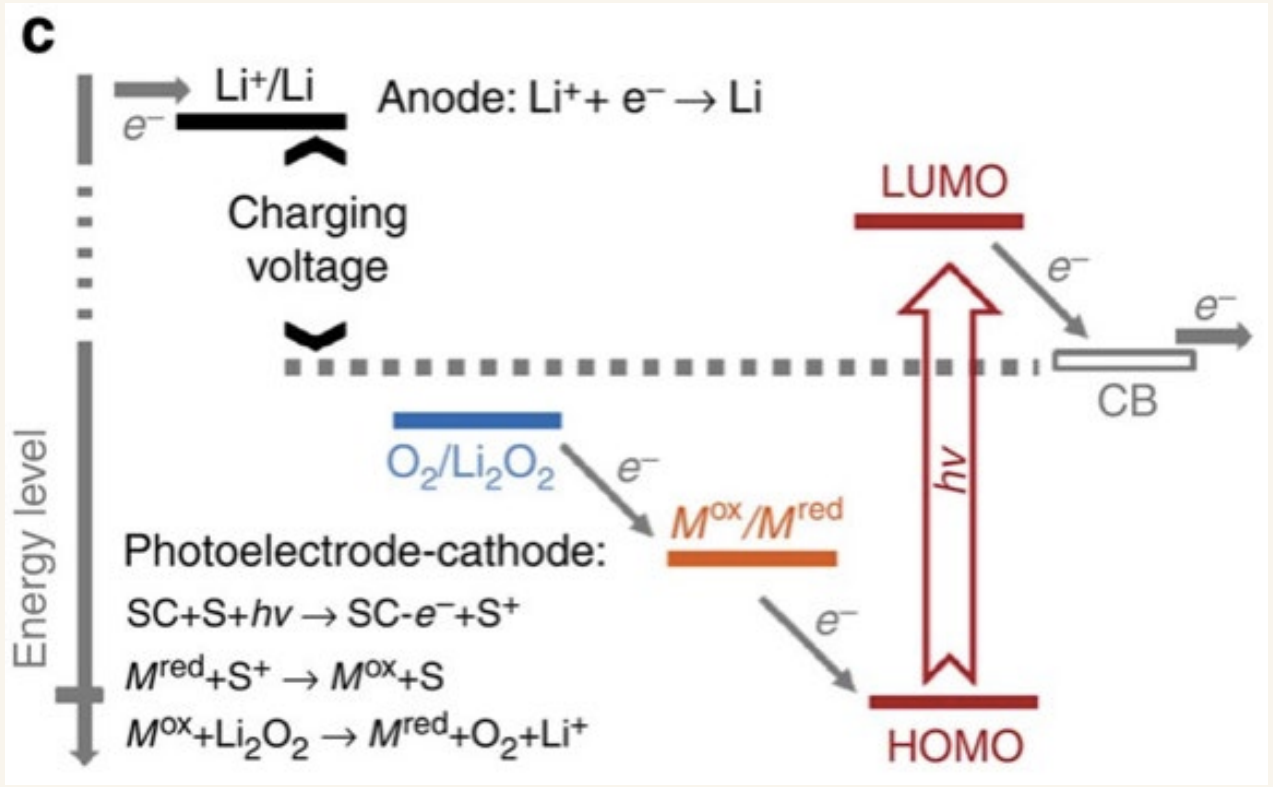
- Discharging
  - Normal Li-air configuration
- Charging
  - Li-metal connected to photoelectrode
- Photoelectrode: Dye-sensitized TiO_2
- Mediator: I_3^-/I^-
  - Redox potential: +3.55V
- Electrolyte: LiI and $LiClO_4$ in dimethylsulfoxide



Yu, M., Ren, X., Ma, L. & Wu, Y. *Nat. Commun.***5,**1–6 (2014).

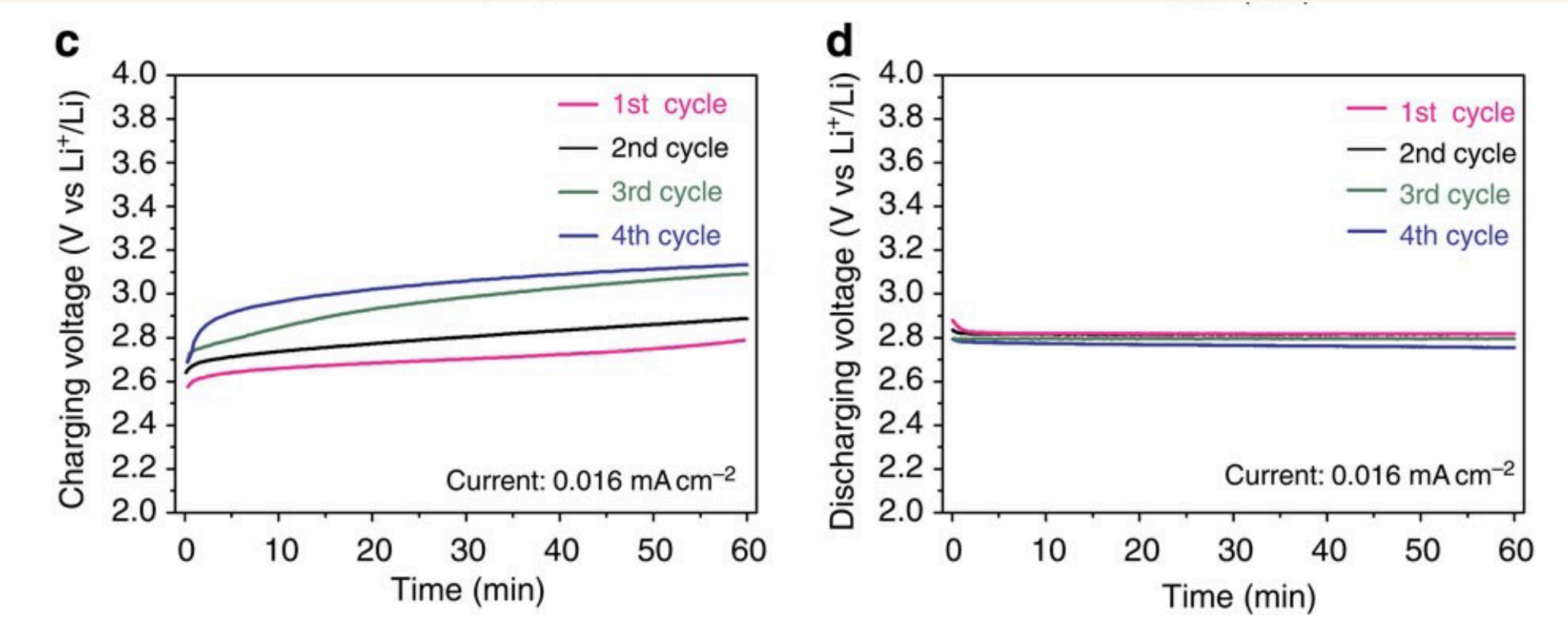
Mediated charging configuration





Yu, M., Ren, X., Ma, L. & Wu, Y. *Nat. Commun.***5,**1–6 (2014).

Mediated Charging



Charging voltage: ~2.6 V

- Theoretical charging voltage: 2.96 V
- Li_2O_2 completely degraded

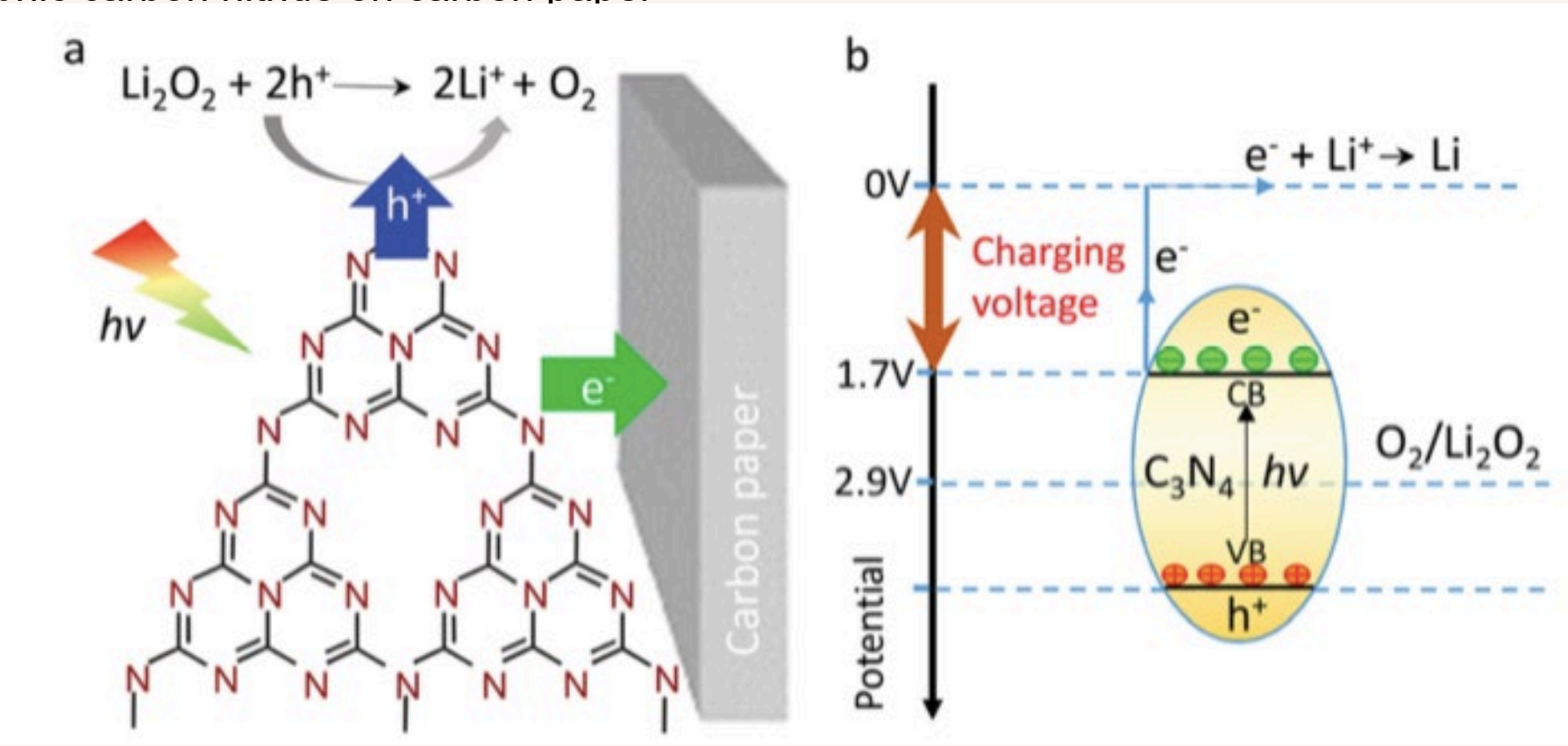
- Stability concerns

Mediators at Li-metal electrode

Yu, M., Ren, X., Ma, L. & Wu, Y. *Nat. Commun.***5,**1–6 (2014).

Unmediated charging

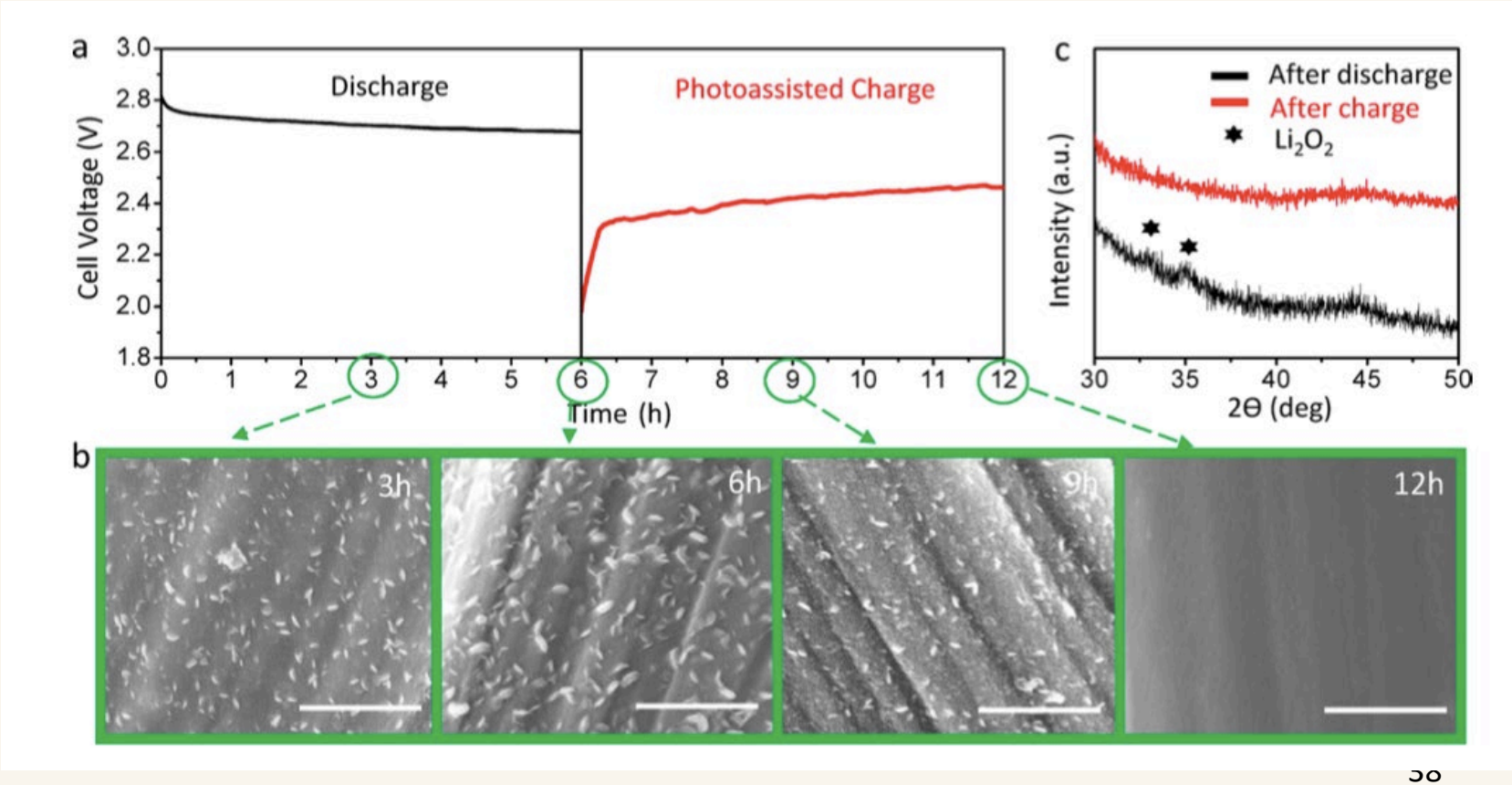
- Electrolyte: LiTFSI in tetraglyme(G4)
- Oxygen electrode also acts as photoelectrode
  - Graphic carbon nitride on carbon paper



Liu, Y. *et al.*. *J. Mater. Chem. A* **4,**12411–12415 (2016).

Unmediated charging

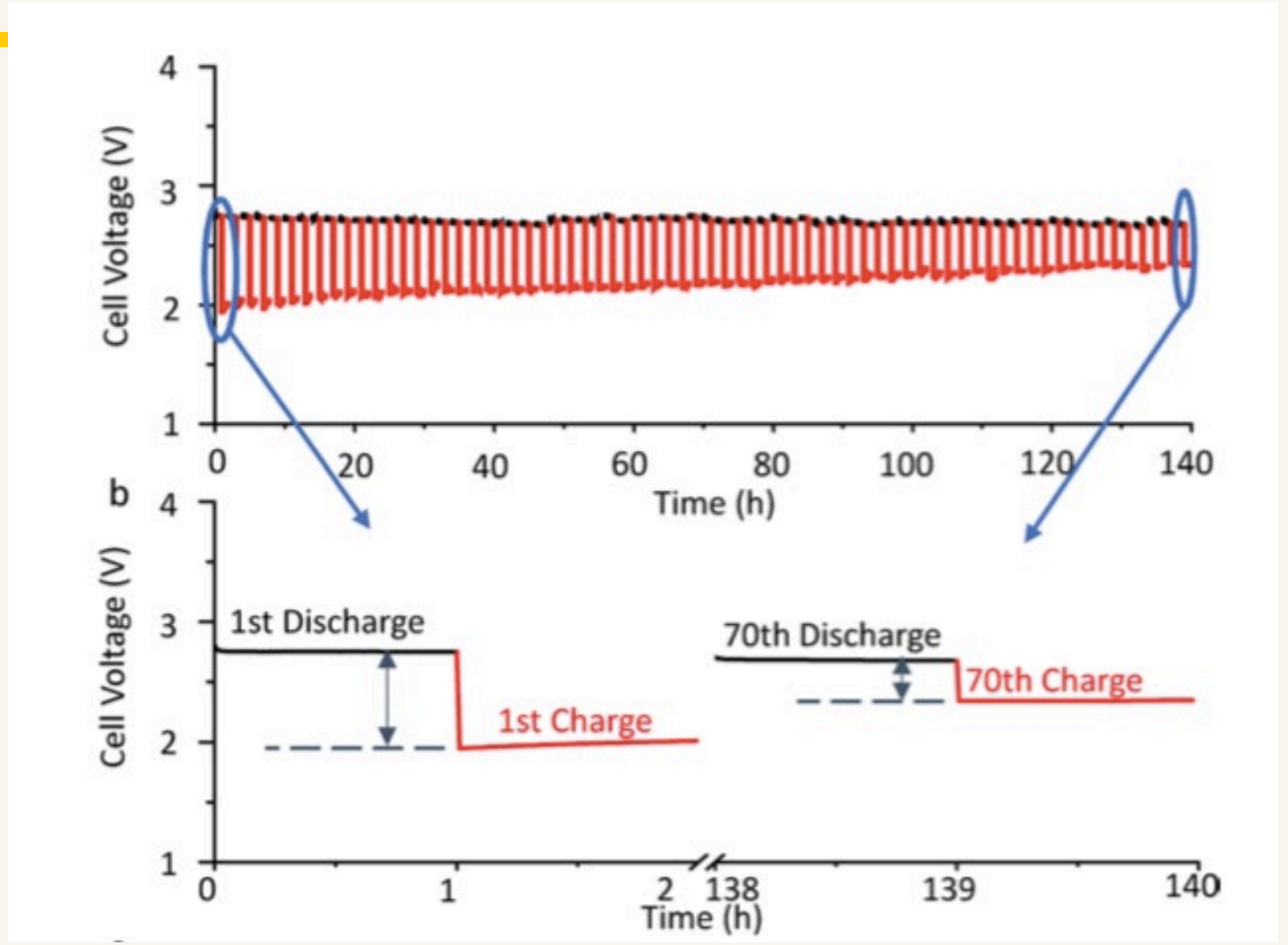
- Charging voltage: 1.96V
- Theoretical charging voltage: 2.96V
- Electrical efficiency: 140%
- Oxidized Li_2O_2 completely



Liu, Y. *et al.*. *J. Mater. Chem. A* **4,**12411–12415 (2016).

