The Materials Challenges in Making Increasingly Better and Better Batteries

Clare P. Grey

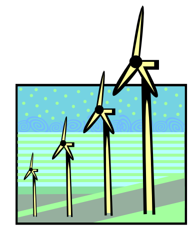
Cambridge University

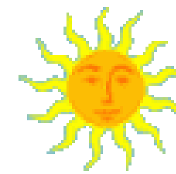
Why is this important?

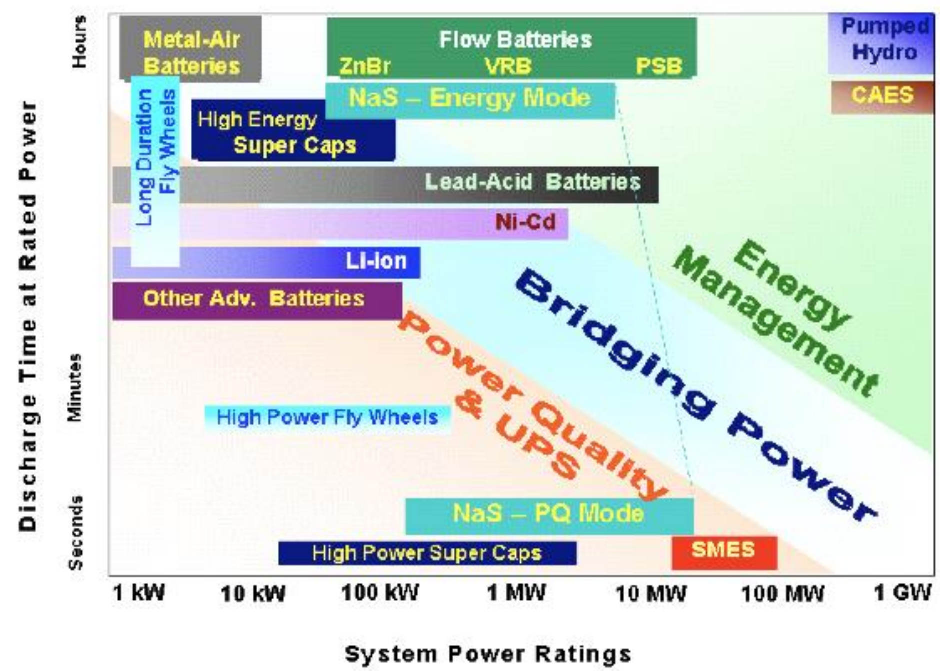
Reducing carbon emissions…. reducing pollution

- Electrification of transport
  Cheaper, safer and longer lasting batteries are critical for widespread adoption

- Storage on the grid is vital if we are to increase the use of renewables
- Current batteries are only suitable for short term back-up and frequency regulation, or on micro-grids