Stability- unmediated charging

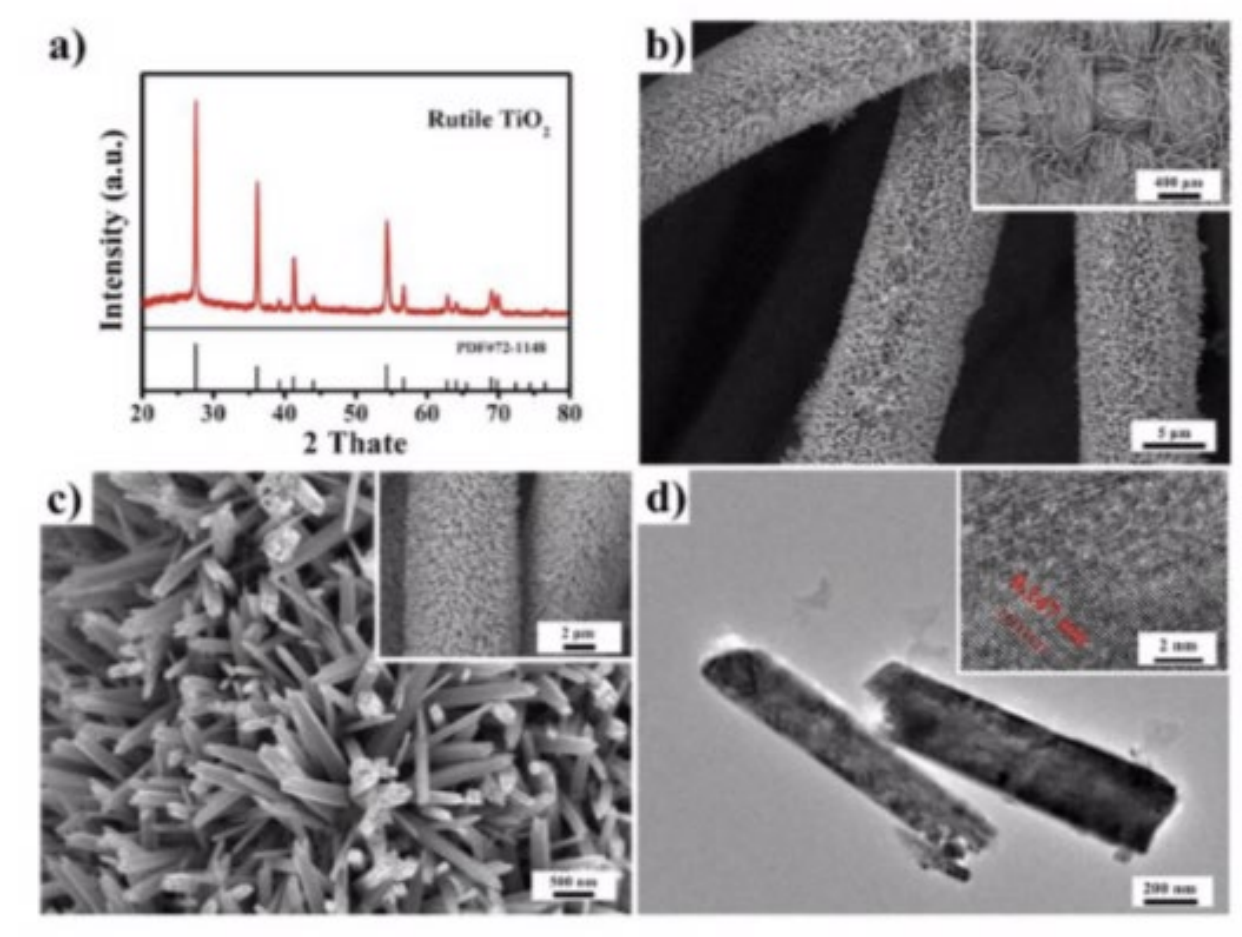
- Stable after 70 cycles at 0.01 mA/cm^2
- Not as stable at 0.03 and 0.05 mA/cm^2
- Charge transport limitations



Liu, Y. *et al.*. *J. Mater. Chem. A* **4,**12411–12415 (2016).

Unmediated charging-nanostructures

- Oxygen electrode acts as photoelectrode
  - Defective rutile TiO2 nanorod assembly on carbon textiles
- Electrolyte: 0.5 M $LiClO_4$ in TEGDME
- Discharge in the dark
- Charge in the light



Gong, H. et al. *Energy Storage Mater.* **13,** 49-56 (2018).

Summary on Li-Air batteries

- Charging is challenge for Li-Air batteries
  - Li_2O_2 overpotential
- This can be mitigated with photon-enhanced charging
  - Mediated and unmediated approaches are available
- Stability could be improved using nanostructures
- Current density enhancement is needed for practical applications

Li-Sulfur

Discharge

Advantage

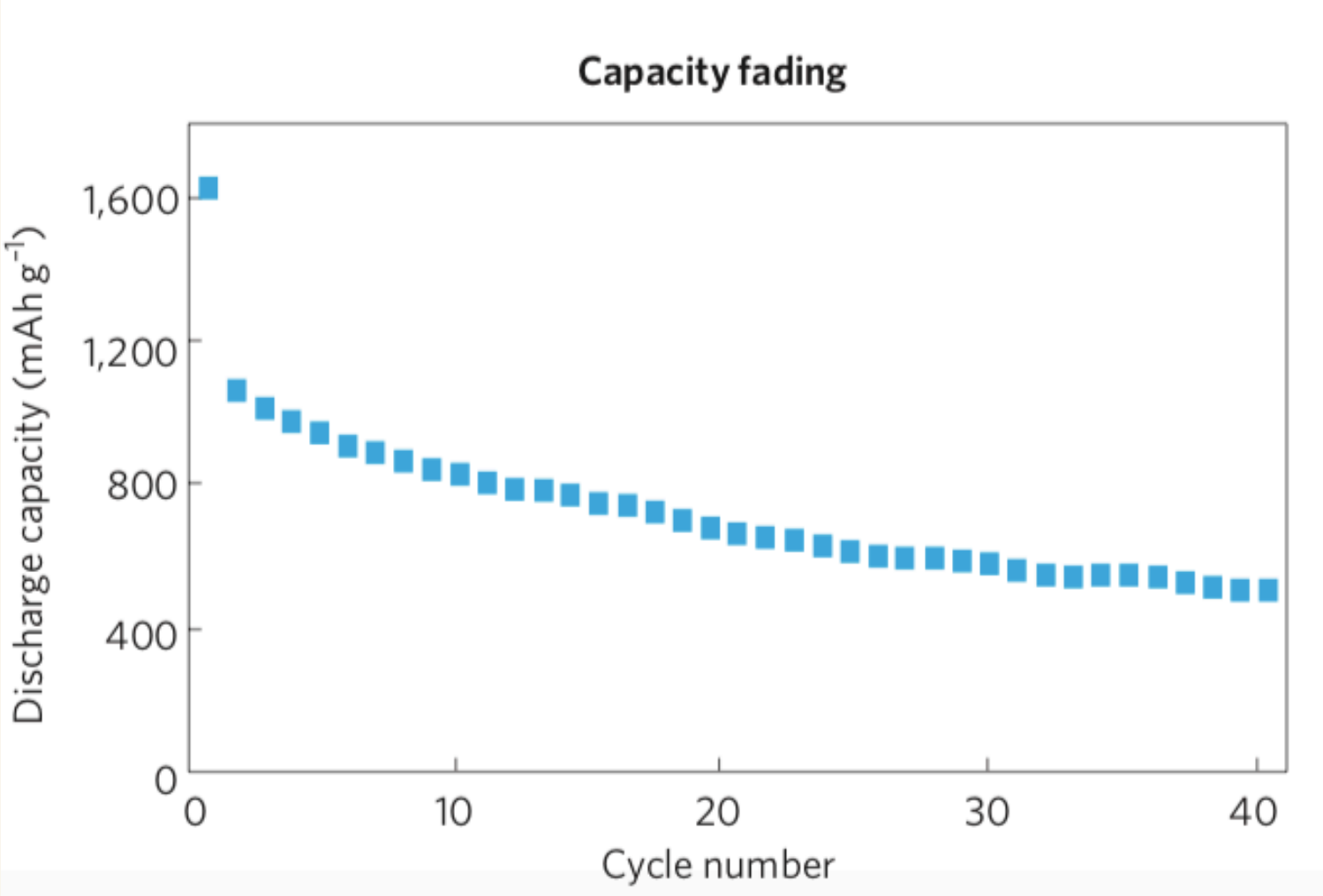
- High specific energy- 2600 Wh/kg
- Cheap, abundant
- Light
- 2 Li for every S(Li_2S)

Disadvantage

- Cycling
- Sulfur conductivity
- Li metal anode stability

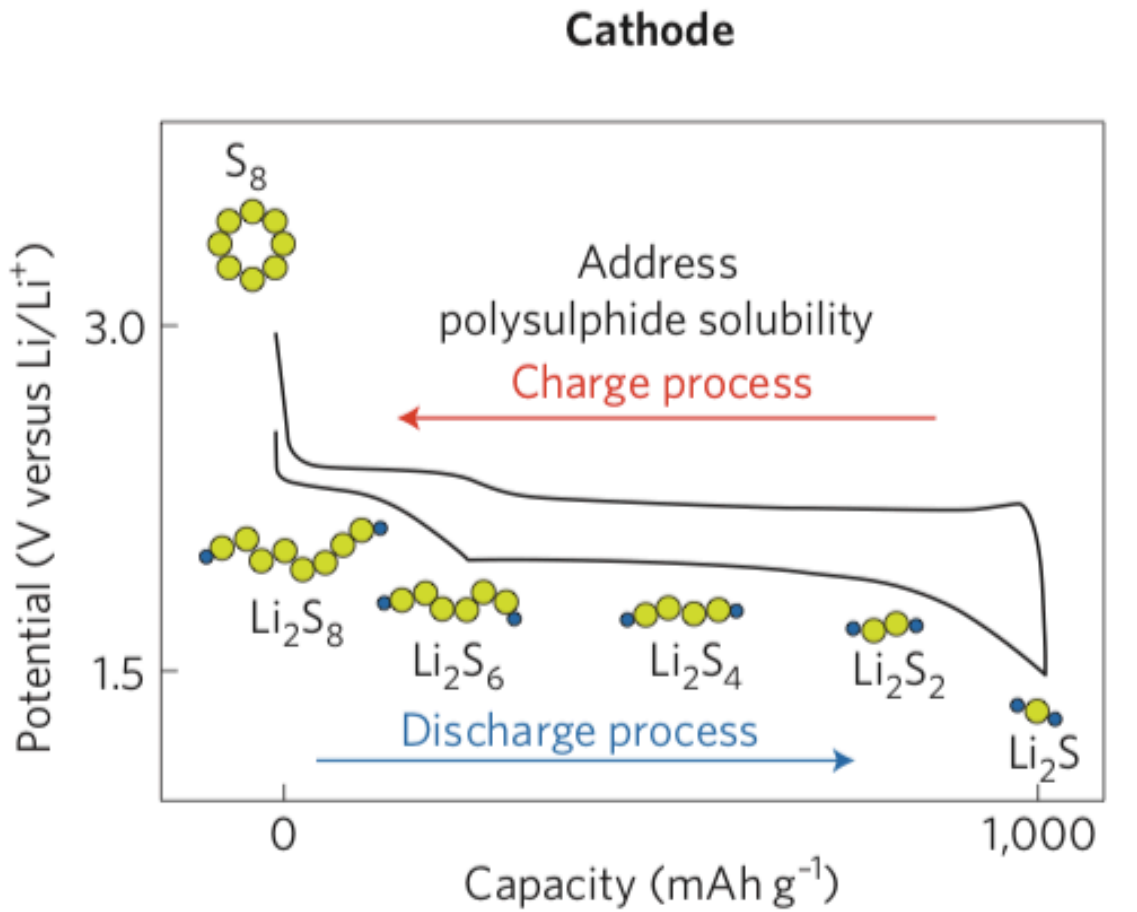
P. G. Bruce et al, Li–O_2 and Li–S batteries with high energy storage," *Nat. Mater.* 2012, *11*, 19-29.

Challenges of Li-S battery



P. G. Bruce et al, Li–O_2 and Li–S batteries with high energy storage," *Nat. Mater.* 2012, *11*, 19-29.

Challenges of Li-S battery



- Formation of insulating Li_2S on the Li anode

P. G. Bruce et al, Li–O_2 and Li–S batteries with high energy storage," *Nat. Mater.* 2012, *11*, 19-29.

Challenges of Li-S battery

Sulfur cathode issue

- Formation of lithium polysulfide (Li_2S_x, $4 \leq x \leq 8$)
  - ↓
- Side reaction with lithium anode
  - ↓ Resulting in :-
- Low energy efficiency
- Self-discharge
- Poor cyclic stability

Lithium anode issue

- Formation of lithium platting
  - ↓
- Irreversible loss of Li^+ - capacity loss
- Degradation of electrodes
- Internal short circuit

Wang, L., Wang, Y., & Xia, Y. (2015) *Energy & Environmental Science*, *8*(5), 1551-1558.

Li_2S as a cathode

Polysulfide I

$$4Li_2S \rightarrow Li_2S_4 + 2Li^+ + 2e^-$$

$$2Li_2S_4 \rightarrow Li_2S_8 + 2Li^+ + 2e^-$$

Polysulfide II

$$Li_2S_8 + 2Li_2S \rightarrow 2Li_2S_2 + Li_2S_6$$

$$2Li_2S_2 + Li_2S_8 \rightarrow 3Li_2S_4$$

$$2Li_2S_4 \rightarrow Li_2S_8 + 2Li^+ + 2e^-$$

$$4Li_2S_6 \rightarrow 3Li_2S_8 + 2Li^+ + 2e^-$$

- The Li_2S cathode must overcome a huge potential (1V) barrier at beginning of delithiation.
- Polysulfide intermediates serving as redox mediators to facilitate the direct electrochemical oxidization of Li_2S.

Wang, L., Wang, Y., & Xia, Y. *Energy & Environmental Science*, **2015**, *8*, 1551-1558.

Battery basics

Solvation

Lecture 4

Richard M. Laine, Eleni Temeche, Xinyu Zhang, Lisa Buch,

Taylor Brandt, Philyoung Kim

Depts of Materials Sci. & Eng. And Macromolecular Sci. & Eng.

University of Michigan

Content

- Diffusion in liquid electrolytes
- How to understand activity
- Diffusion in liquid, polymer and solid, electrolytes
- Summary

In liquid electrolytes Li^+ diffusion governed by:

- Chemical potential
- Solvent polarity (dielectric constant)
- Viscosity
- Solvation sphere
- Temperature
- Counterions

Mechanism of ionic transport in liquids

- Li^+ transport in liquids involves diffusion of solvated Li^+.
- $\sigma_{Li}{}^+$ in aprotic electrolytes controlled/enhanced by:
  - Increasing salt/ion dissociation- e.g. *by increasing dielectric constants*
  - Promoting mobility of solvated *ions*-*lowering solvent viscosity*

$$D_o = \frac{k_B T}{6\pi\eta Ro}$$

η – Viscosity

R_o – Radius of solvating cation

k_B - Boltzmann constant

D_o - Diffusion coefficient

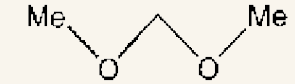
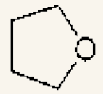
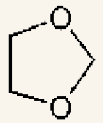
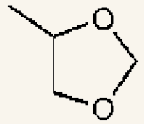
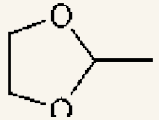
J.C. Bachman et al Chem. Rev. (2016).

Traditional liquid electrolytes

- Are low viscosity, polar liquids capable of dissolving M^{+}/M^{2+} and anions.
- Operational windows from -40 °C to ≈ 60 °C.
- Typical Li^{+} diffusion rates
- Low flammability

K. Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” *Chem. Rev*. **2004**, 104, 4303−4417

Traditional liquid electrolytes

Solvent	Structure	M. Wt	T_m/ °C	T_b/ °C	η/cP 25 °C	ε 25 °C	Dipole Moment/debye	T_f/ °C	d/gcm^{-3}, 25 °C
DMM		76	-105	41	0.33	2.7	2.41	–17	0.86
DME		90	-58	84	0.46	7.2	1.15	0	0.86
DEE		118	-74	121				20	0.84
THF		72	-109	66	0.46	7.4	1.7	-17	0.88
2-Me-THF		86	-137	80	0.47	6.2	1.6	-11	0.85
1,3-DL		74	-95	78	0.59	7.1	1.25	1	1.06
4-Me-1,3-DL		88	-125	85	0.60	6.8	1.43	-2	0.983
2-Me-1,3-DL		88			0.54	4.39			

K. Xu, “Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries,” *Chem. Rev*. **2004**, 104, 4303−4417

What creates the electrochemical driving force that allows batteries to function?

- Chemical driving force across battery is Δ in chemical potential between two electrodes.
  - Expressed as the standard Gibbs free energy/mol of reaction.
- Basically $\Delta G_{free\ energy}$ of products and reactants that occur at neutral electrodes.

$$\Delta G_{reaction} = -zFE = \Delta\mu$$

Z = the charge number of mobile ion

F = Faraday's constant 96,500 coulomb/mol

E = Voltage between electrodes

$\Delta\mu$ = chemical potential – ability to be oxidized/reduced

How to understand activity

The chemical potential of a system is $\mu_i = \partial G_j / \partial n_i = \Delta Gj$

mole fraction *n* of each phase *j* contributing to free energy

Free energy and chemical potential change as cell discharges charges

Moreover, chemical potential of each component *j* is not unity for that mole fraction.
basically, *μ* depends on activity of the species *j:*

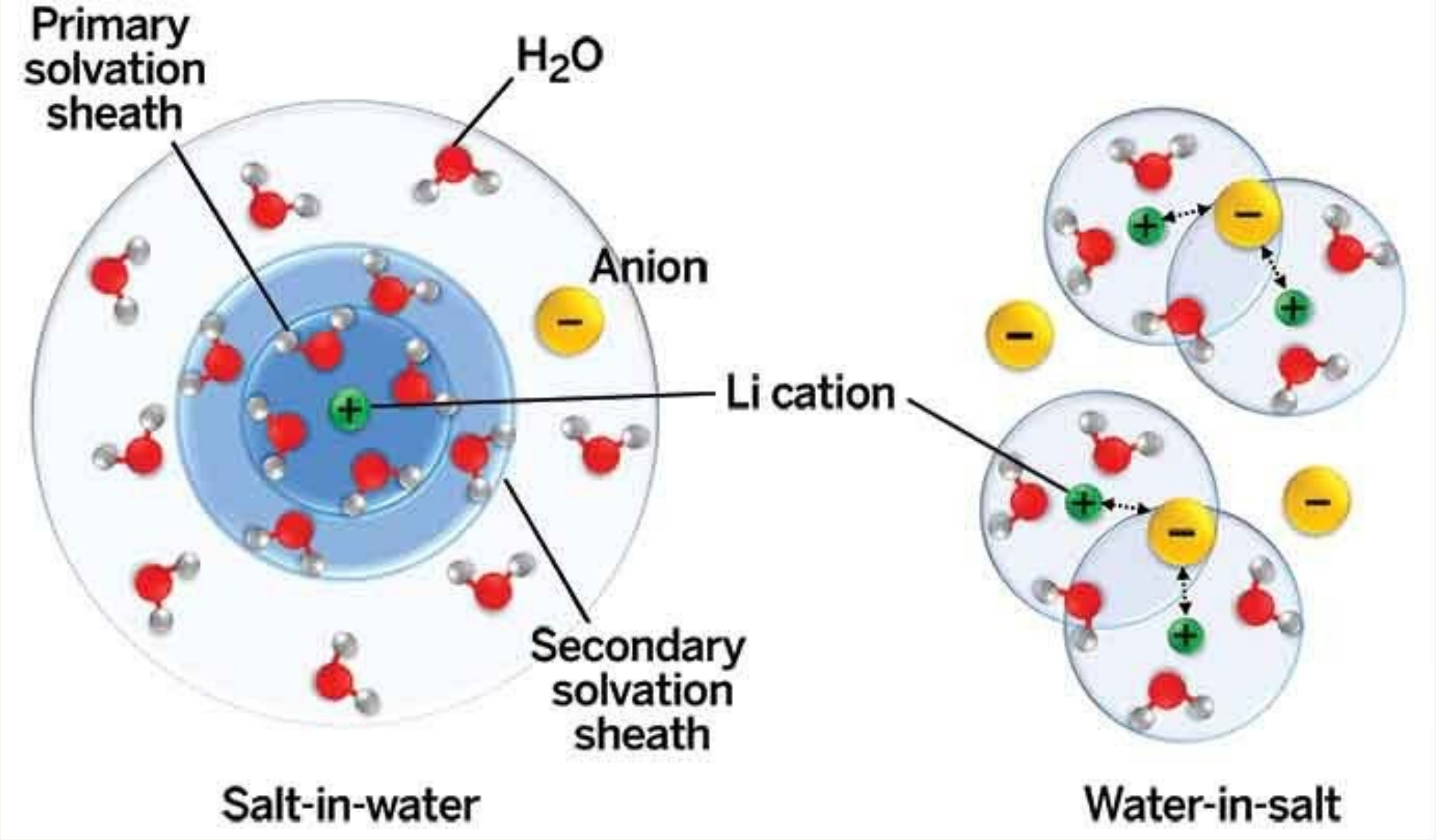
$$\mu_i = \mu_i^\circ + RT \ln a_i$$ *a is activity, what is it?*

In order to understand why activity is not = 1, we can look at Li^+ solvation in liquid electrolytes

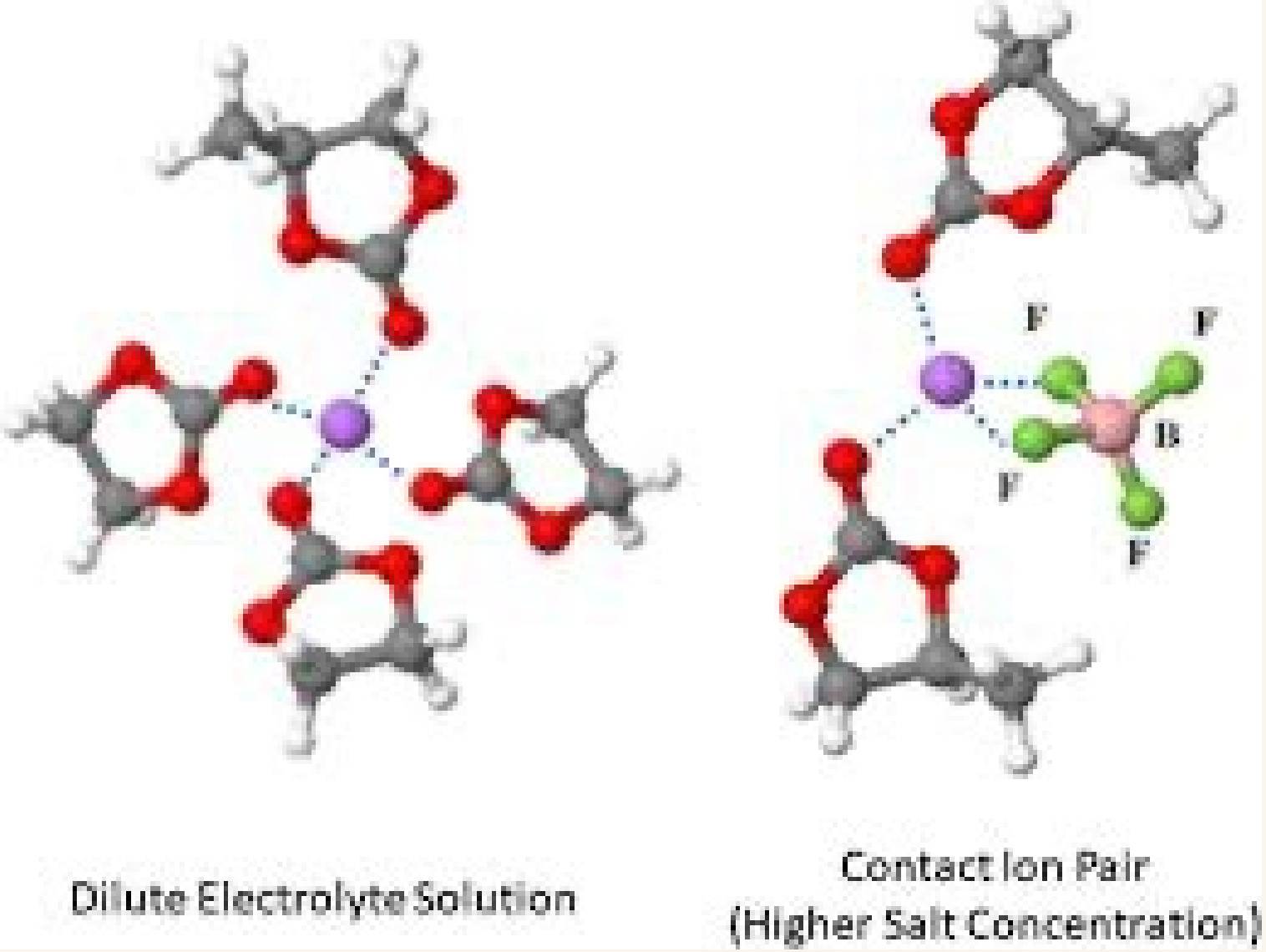
Concentration vs activity

- In liquid electrolytes Li^+ diffusion (activity) is governed by:
  - Solvent polarity (dielectric constant)
  - Viscosity
  - Solvation sphere
  - Temperature
  - Counterion