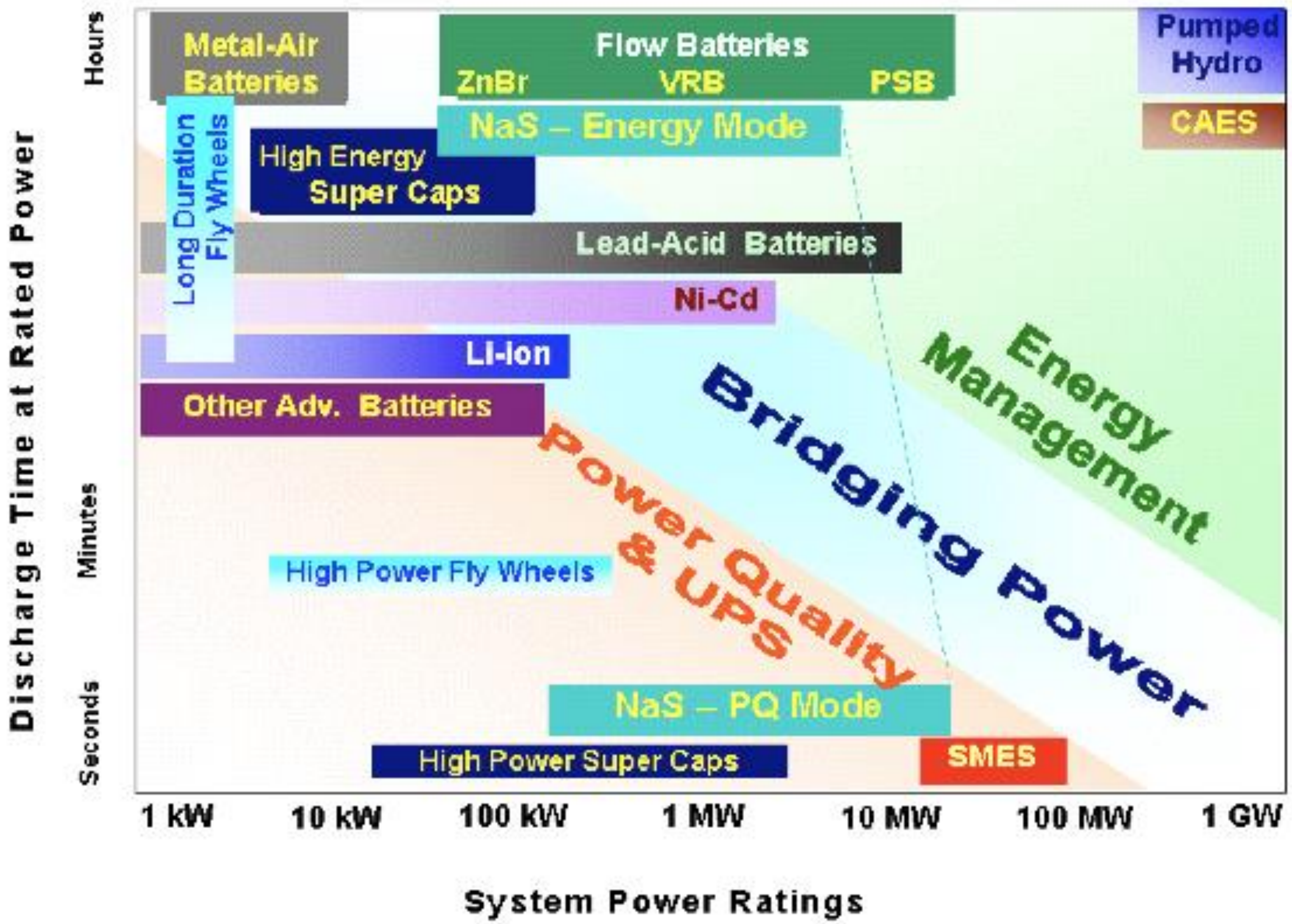
I Gyuk, A. Nourai and C. Shafer, 2009

Sustainability of resources

Why is this important?

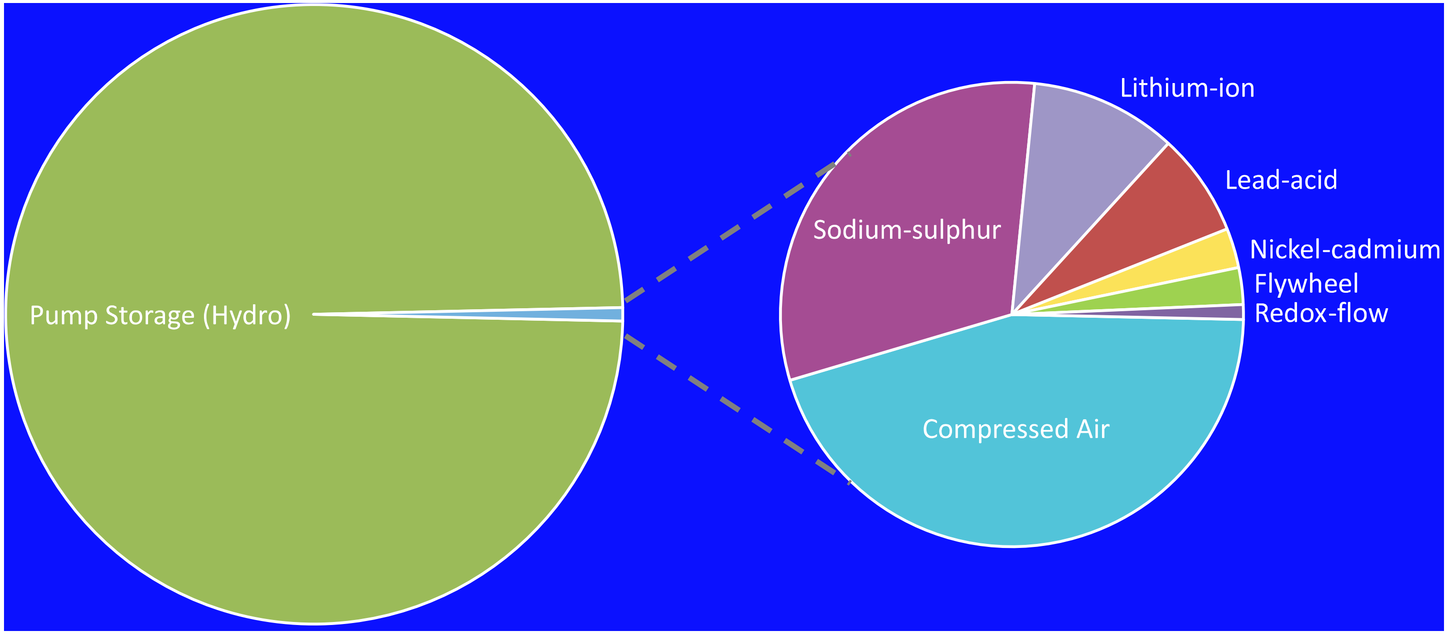
Reducing carbon emissions…. reducing pollution