Solvation sphere—not just cation that moves

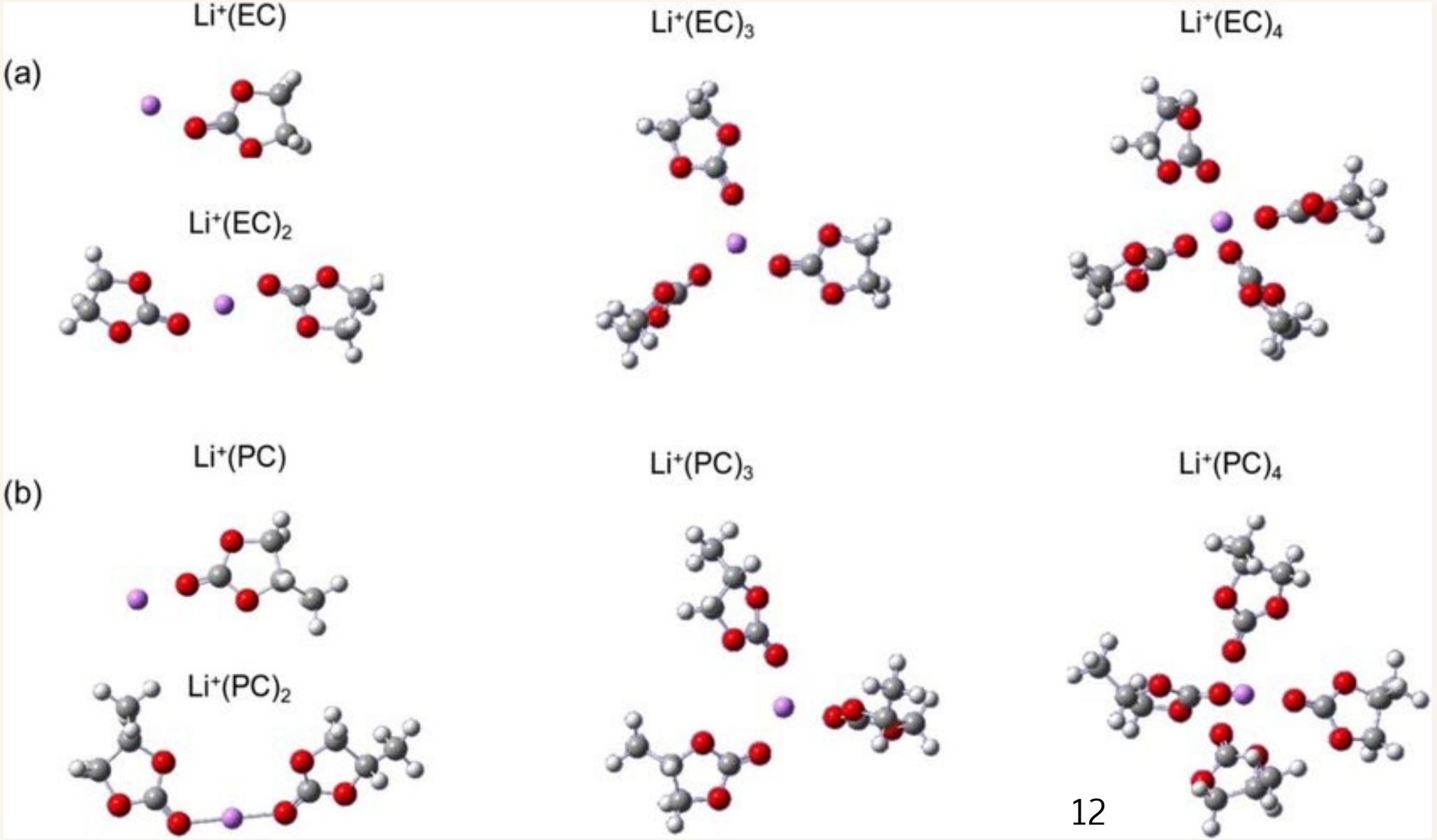


Solvation sphere vs. concentration

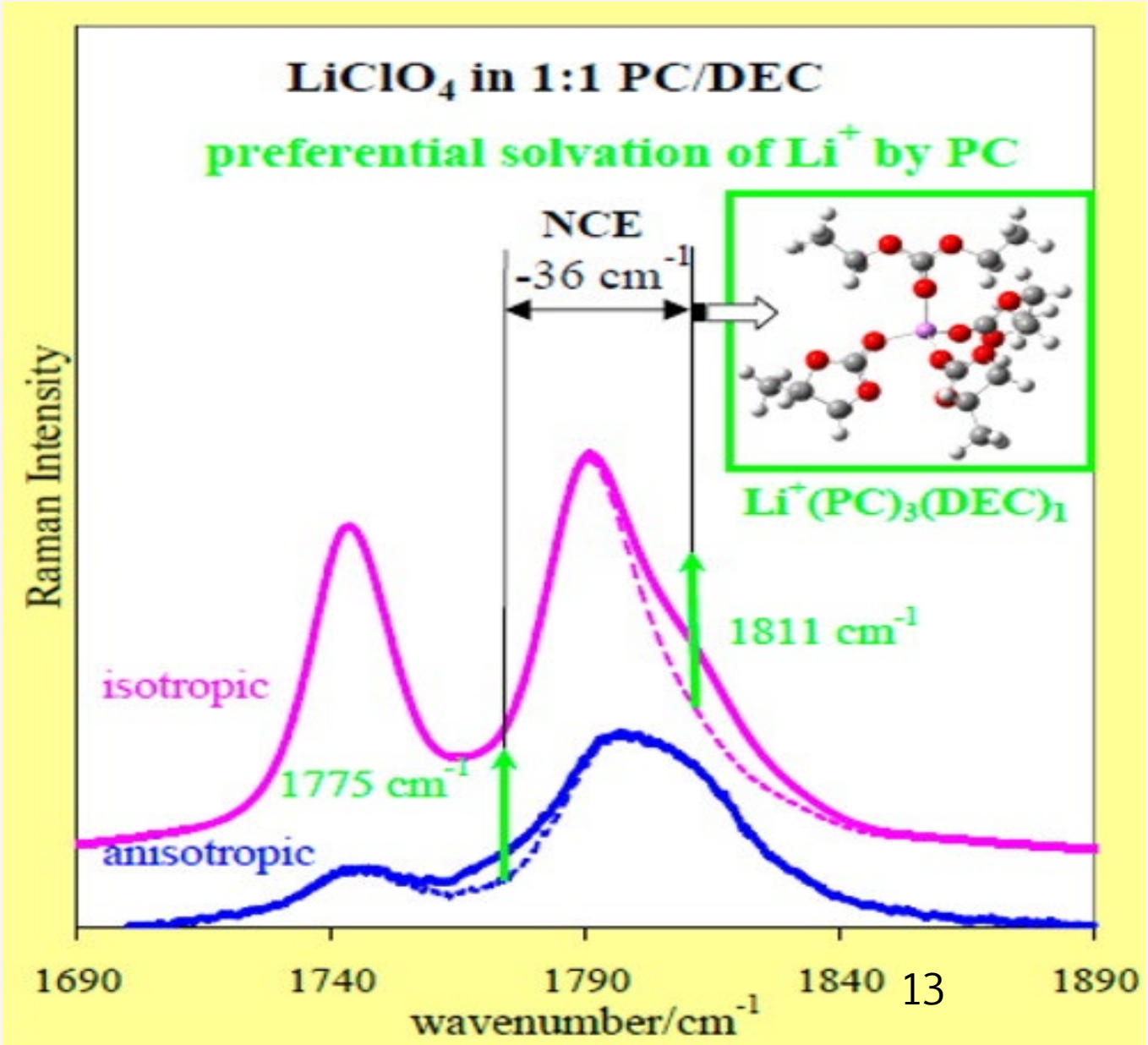


EC = ethylene carbonate

Activity as a function of solvation sphere

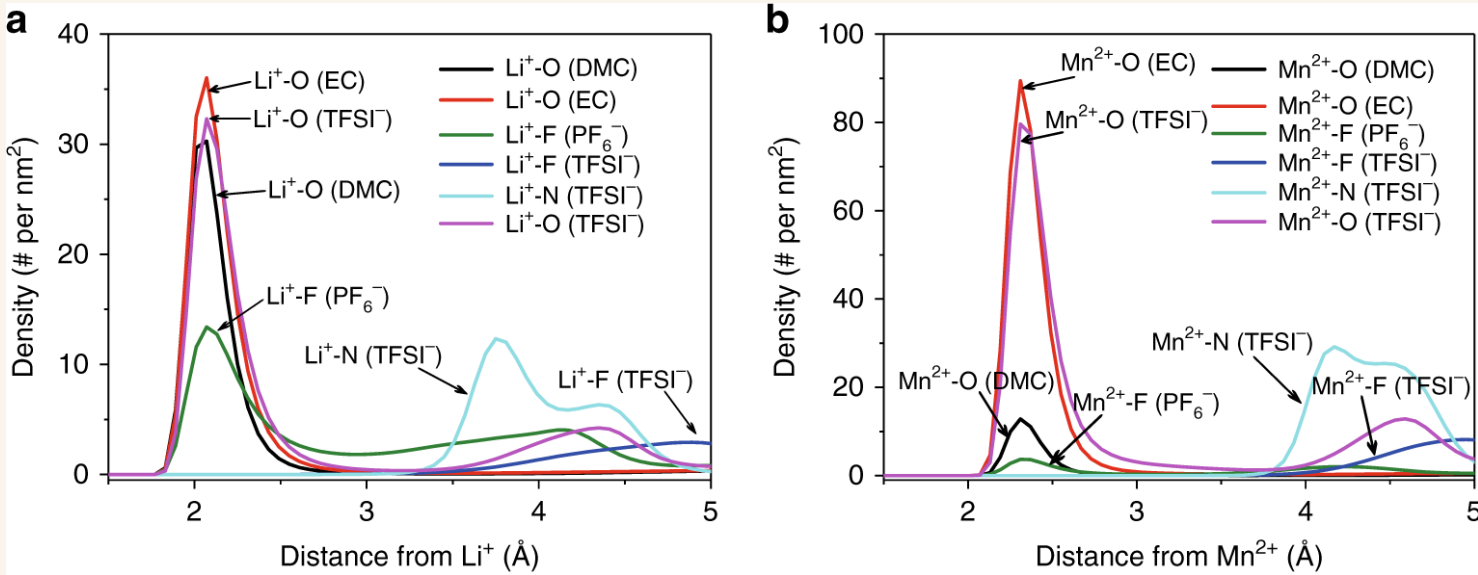


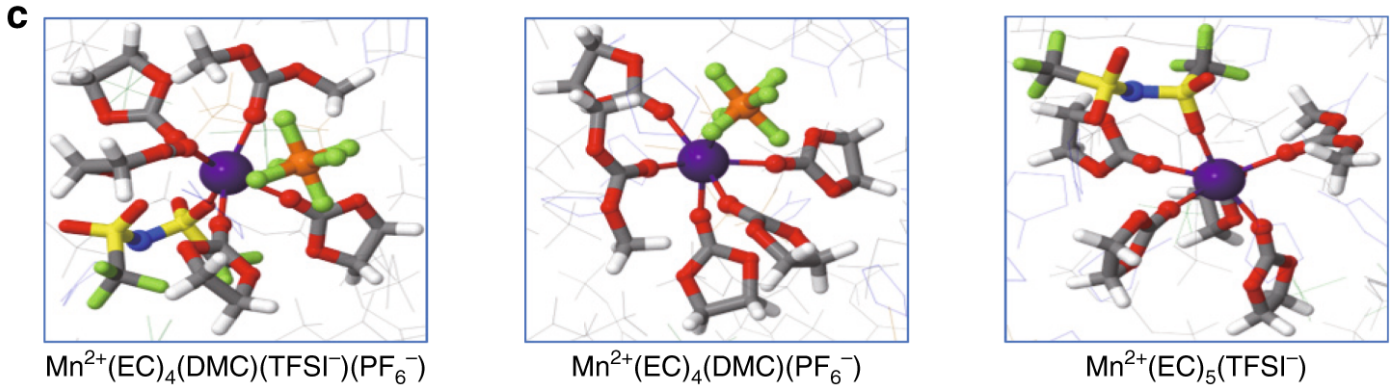
Solvation sphere probed using Raman

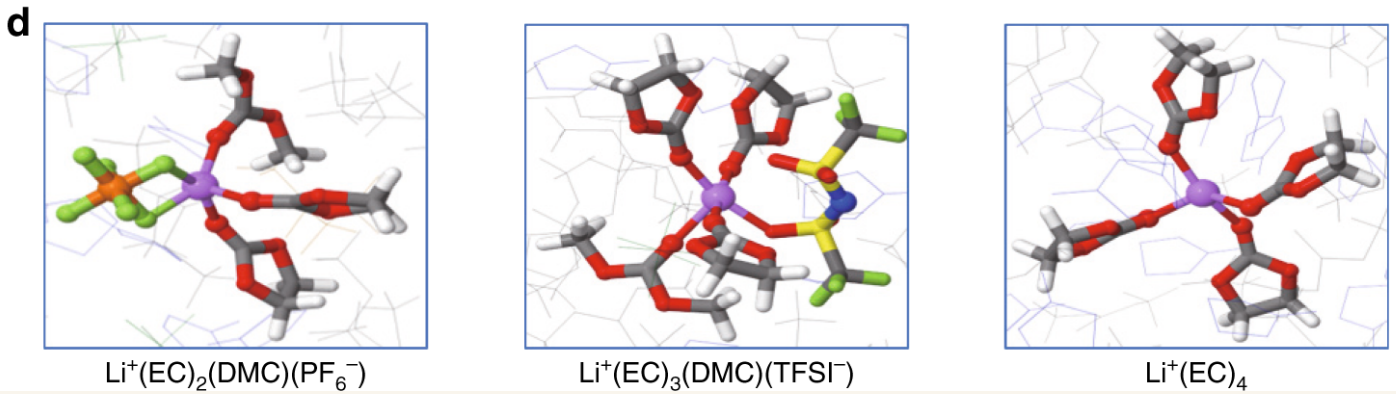


Activity as a function of solvation sphere

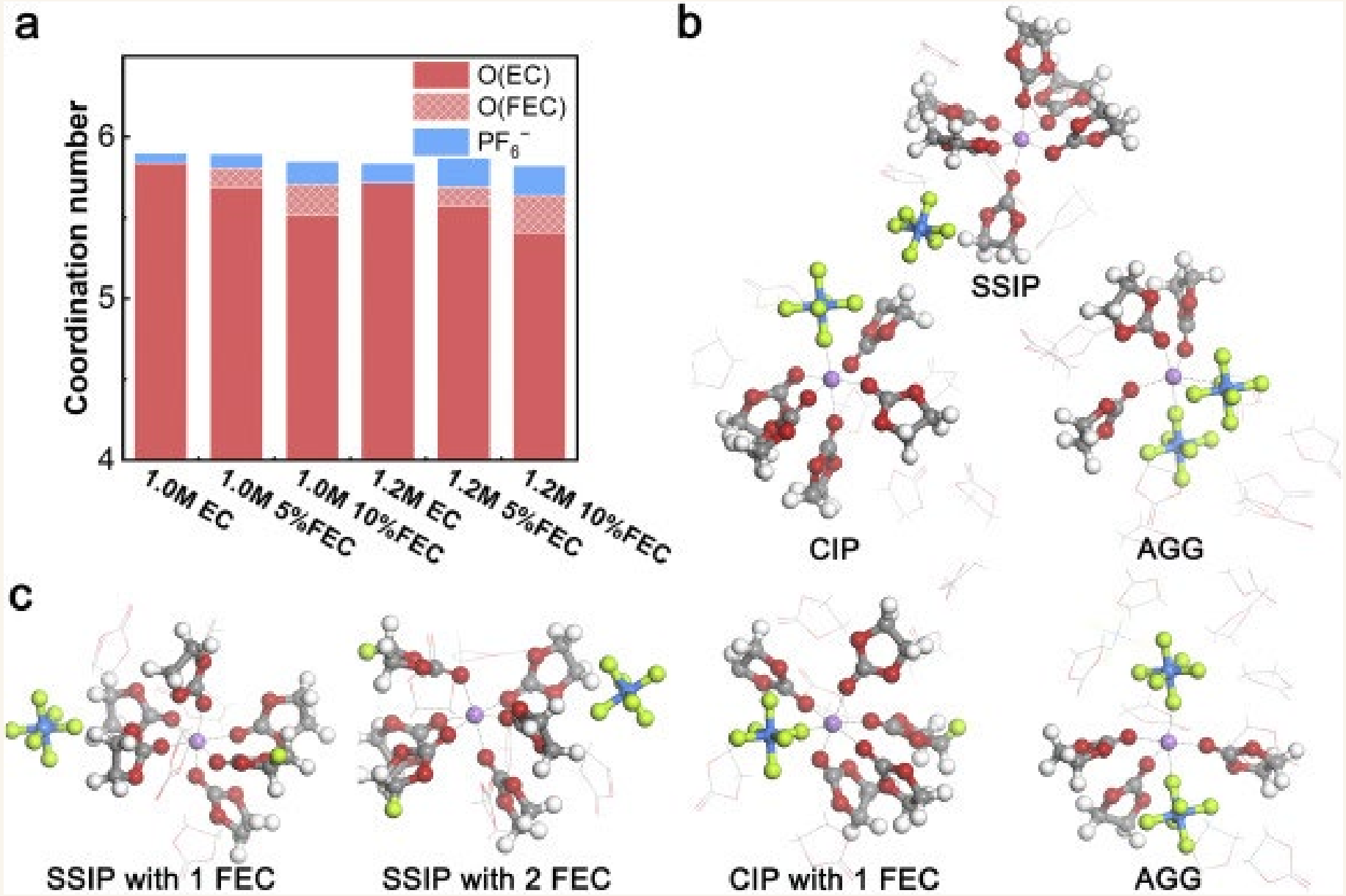
and counterions







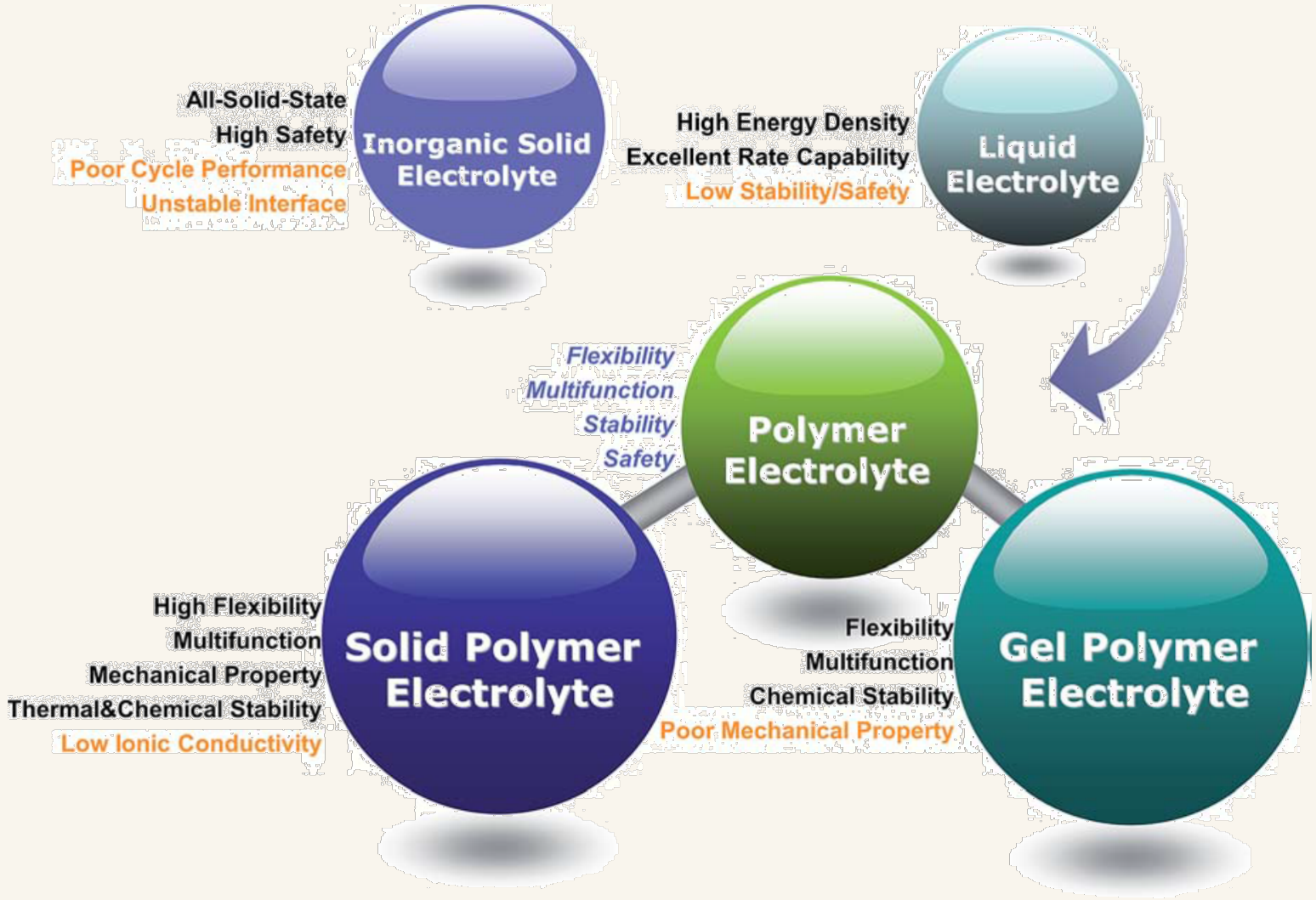
Influence of FEC



Ionic conduction mechanism in polymer electrolytes

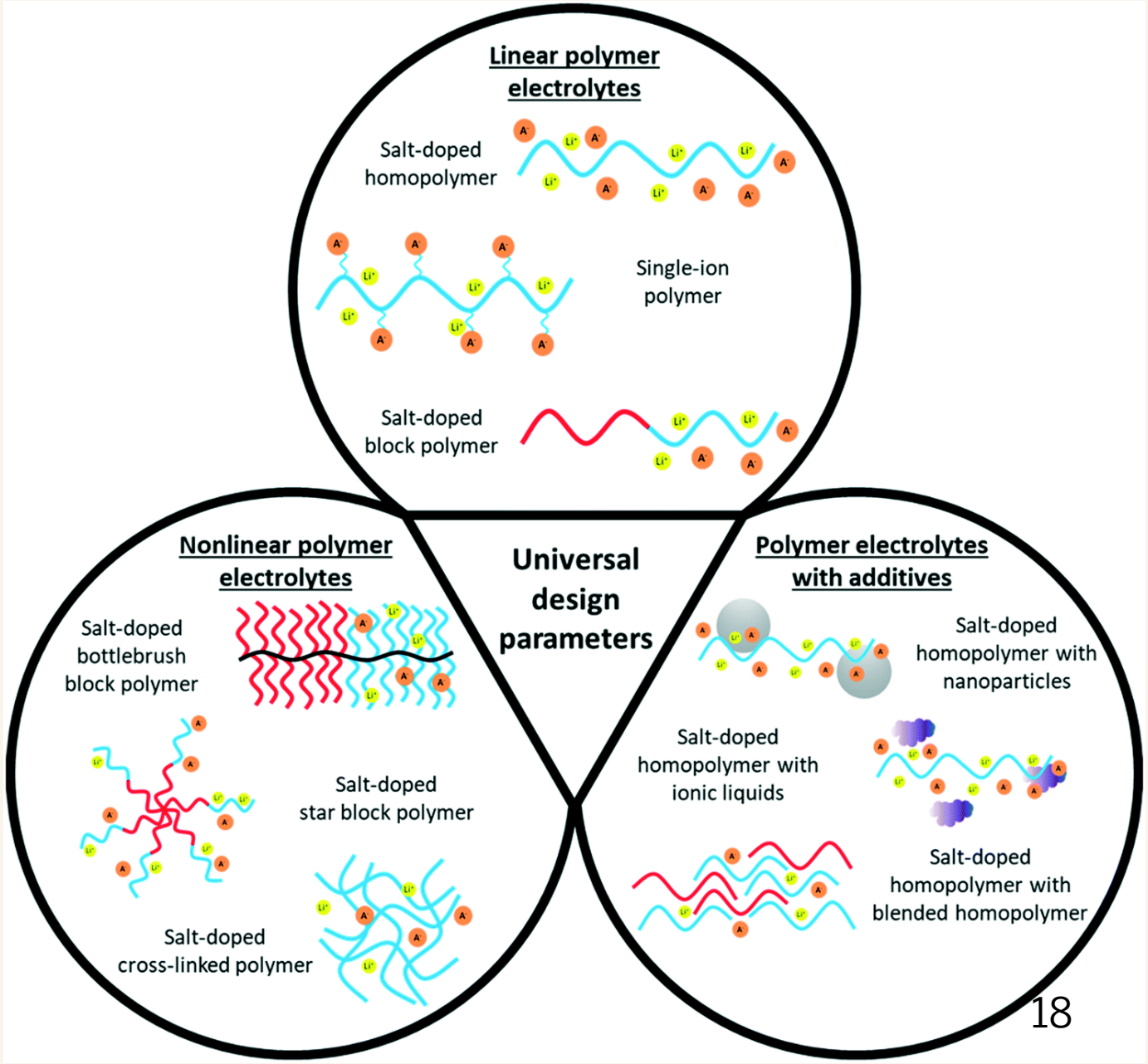
Polymer electrolytes

- Multifunctional
- Flexible
- Good mechanical properties
- Moderate thermal stability
- Safe

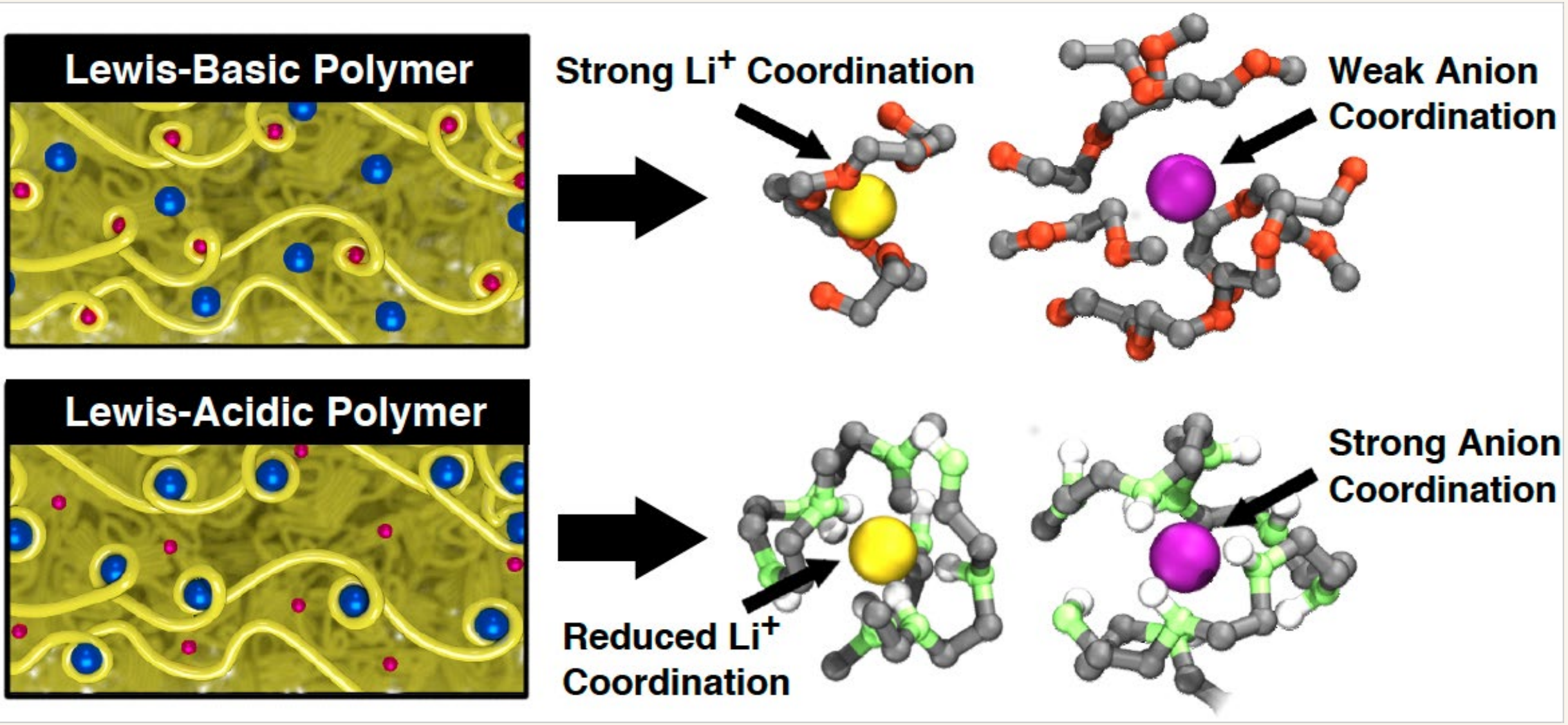


Z. Xue, et al., *J. Mater. Chem. A* **2015**, 3, 19218–19253

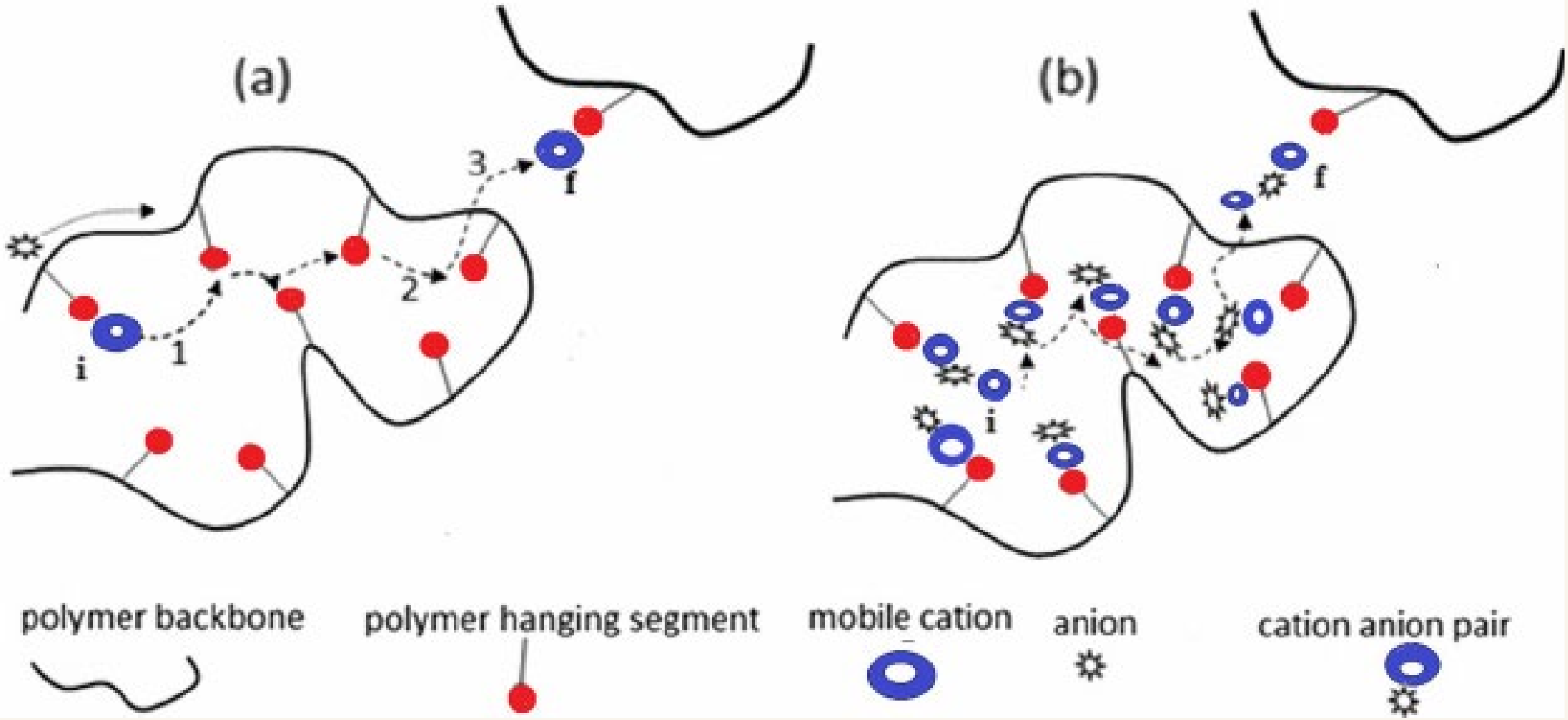
Solvation sphere w/polymers



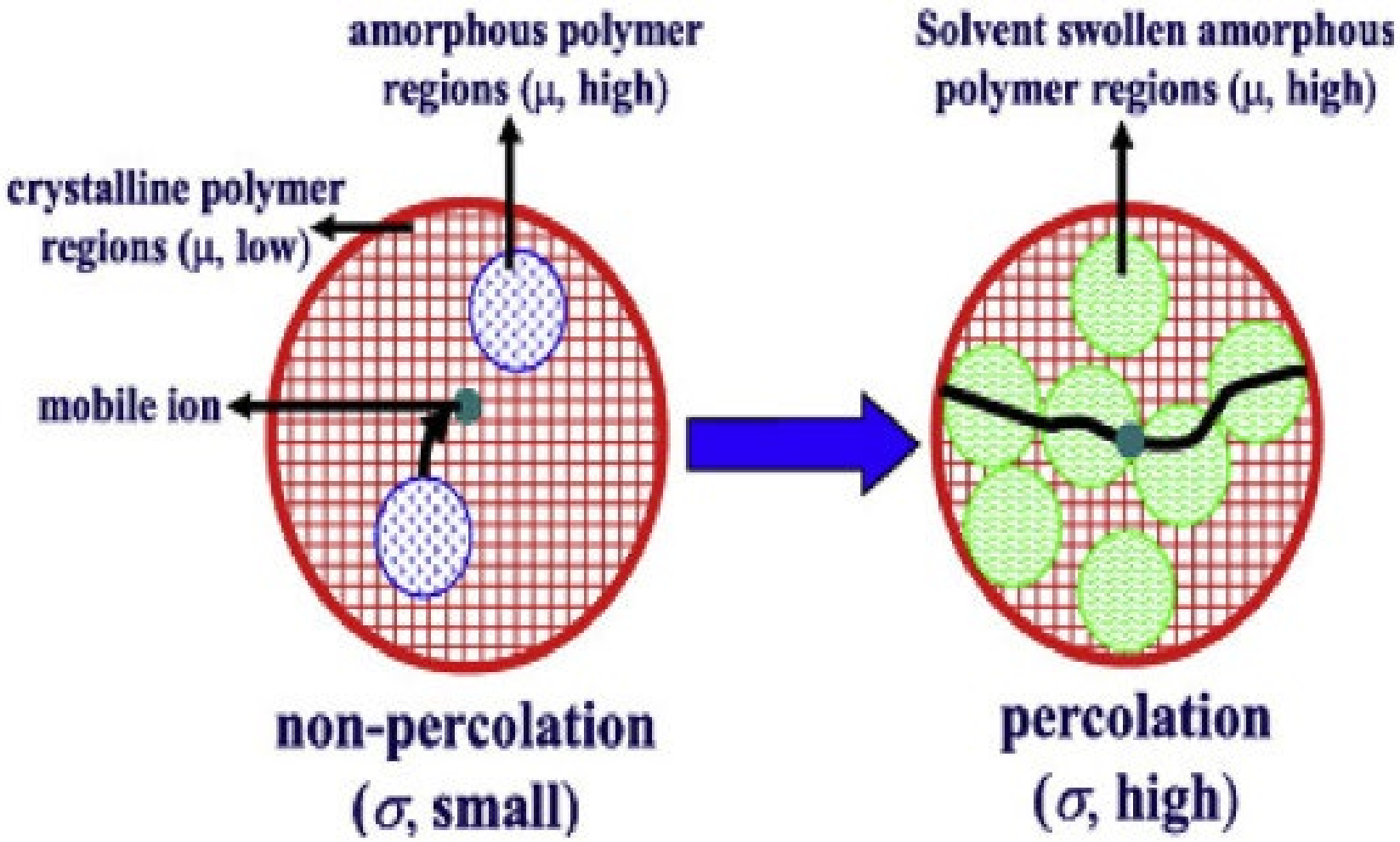
Solvation sphere w/polymers



Solvation sphere w/polymers



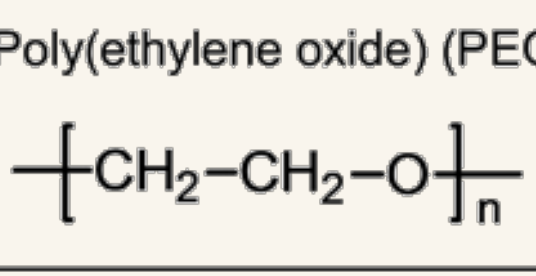
Solvation sphere w/polymers



PEO-based polymer electrolytes

- Flexible EO segments and ether oxygens:
- Strong donor character
- Readily complexes metal salts
- Commercially available, low cost

Matrix: Poly(ethylene oxide) (PEO)

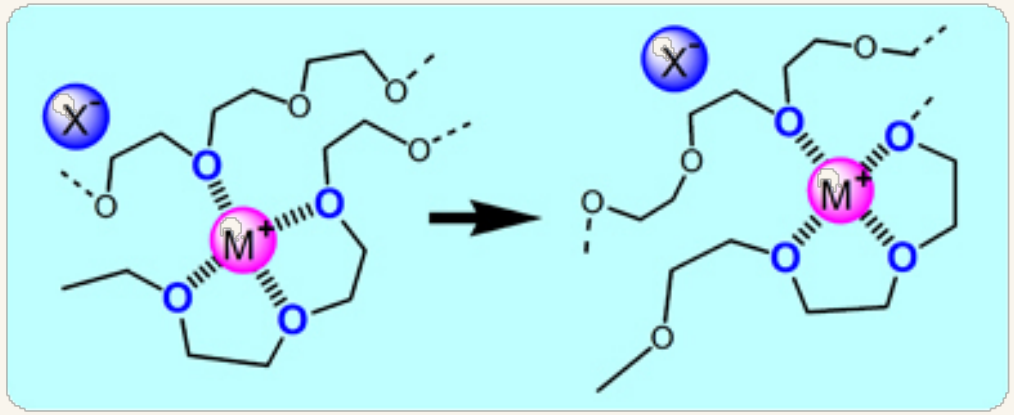


+

Ion source: Alkali metal salts (M^+X^-)

M^+ : Li^+, Na^+, K^+, etc.

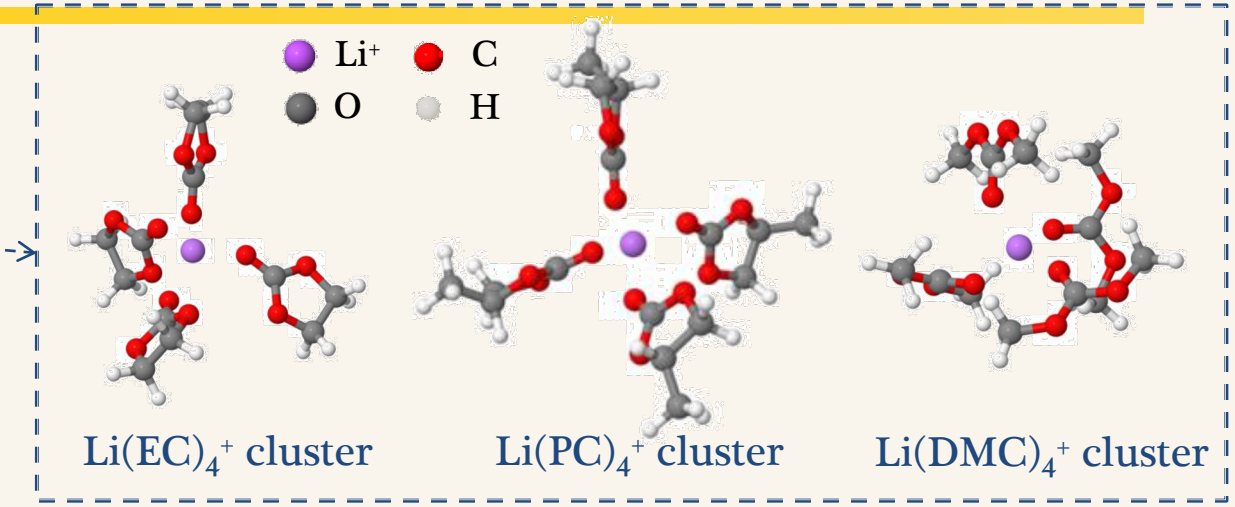
X^- : $(CF_3SO_2)_2N^-$, ClO_4^-, PF_6^-, etc.

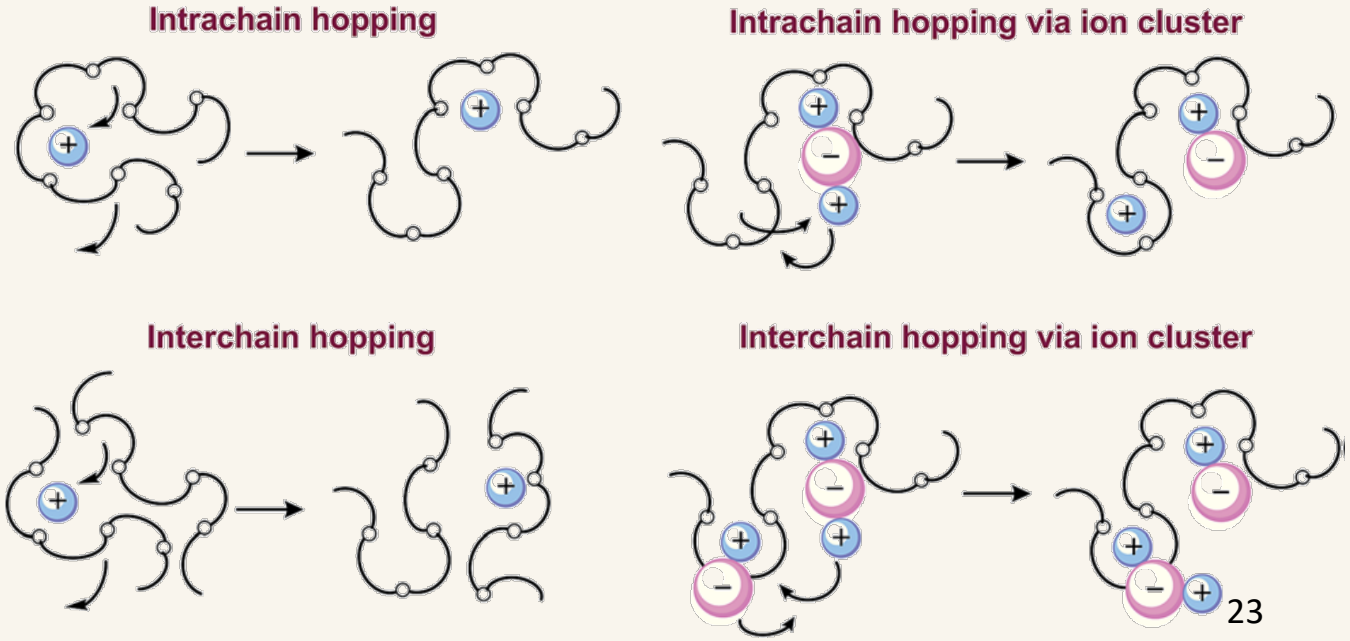


Y. Tominaga, Y. Izumi, G. H. Kwak, S. Asai and M. Sumita, *Macromolecules*, 2003, **36**, 8766–8772.

M^+ Ion diffusion mechanism in PEO

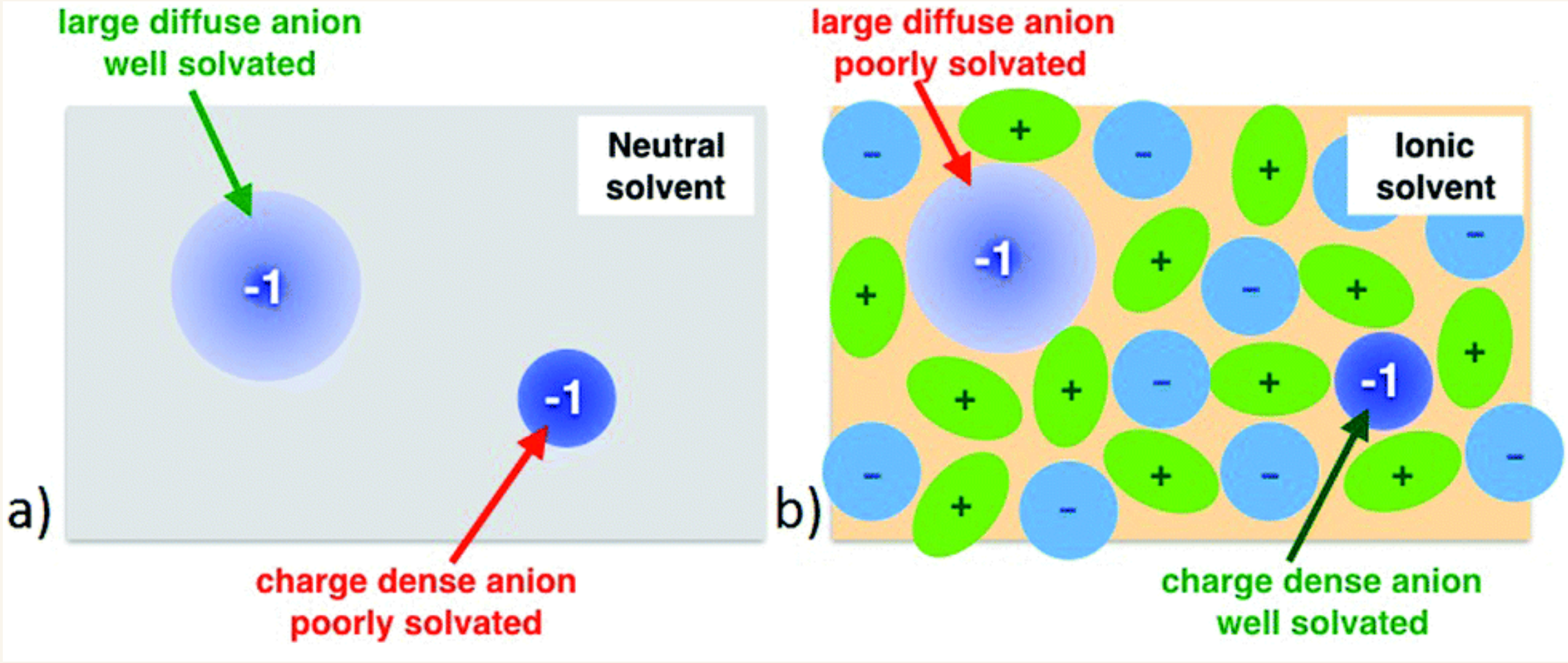
- M^+ coordinated by ether oxygens:
  - Similar to M^+ complexation by organic carbonates in liquid electrolytes.
- Ion transport occurs by breaking/forming M-O electrostatic interaction, either intrachain or interchain looping.
- Continuous segmental motion results in a long-range movement of M^+.