- Storage on the grid is vital if we are to increase the use of renewables
- Current batteries are only suitable for short term back-up and frequency regulation, or on micro-grids



I Gyuk, A. Nourai and C. Shafer, 2009

We have a long way to go: just 0.4% of current grid storage capacity comes from electrochemical devices



International Energy Agency Technology Roadmap 2014

Yet the societal (health) and environmental impacts are enormous

Batteries for Transportation Play Also an Important Role in CO_2 Emissions Reduction

Mild Hybrid (Stop-Start)

Efficiency gains (regenerative braking)

need high power battery

EM assists in acceleration
Smaller IC required

Electric Vehicles (EV)

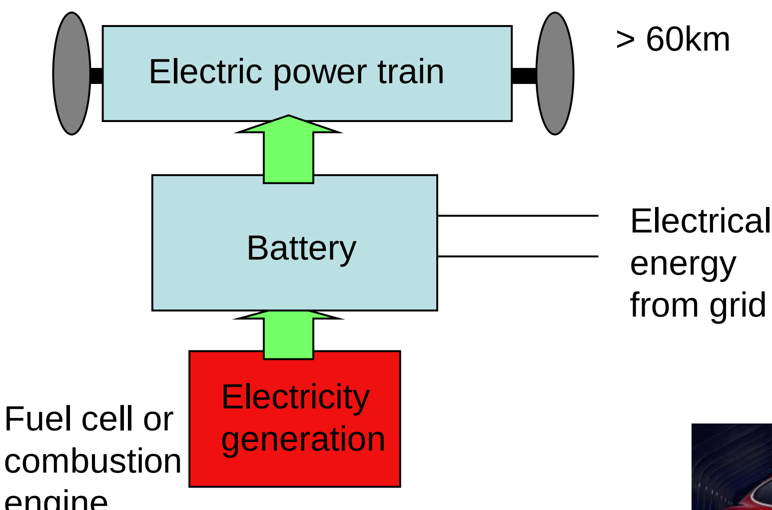
Fuel Diversification

Nissan Leaf: from £16,680*
(+4.5 k incentive)
124 - 155 miles on 24 -30 kWh

300 kg

Hybrid Electric Vehicles (HEV)

Plug-in Hybrid Electric Vehicles (PHEV)

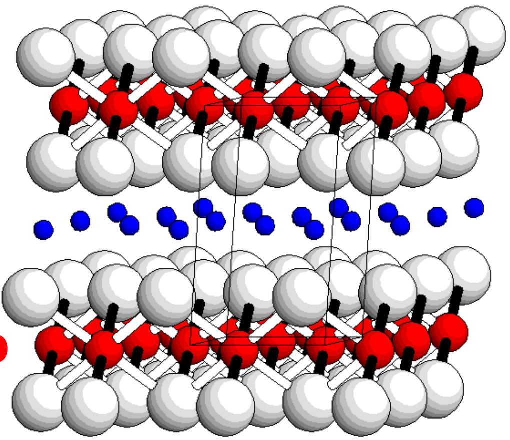


> 60km

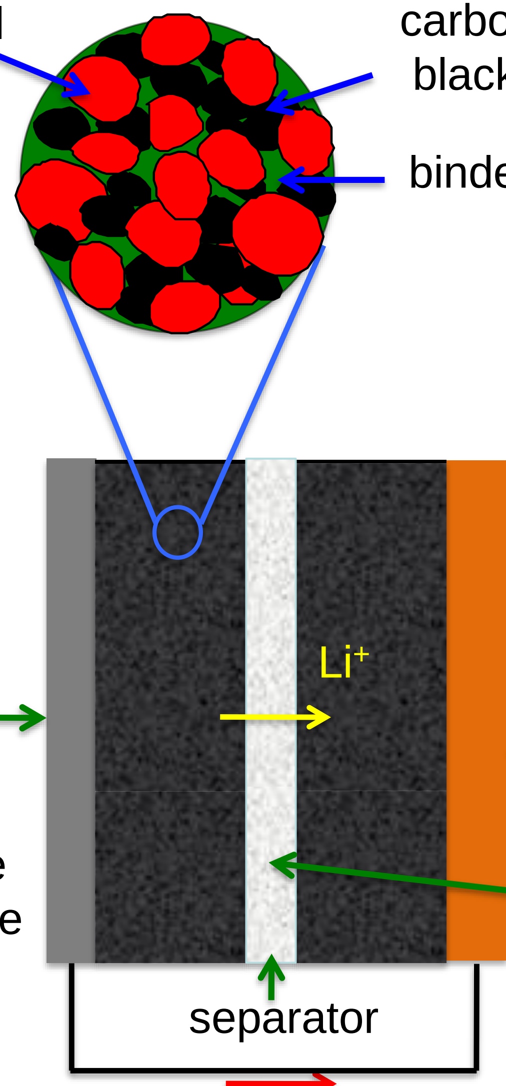
Both **Energy** and **Power** are important

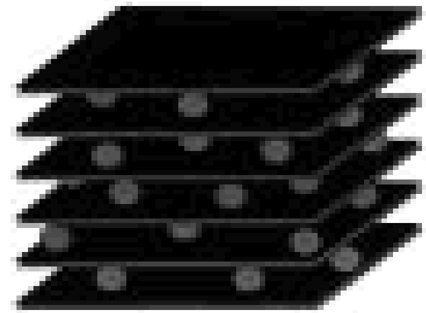
208 - 270 miles

What is a Battery?
The SONY "Rocking-Chair" battery (1990)



$LiCoO_2$





Negative (anode)
Li_xC_6

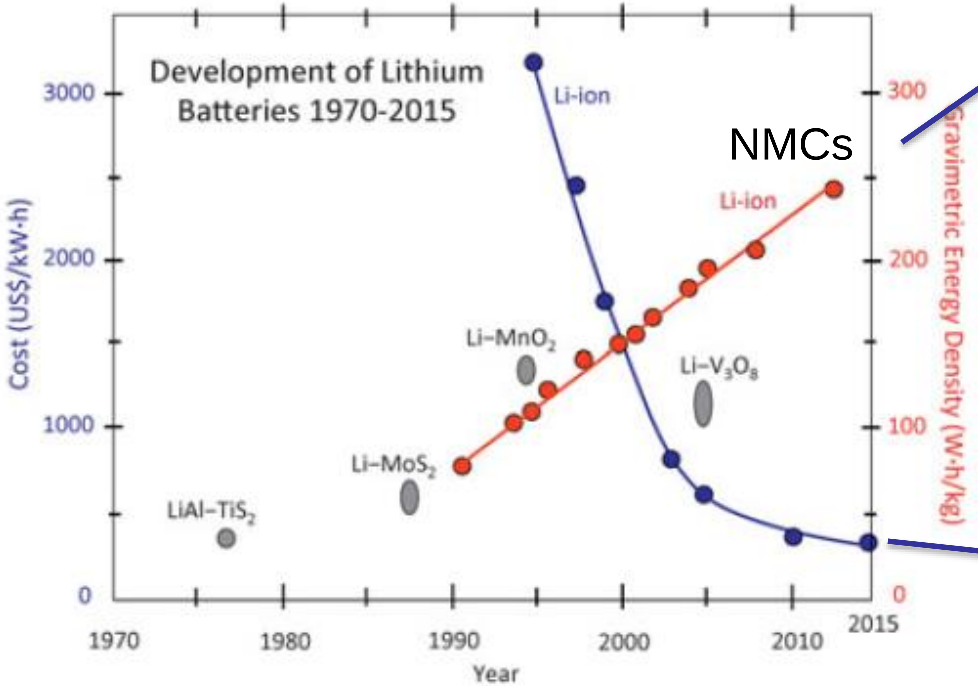
Lithium shuttles backwards between two layered compounds

Positive (cathode)
$LiCoO_2$

- $LiCoO_2$, J. Goodenough (1980); 2ndary host material, Murphy et al., and Scrosati et al. ('78 and '80)

- Very high voltage (4 V;
- cf Ni/Cd @ 1.35 V)

We are reaching the theoretical limits and new approaches are required



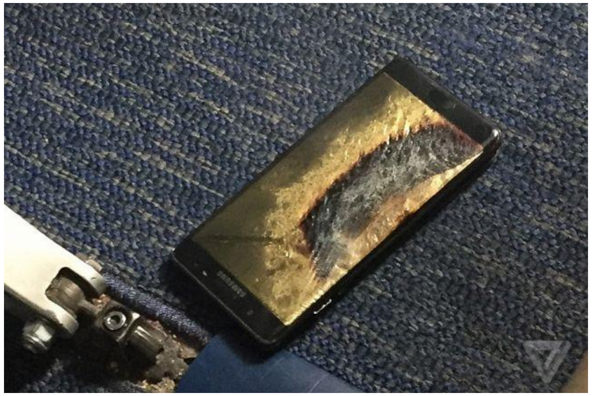
NMCs

Li air, Li S, Mg etc.

Tesla projects (gambles) that battery costs will drop to $100/KWh by 2020

G. Crabtree, E. Kocs, L. Trahey, 2015

Pushing the limit has safety consequences



Critical need to increase battery longevity and monitor state of health (SoH):

- cost,
- sustainability,
- safety
- second-hand use etc.

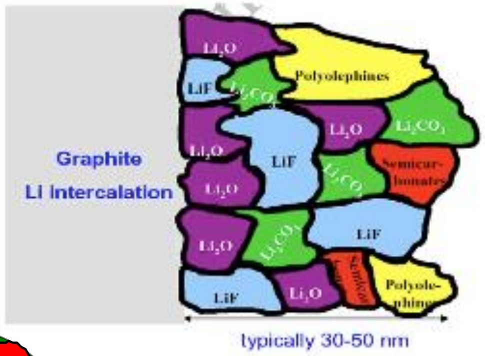
Why do batteries fail?