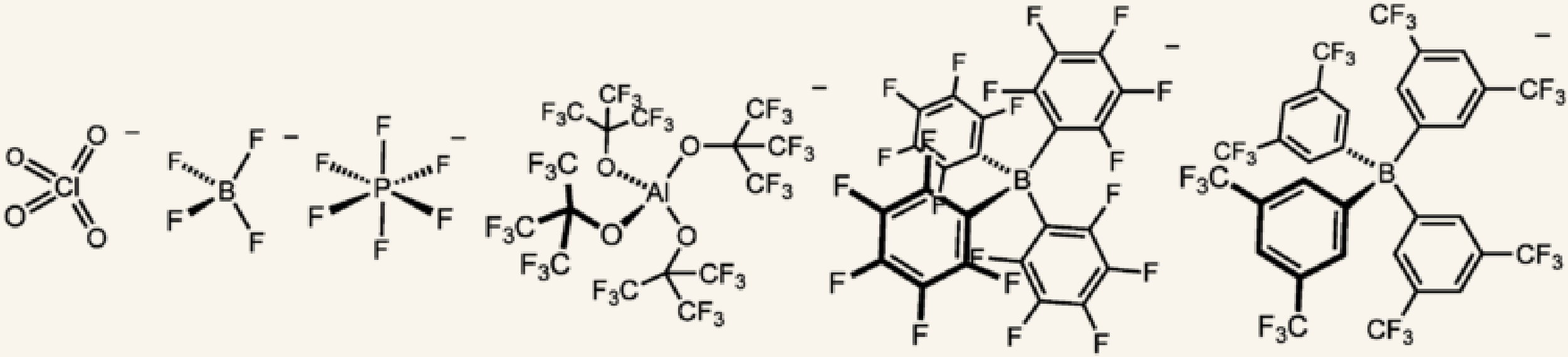


Reference 1,11

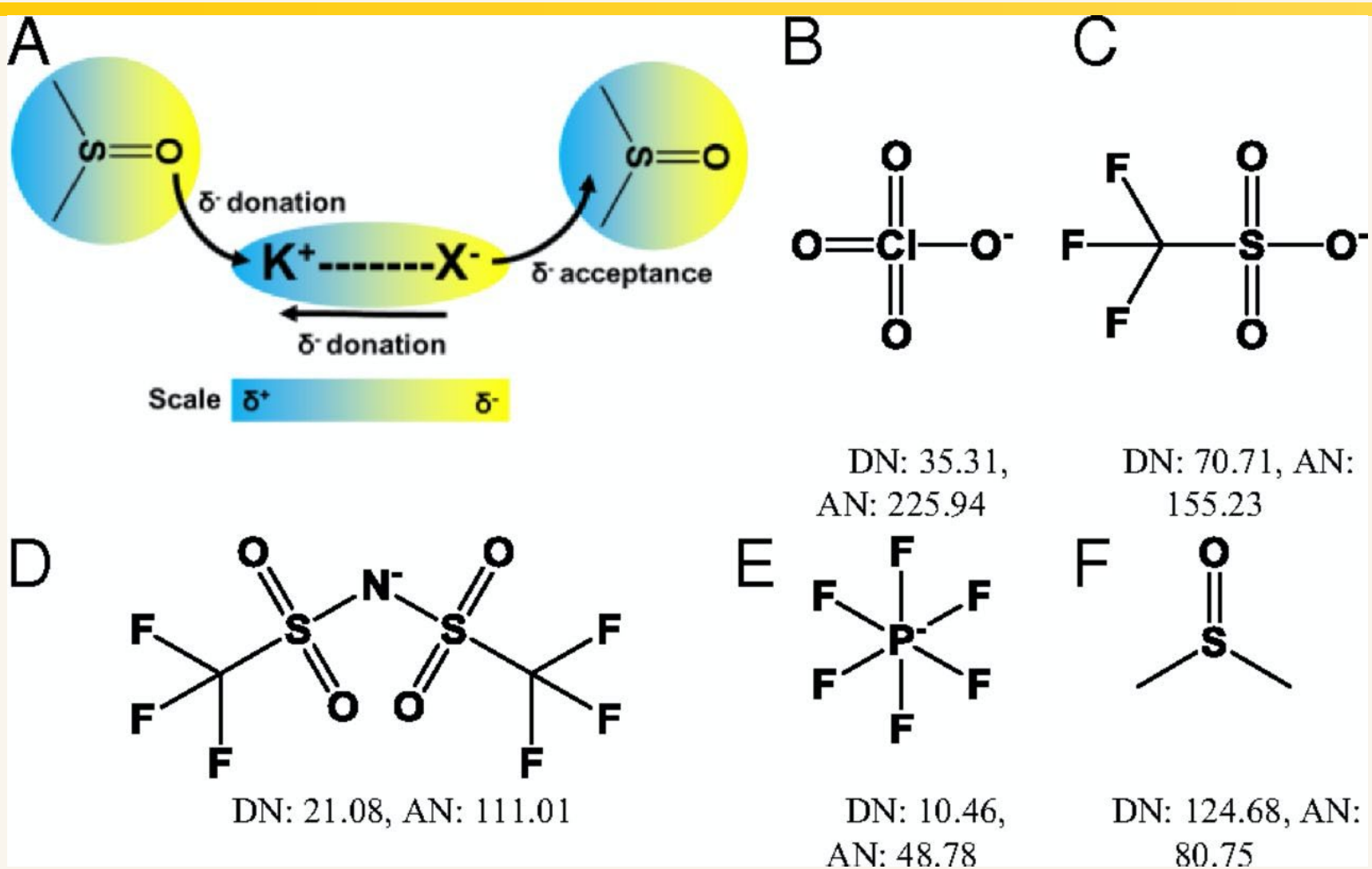
Anions


large diffuse anion
well solvated
Neutral
solvent
-1
-1
a)
charge dense anion
poorly solvated
large diffuse anion
poorly solvated
Ionic
solvent
-1
-1
b)
charge dense anion
well solvated

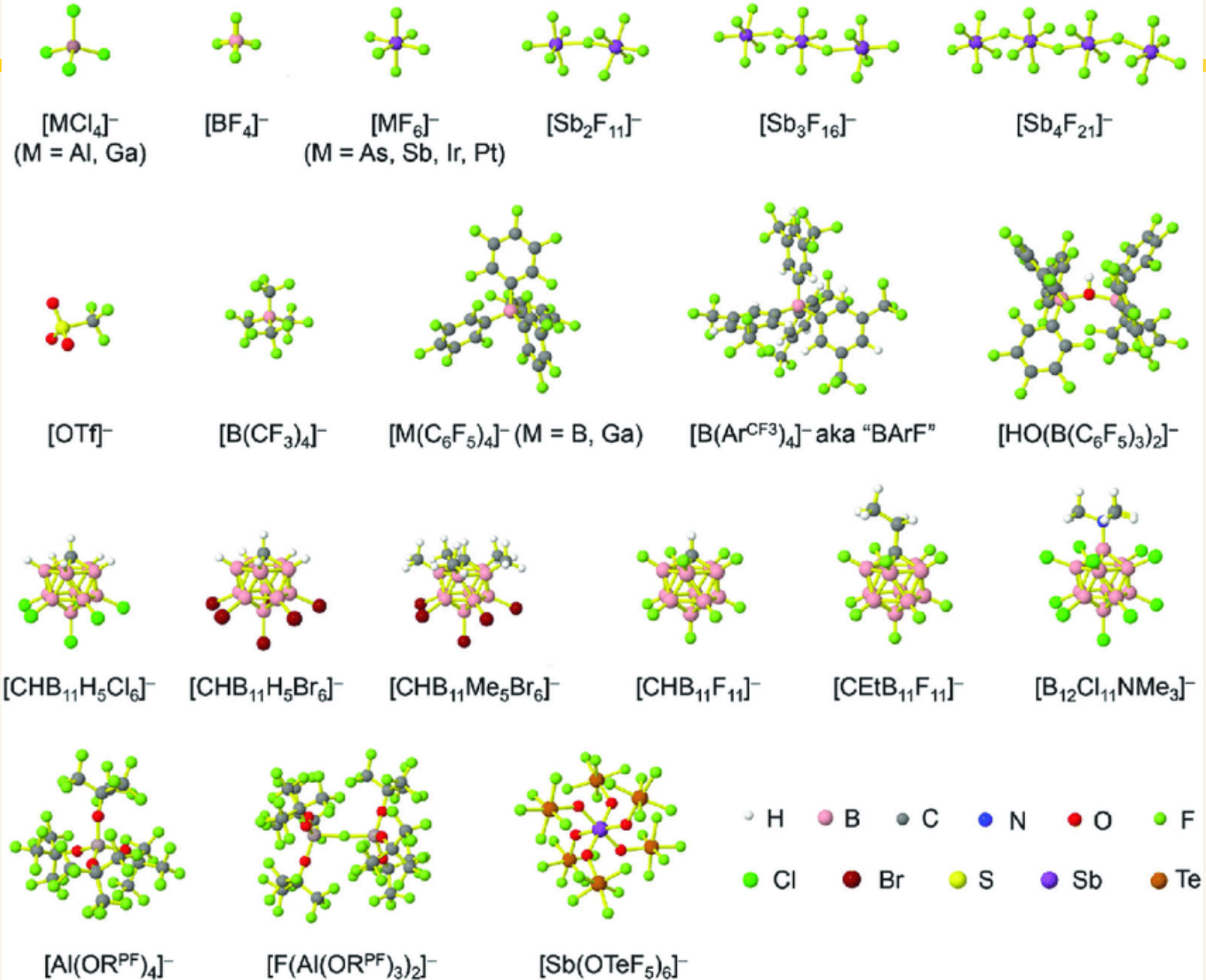
Anions



Diffuse anions—poorly coordinating

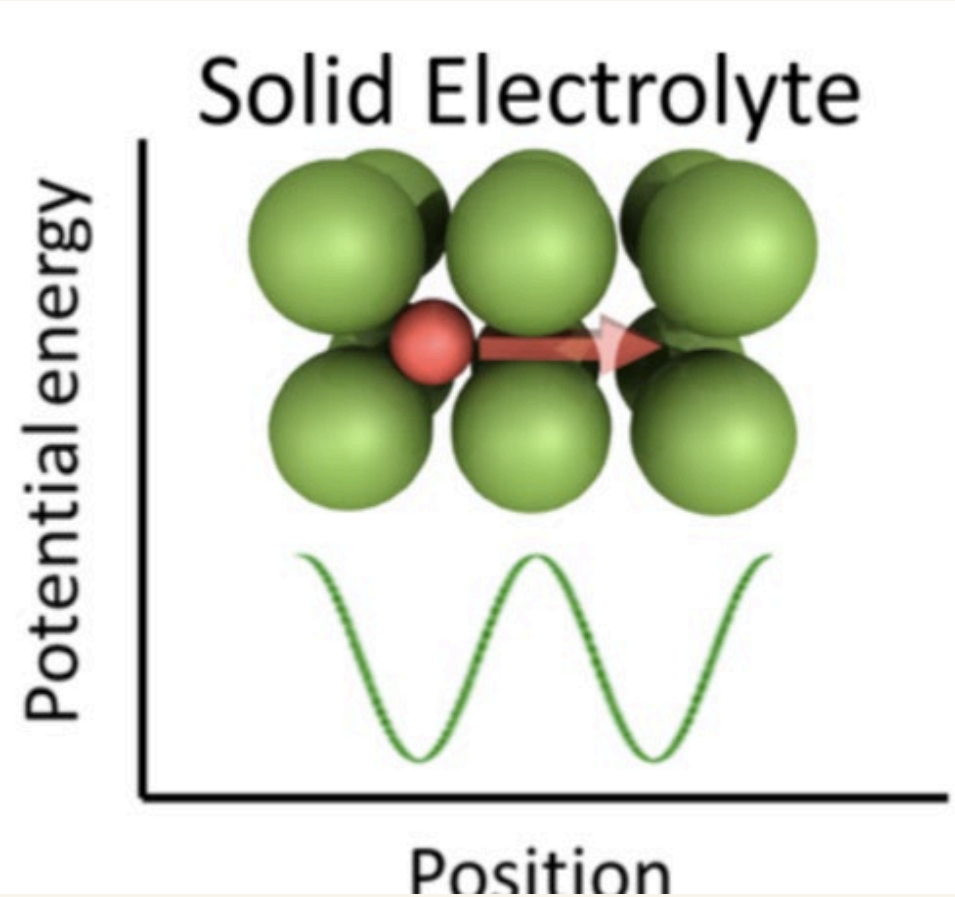


Diffuse anions—poorly coordinating



Ionic conduction mechanism in solid electrolytes

Mechanism of ionic transport in solids

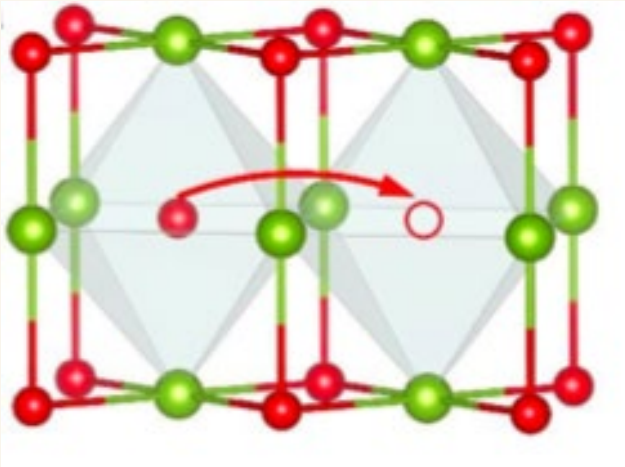


- Relies on concentration and distribution of defects
  - E.g. Schottky and Frenkel point defects
- Mobile species *must pass through periodic bottlenecks*
- Low migration energy (E_m) leads to high ionic mobility

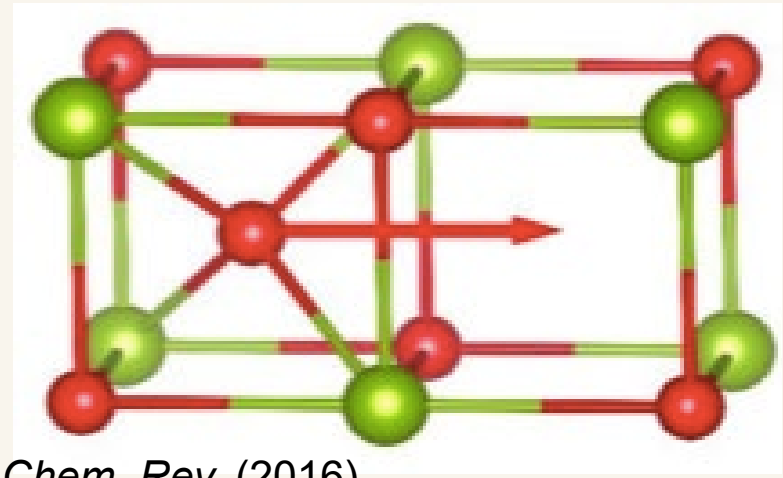
J.C. Bachman et al *Chem. Rev.* (2016).
A. Manthiram et al. *Nat. Rev. Mater.* (2017).

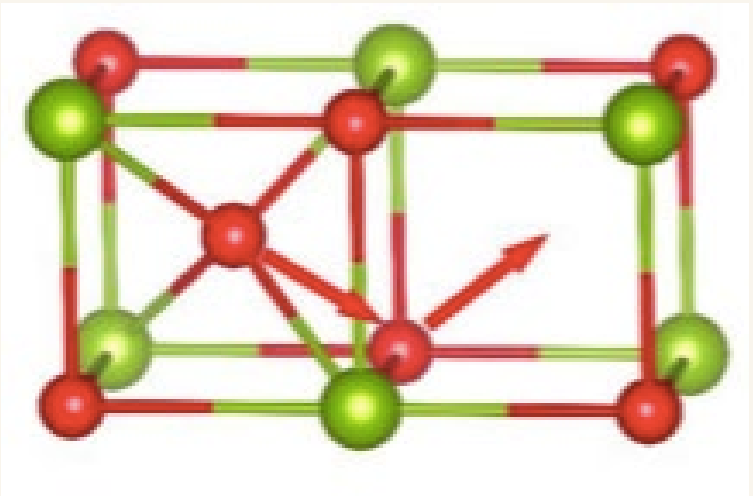
Ion migration within a crystalline solid

- Schottky defects - random jumps between vacant sites



- Frenkel defects - direct interstitial jumps and migration

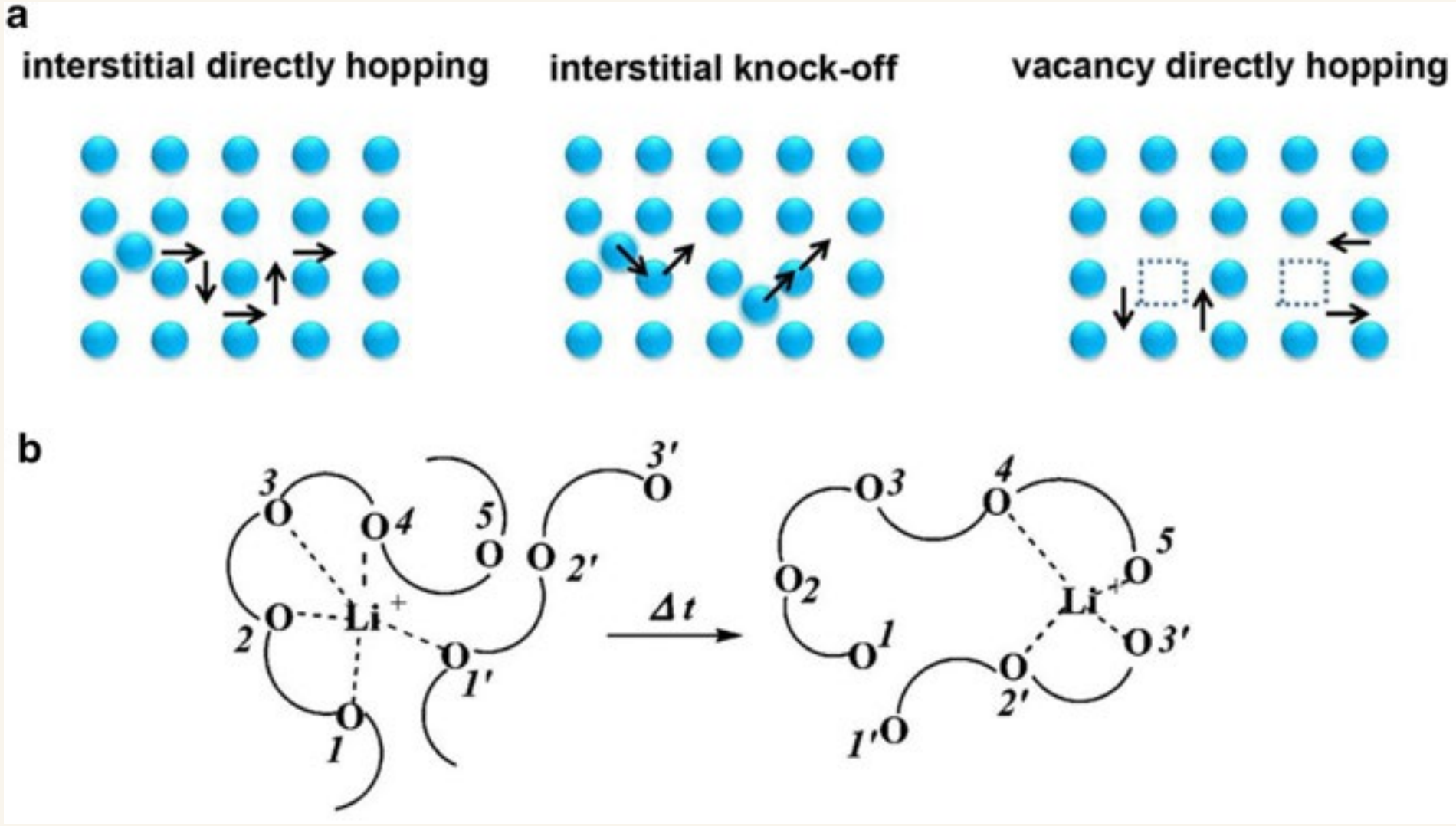




J.C. Bachman et al *Chem. Rev.* (2016).