•**Electrolyte** is only metastable when battery charged

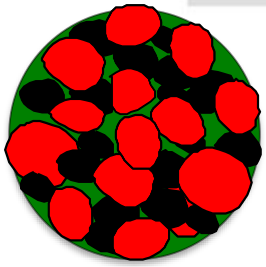
•*Multiple organic degradation products are formed*

•Surface electrolyte phase (**SEI**) film forms on the anode (and cathode) preventing further electrolyte decomposition

•*SEI removes Li from the cell*



E. Peled et al. JES 1979



•**Particle expansion** on cycling leads to cracking and movement of particles and "dead lithium"

Disadvantages of the $LiCoO_2$ Cell

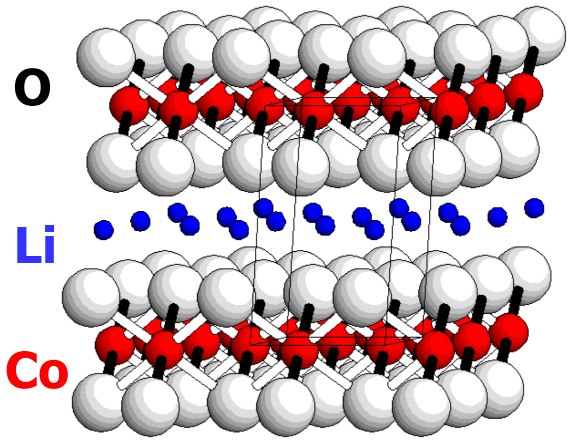
- COST: Co is toxic and expensive; electronic circuitry *etc.*
- MATERIALS RESOURCES
- CAPACITY (how many electrons can be stored): Only 0.5 of the Li can be removed from $LiCoO_2$ (120 – 140 $mAhg^{-1}$). I.e., low capacity (vs. graphite – 372$mAhg^{-1}$)
- POWER (rate): slow to charge and discharge (low power) - not suitable for EV.s, PHEVS, HEV.s or other high power applications
- SAFETY: Li-plating can occur on rapid charging; short circuits and thermal stability in charged state..

•**Charged** materials are generally metastable

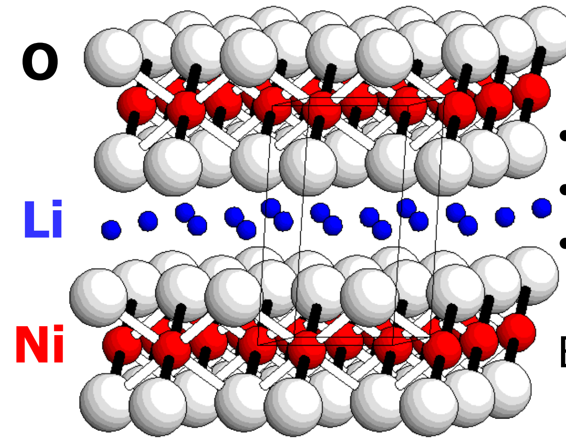
•$6Li_{0.5}CoO_2$ -> $3LiCoO_2 + Co_3O_4 + O_2$ **+ heat**