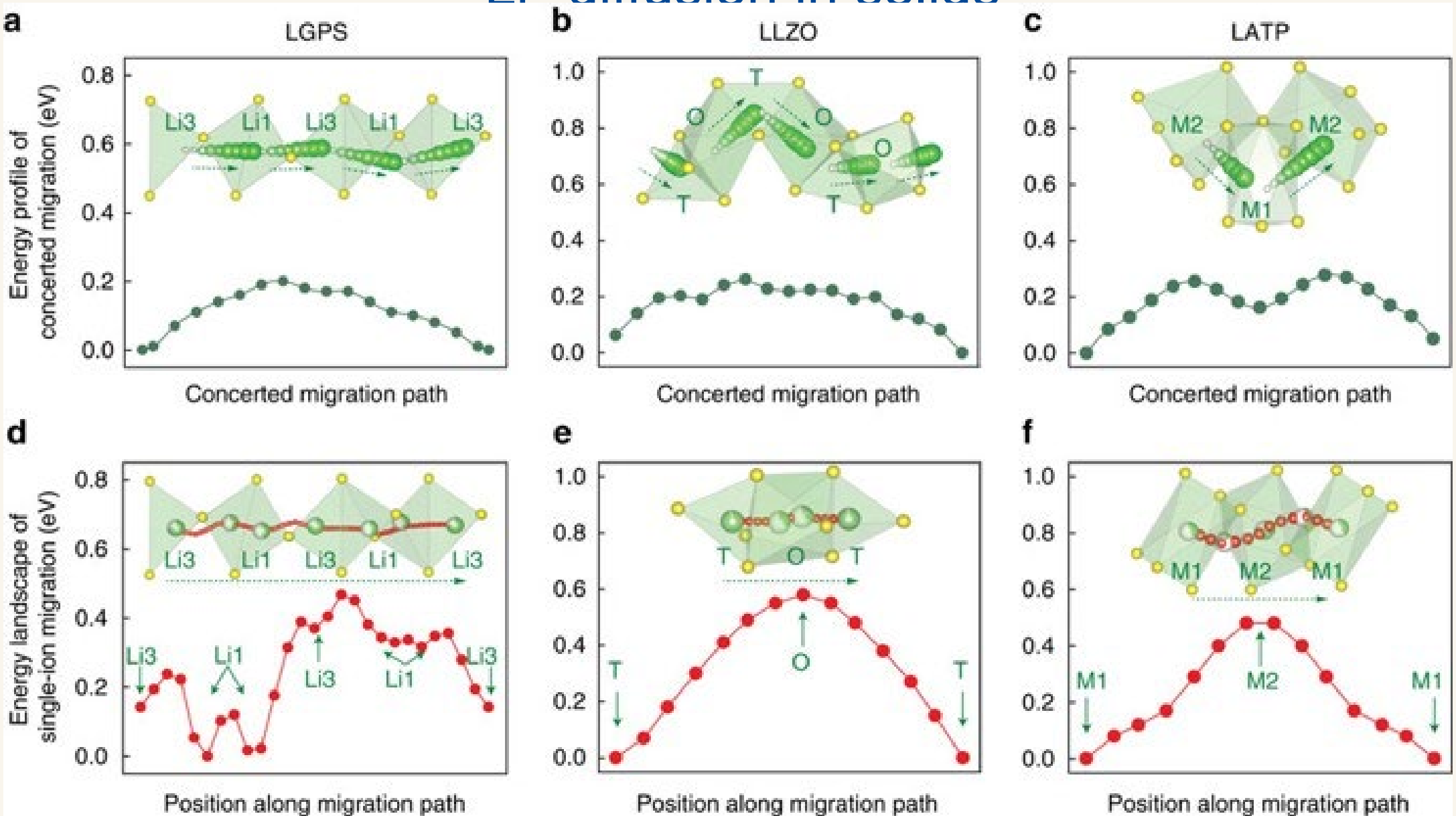
Activity in solid electrolytes

Li^+ diffusion in solids



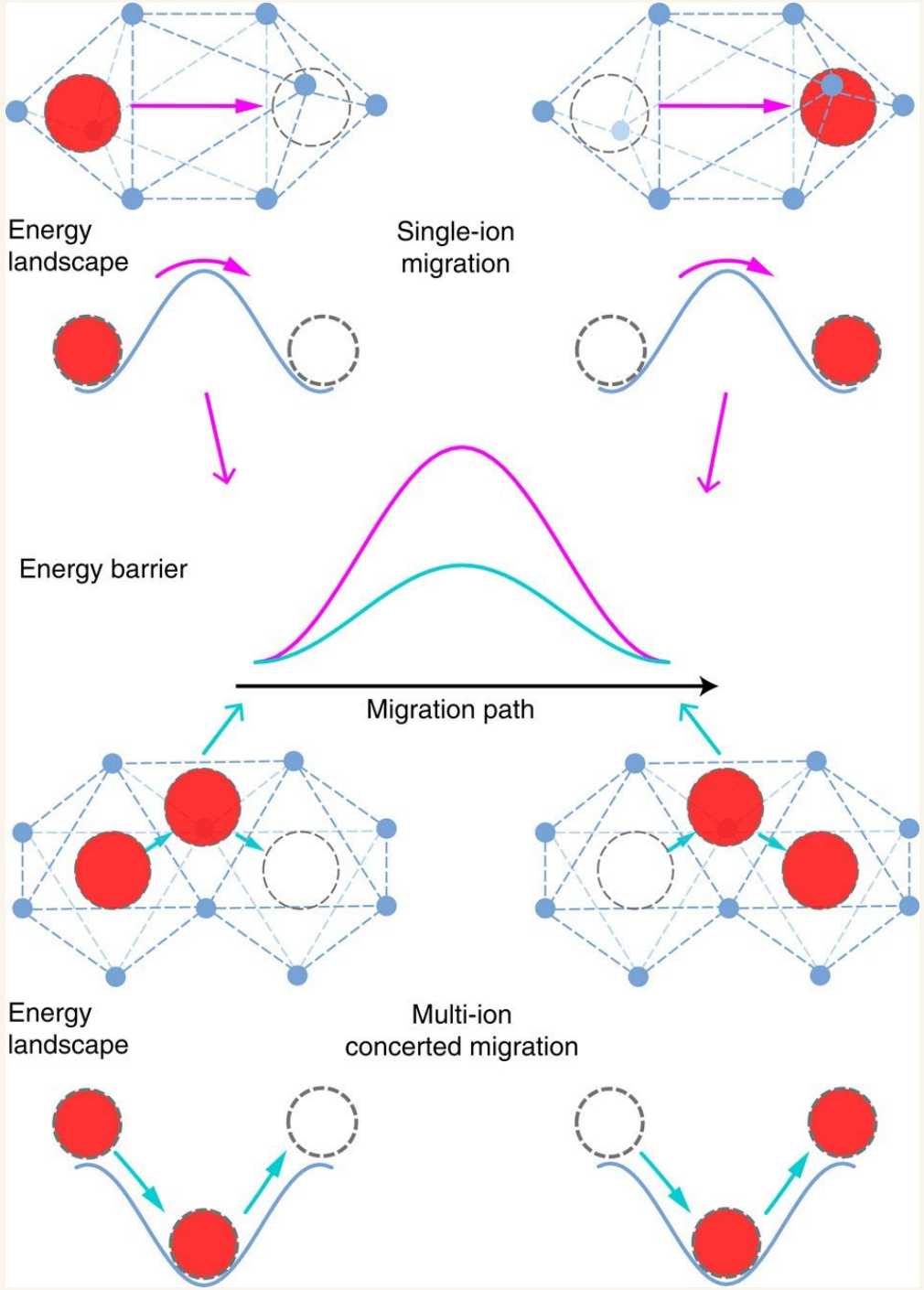
Activity in solid electrolytes

Li^+ diffusion in solids



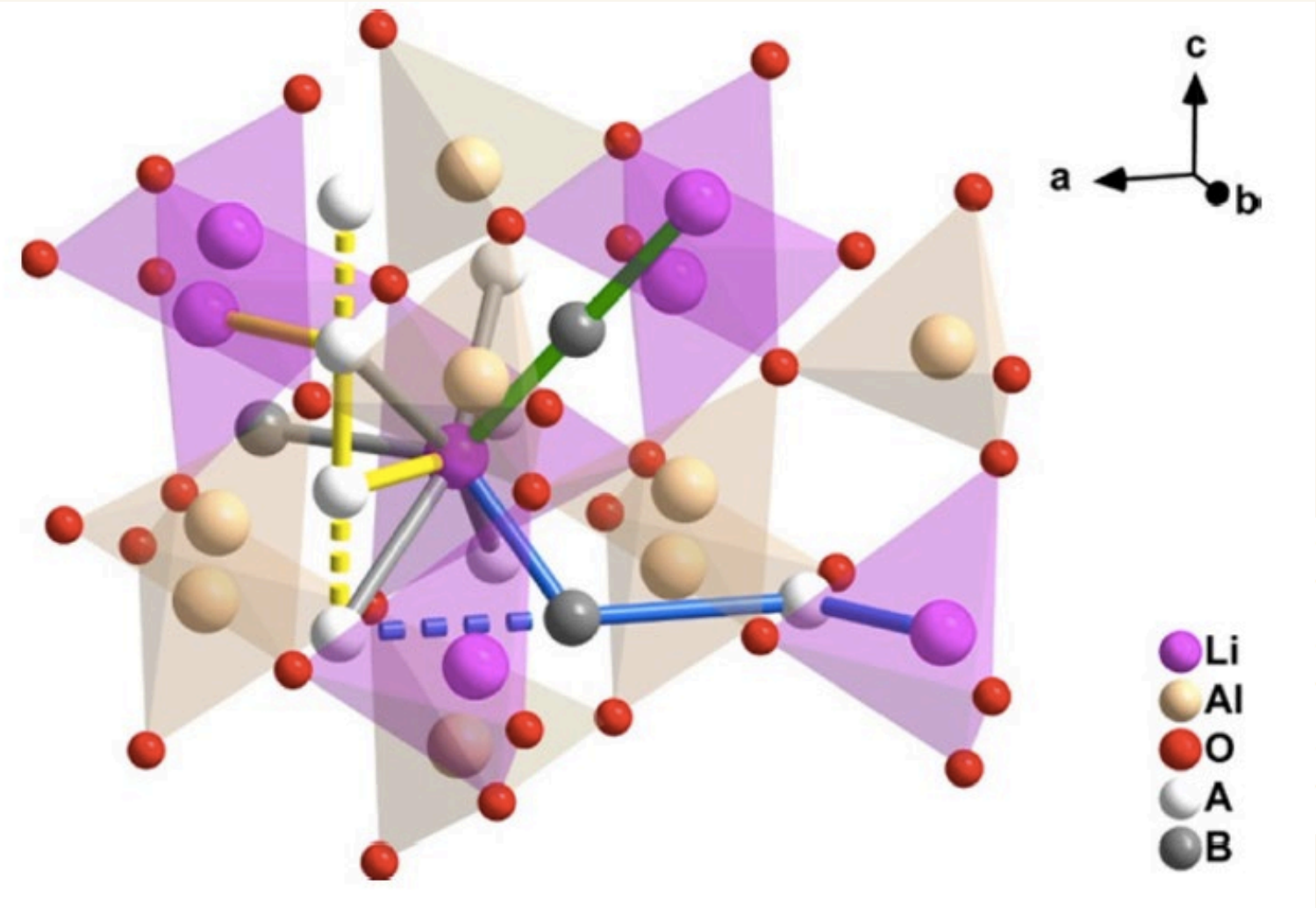
Activity in solid electrolytes

- Li^+ diffusion in solids
- Size of channel for movement
- Distance ion has to hop
- Electrostatic repulsion of Al^{3+}, Ti^{4+}, Zr^{4+}, Si^{4+}, etc.
- All of these interfere, aid diffusion and control apparent activity



https://doi.org/10.1038/ncomms15893

Proposed Li^+ diffusion pathways in γ-$LiAlO_2$



Yellow: P1

Green: P2

Blue: P3

Gray: disfavored jumps

Dashed lines: possible

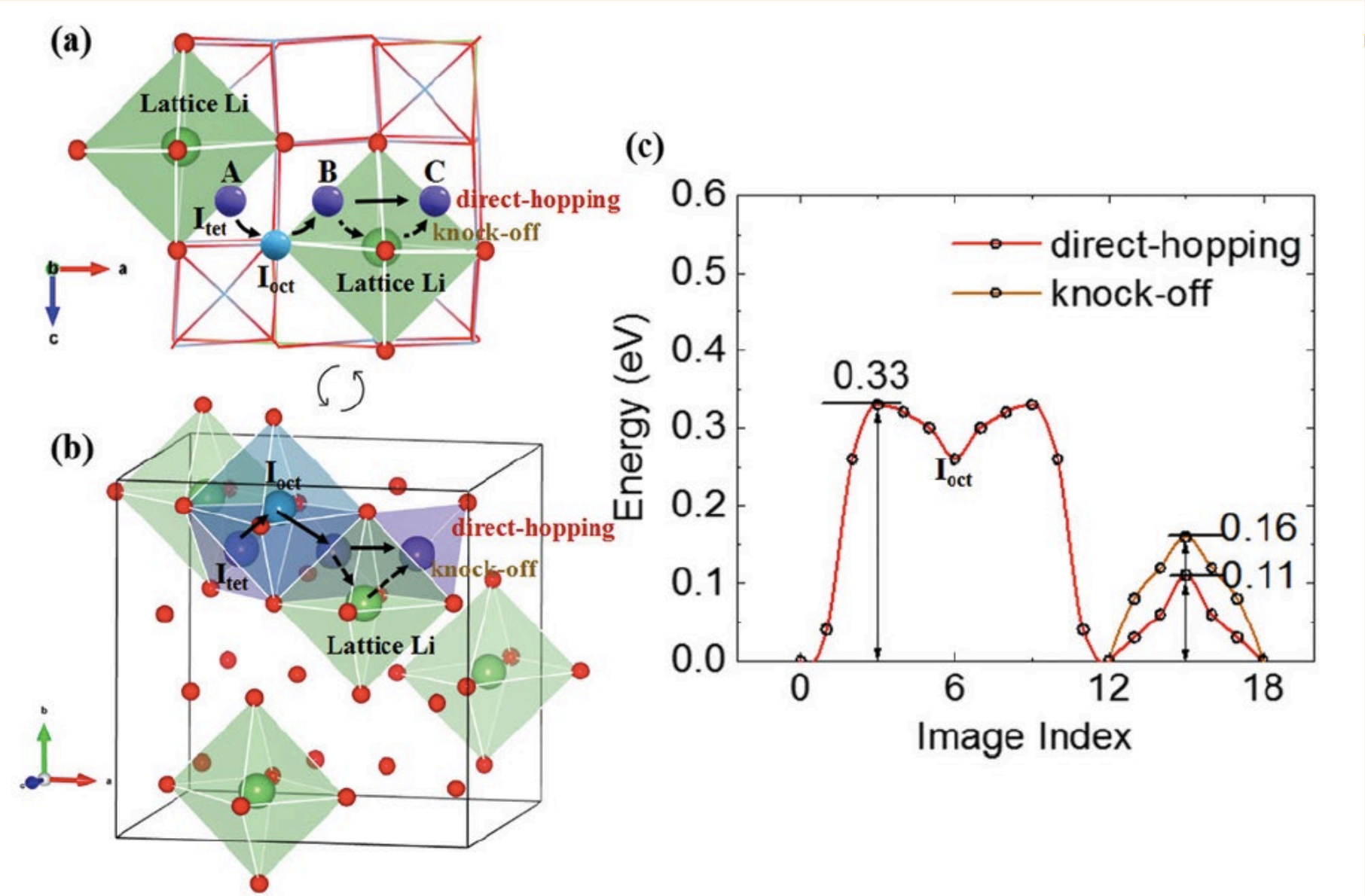
$$\mathrm{Li} \rightarrow \mathrm{A} \rightarrow \mathrm{A}' \rightarrow \mathrm{Li}' \qquad (\mathrm{P1})$$

$$\mathrm{Li} \rightarrow \mathrm{B} \rightarrow \mathrm{Li}'' \qquad (\mathrm{P2})$$

$$\mathrm{Li} \rightarrow \mathrm{A} \rightarrow \mathrm{B} \rightarrow \mathrm{Li}''' \qquad (\mathrm{P3})$$

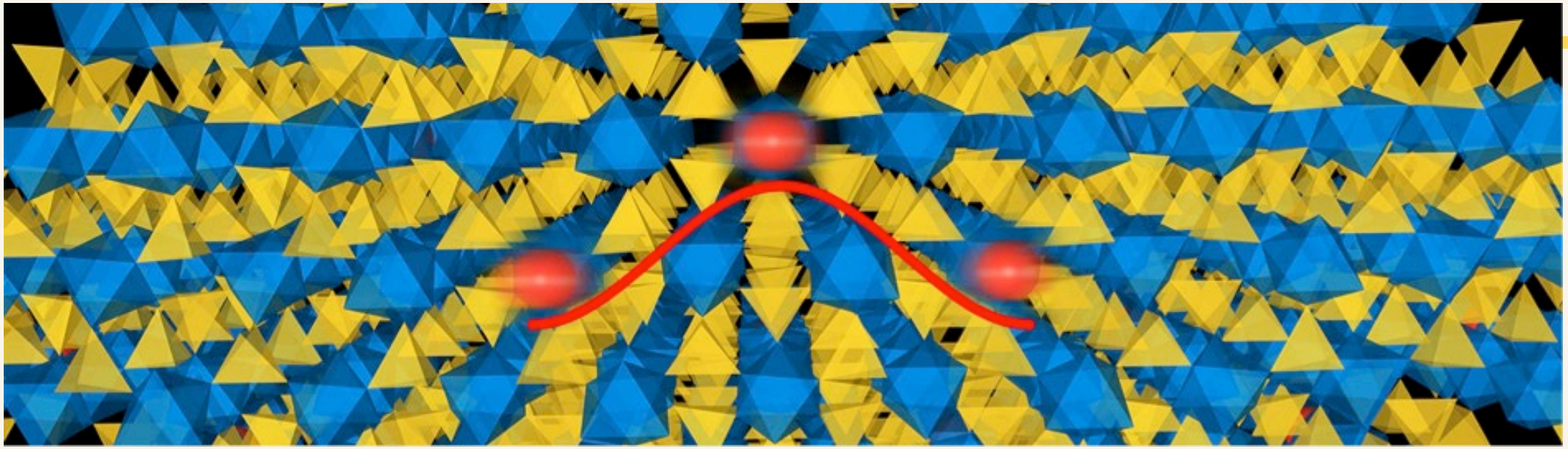
Wiedemann et al,*Chem. Mater.* **2016**.

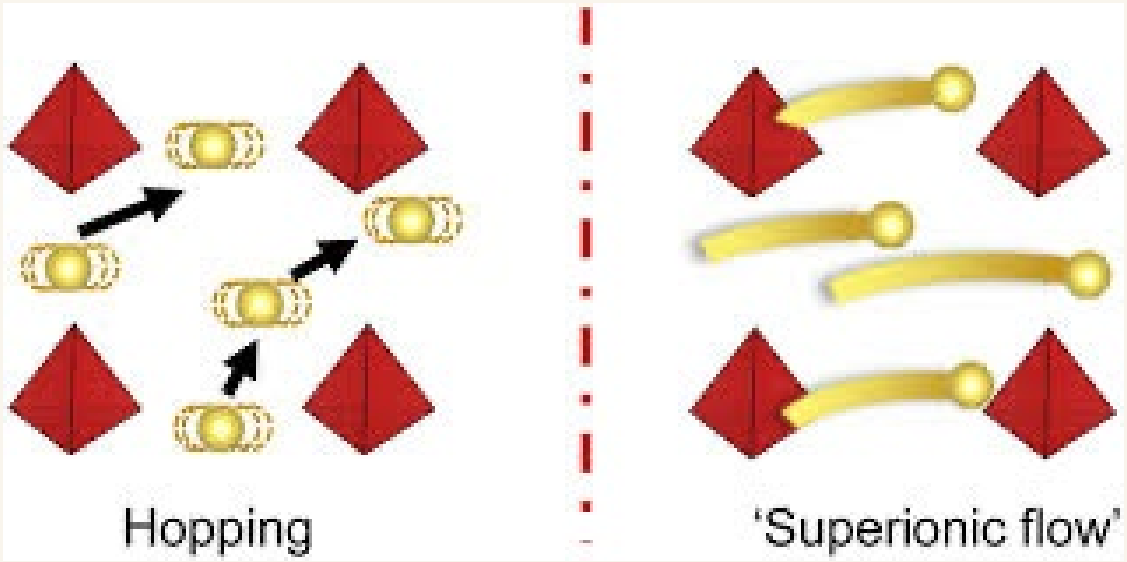
Proposed lithium diffusion pathways in $LiAl_5O_8$



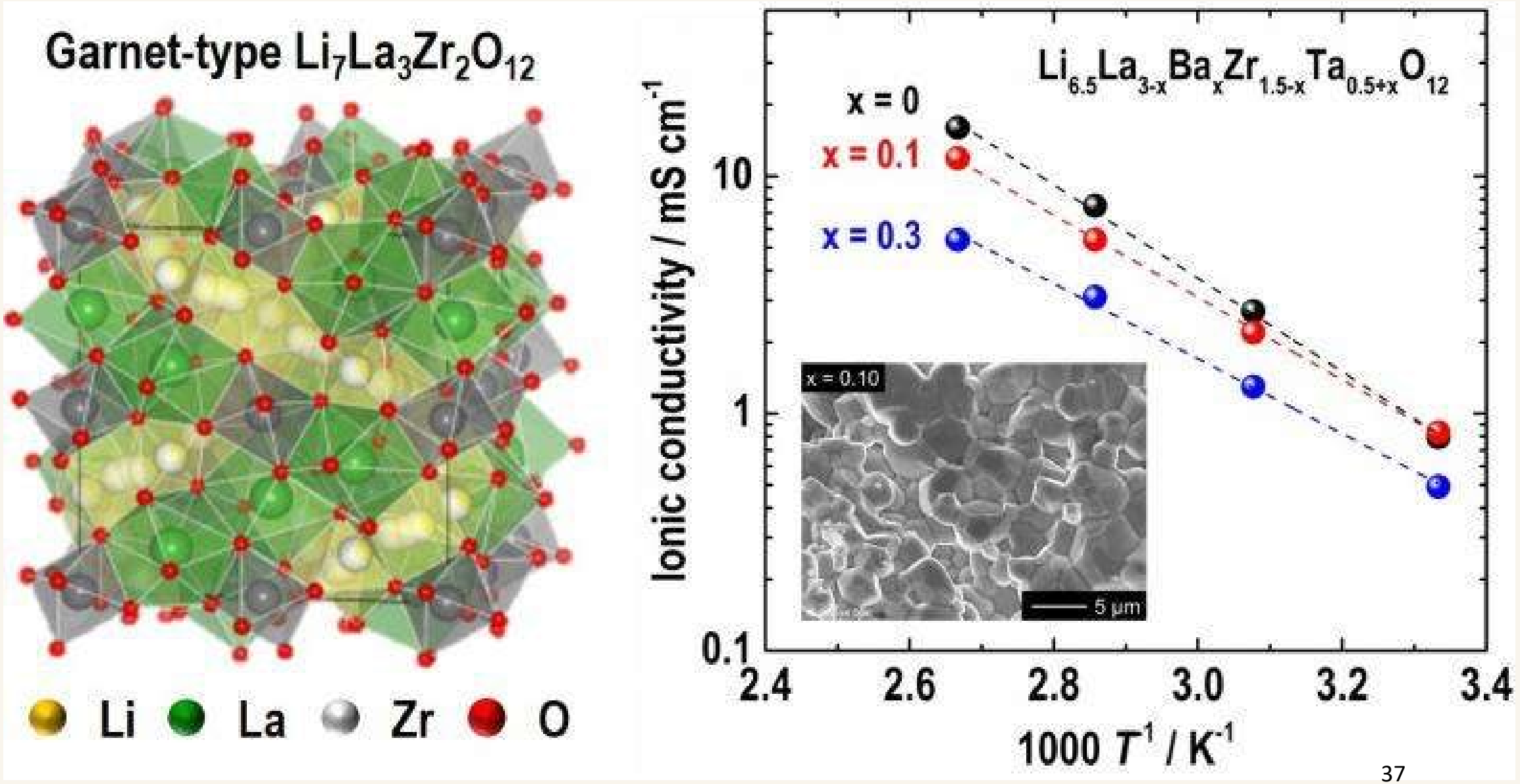
https://doi.org/10.1039/c9cp02650a.

Li diffusion in solids

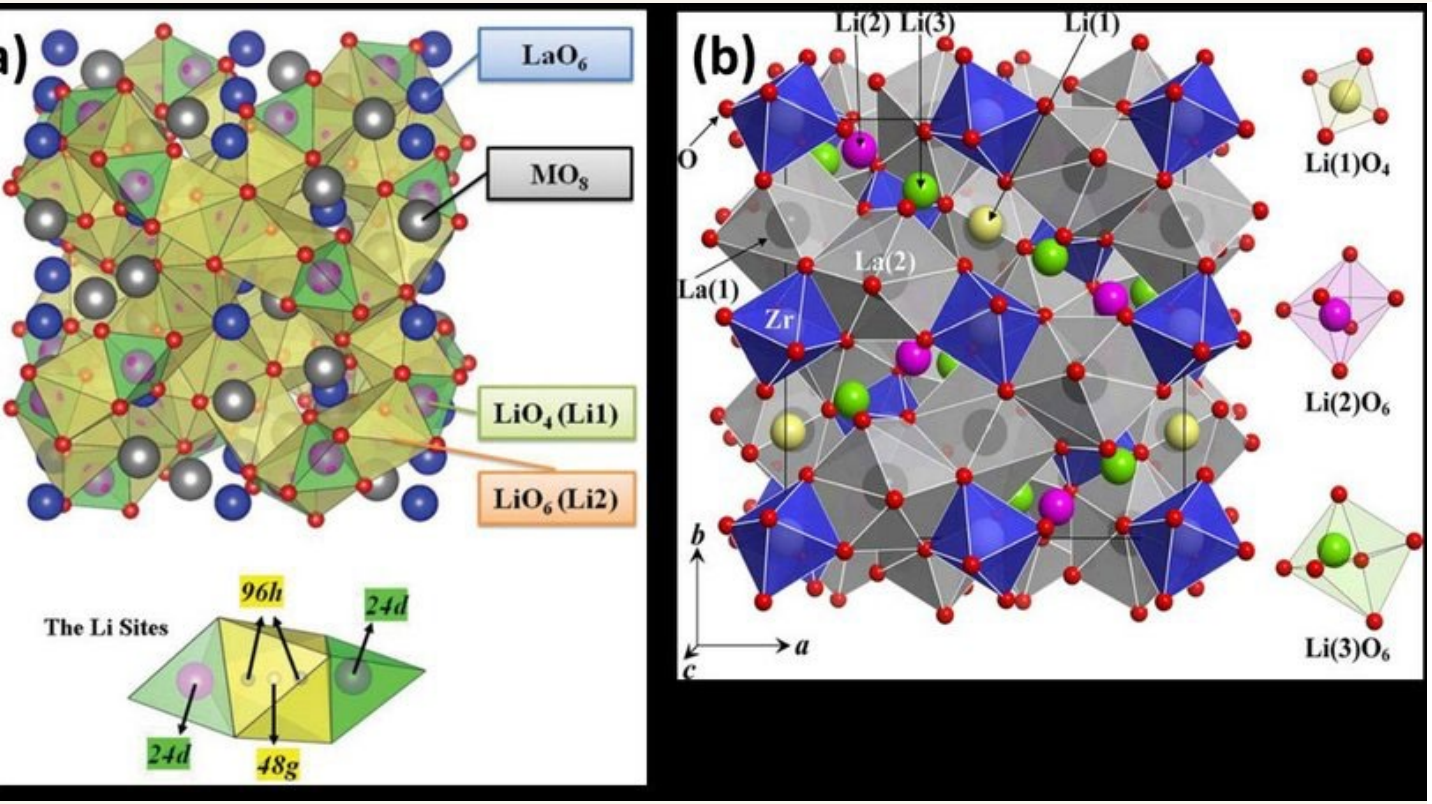


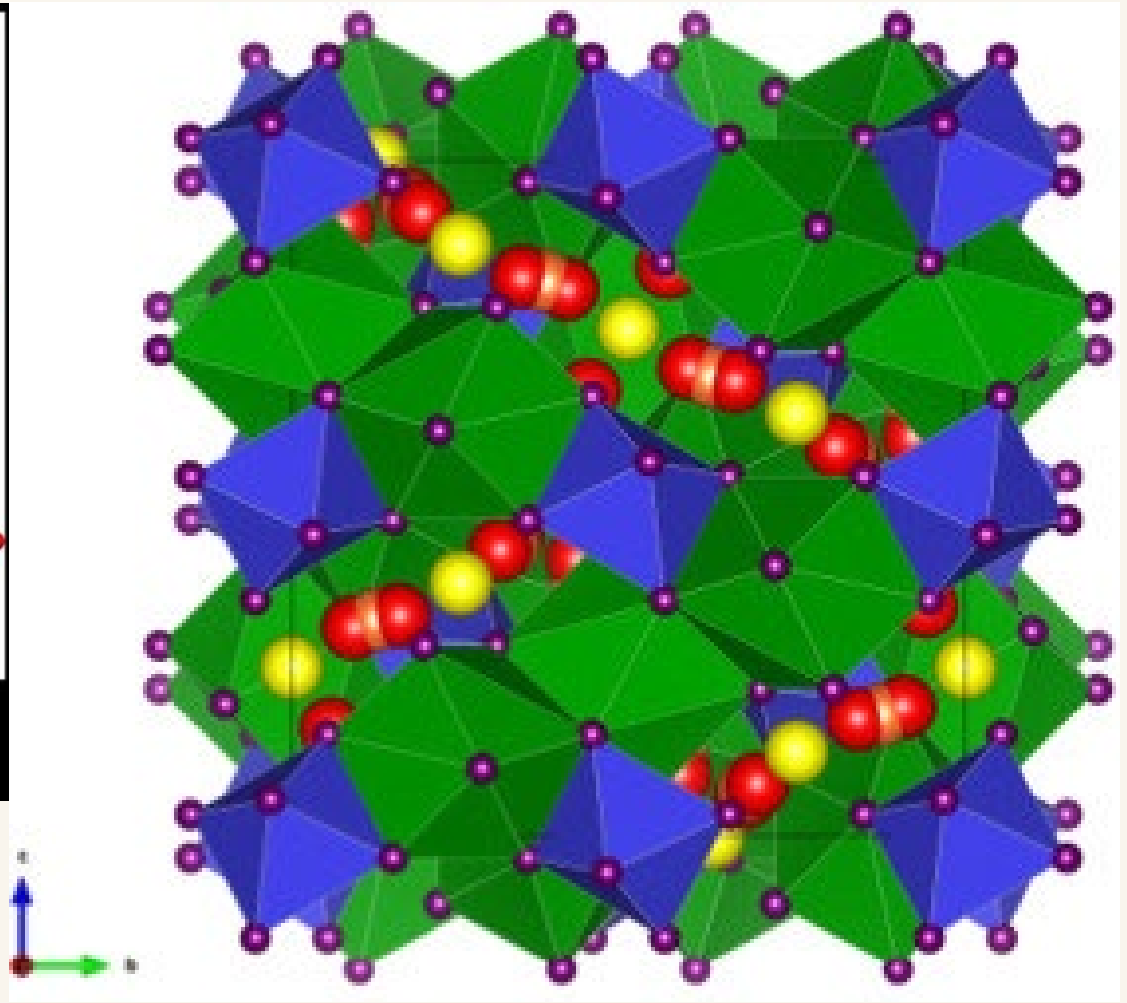


Li diffusion in solids

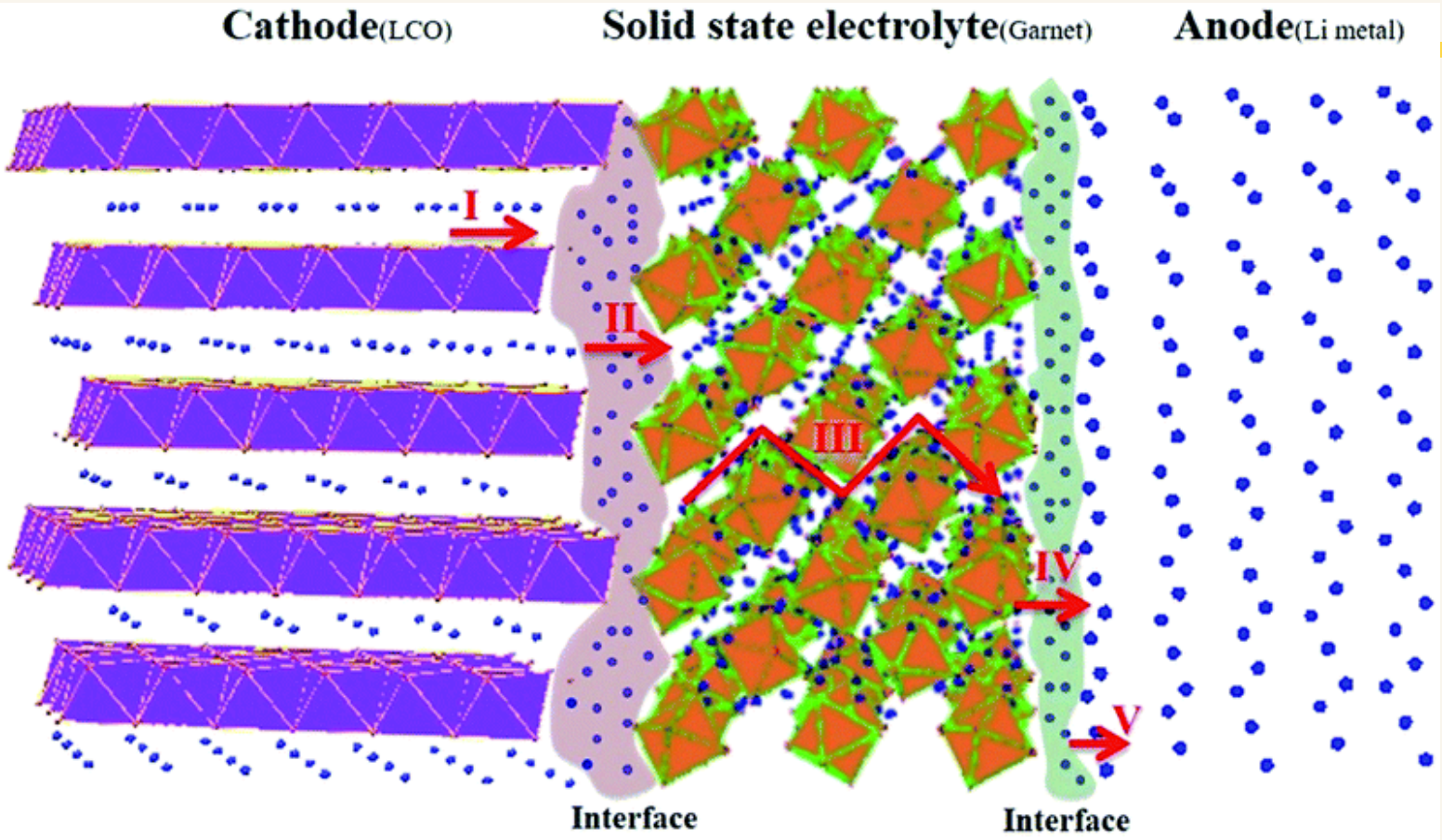


Li diffusion in solids





Li diffusion in solids



I: Li^+ cations come out of the lattice structure of cathode;
II: pass through cathode/SSE interface;
III:cross SSE structure (crystalline or amorphous);
IV:move across the SSE/anode interface;
V: finally deposit onto the Li metal anode.

Li diffusion in solids—intercalation processes