Batteries for EVs

120 - 140 $mAhg^{-1}$



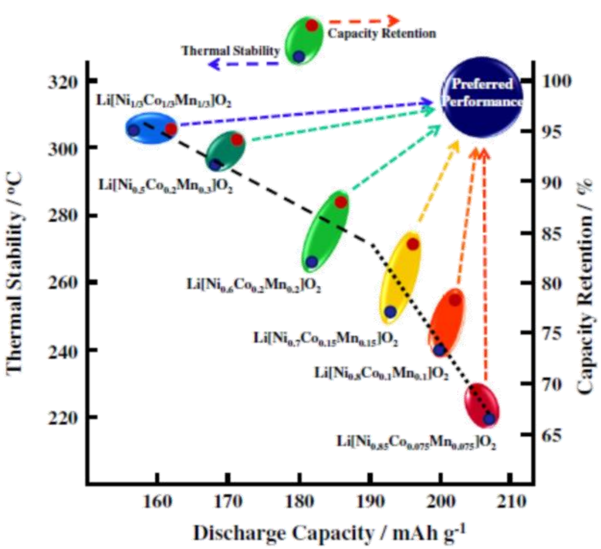
$LiCoO_2$



$LiNiO_2$

- Replace Co by Ni
- Higher rate
- Cheaper

But unstable



Increase stability

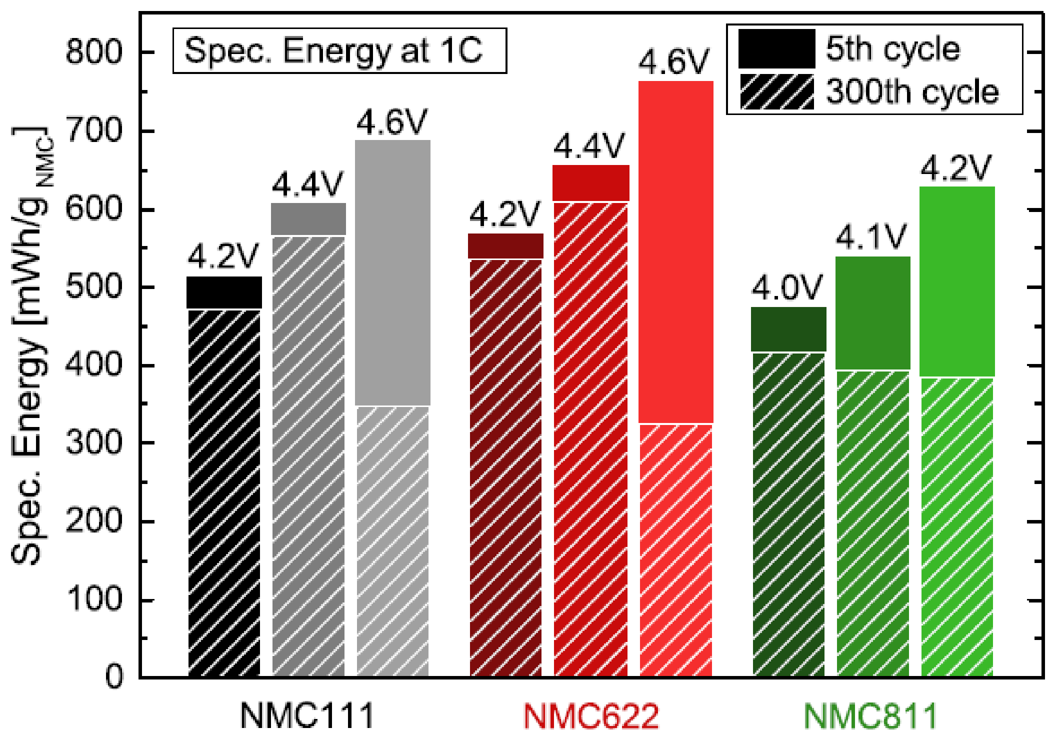
$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$ (NCA)

Increase capacity
Increase stability
But increase cost

$Li(NiCoMn)_{0.33}O_2$ (NMC)

Some current directions in the battery field

Pushing the limits of the current technology



Reduce Co content (cost)

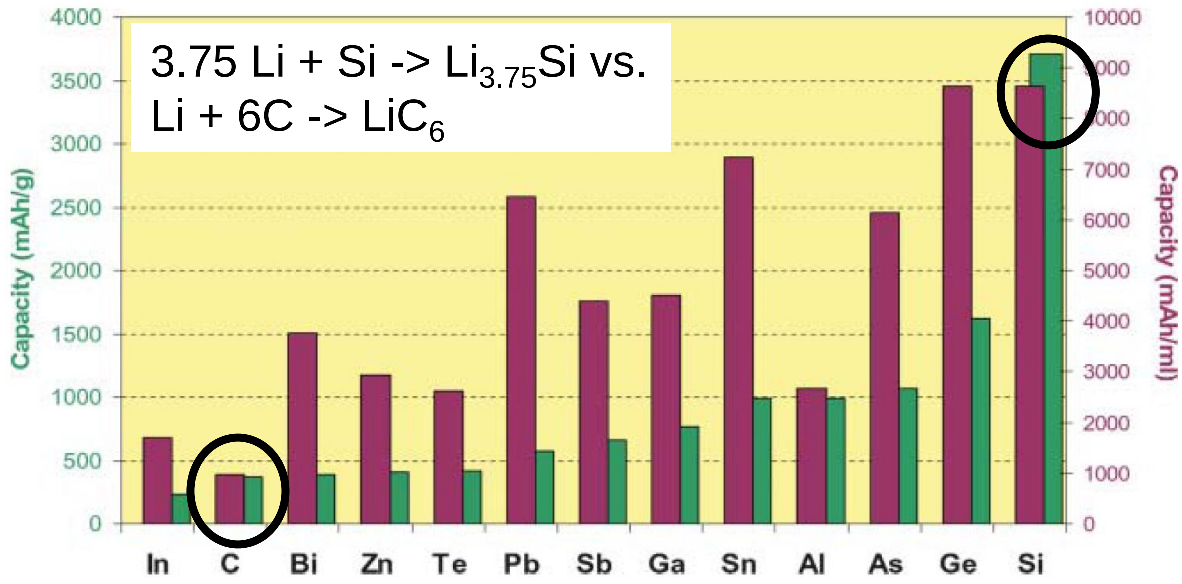
Increase capacity at lower voltage (less electrolyte decomposition)

Jung, R.; Metzger, M.; Maglia, F.; Stinner, C.; Gasteiger, H. A. *J. Electrochem. Soc.* **2017**, *164* (7), A1361.

Some current directions in the battery field

Pushing the limits of the current technology

E.g., high capacity anodes (Si, Sn) vs. layered nickel manganese oxides



	Carbon	Silicon
Gravimetric Capacity (mAh/g)	372	3572
Volumetric Capacity (mAh/cm^3)	843	8322

Ways to Reduce Cost

- Cheaper materials
- Thicker electrodes – reduce amount of separator, current collector, packaging *etc.*
- Increase capacity
- Increase energy density (capacity x voltage)
- Increase longevity (calendar life and cycle no. – often require different chemistries)
- 2nd hand market for batteries
  - Insurance
  - Pricing
  - Guaranteeing longevity

Motivates need for sustainable chemistry …
And for longevity/second use

Life Cycle Analysis

- Today's battery assembly process requires 400 kWh of energy to make batteries that deliver 1 kWh of energy, releasing 75kg of CO_2.

Ishihara, K., Kihira, N., Terada, N., Iwahori, T. & Nishimura, K. Life cycle analysis of large-size lithium-ion secondary batteries developed in the Japanese national project. *Proceedings from 5th Ecobalance conference.* (2002).

Shortage vs. Reliability of Source?

World Lithium Production and Reserves (t)

	Mine Production		Reserves
	2012A	2013A	
Chile	13,200	13,500	7,500,000
China	4,500	4,000	3,500,000
Australia	12,800	13,000	1,000,000
Argentina	2,700	3,000	850,000
Portugal	560	570	60,000
Brazil	150	150	46,000
United States	*	*	38,000
Zimbabwe	1,060	1,100	23,000
World total (rounded)	**35,000***	**35,000***	**13,000,000**

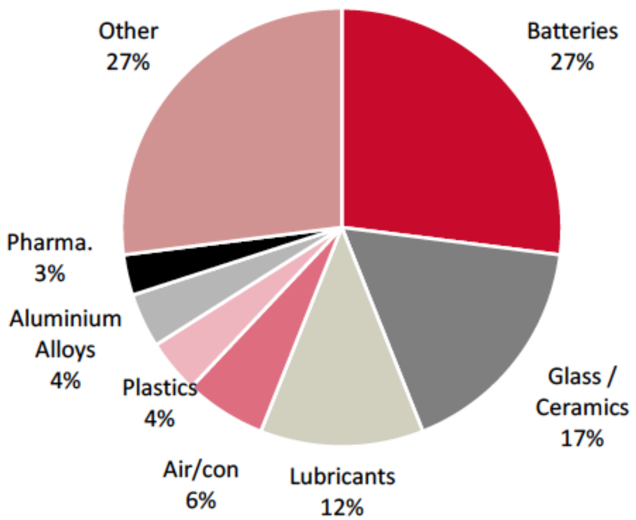
NOTE: **US production withheld to avoid disclosing company proprietary data, and excluded from total.*

SOURCE: *US Geological Survey, from government sources.*

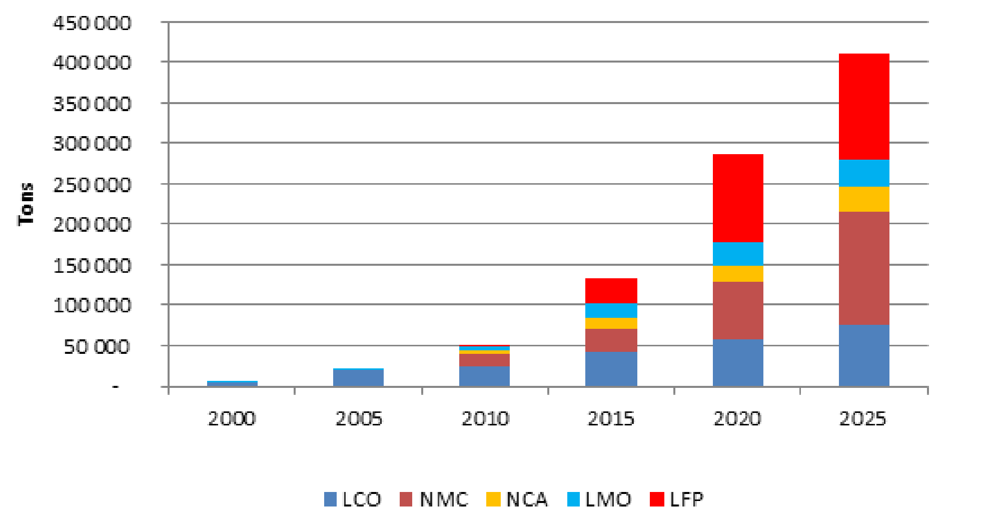
Batteries currently use up approximately one third of the world Li production, but their use is predicted to explode.. ☺

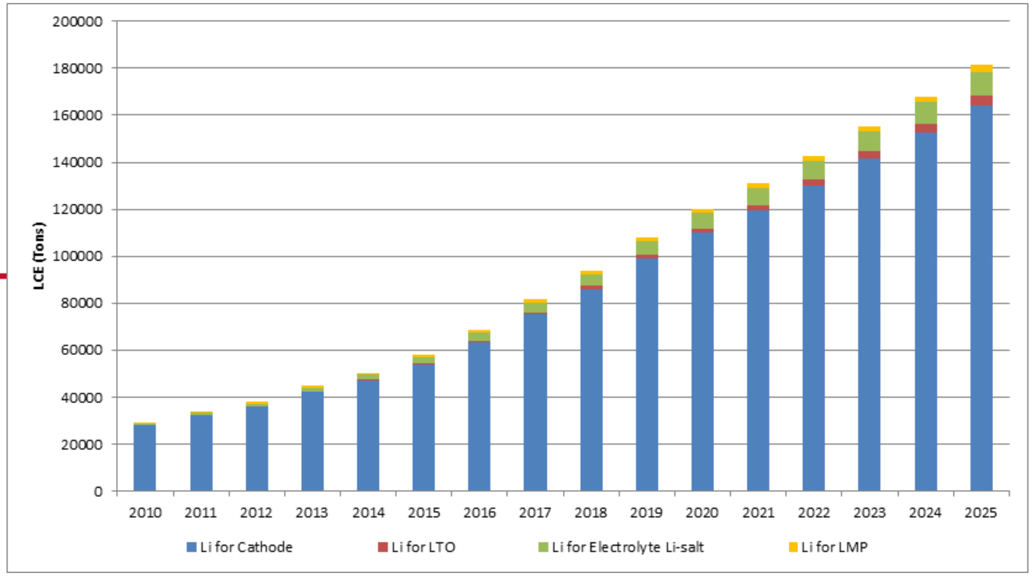
Recycling/2nd life possible

Lithium Usage Worldwide, by Application (2013)



***NOTE:** Other includes rocket fuel and laser applications.*
***SOURCE:** http://www.statista.com/.*



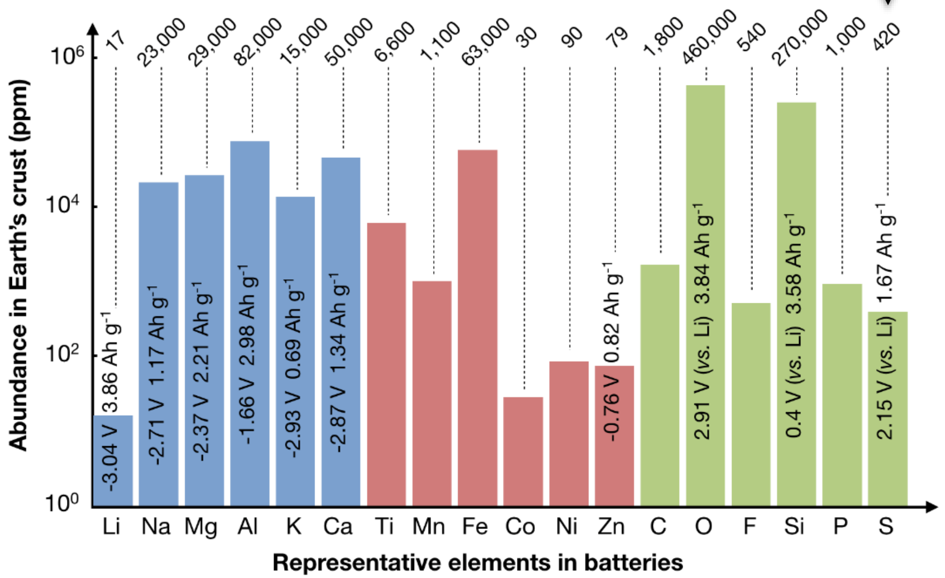


Christophe PILLOT, AVICENNE Energy analysis, April 2016

Some current directions in the battery field

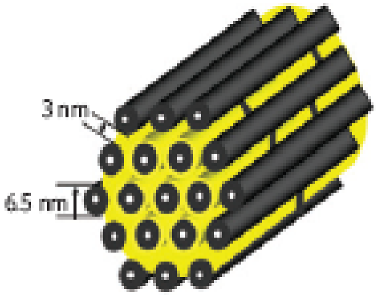
Beyond Conventional Li-ion?

Cheaper, More Abundant Materials:



C.P. Grey, J.M. Tarascon, *Nat. Mater.* (2016).

Lithium Sulfur Batteries



$2Li + S \rightarrow Li_2S$

X. Ji... L. Nazar *Nat. Mater.* (2009)

Cheap and high energy density

- But soluble polysulfides cross over to the negative electrode

Some current directions in the battery field

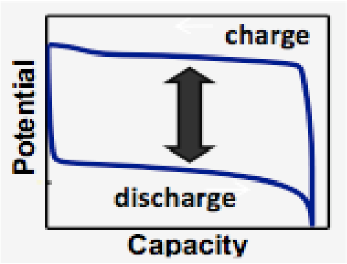
The Highest Energy Density?

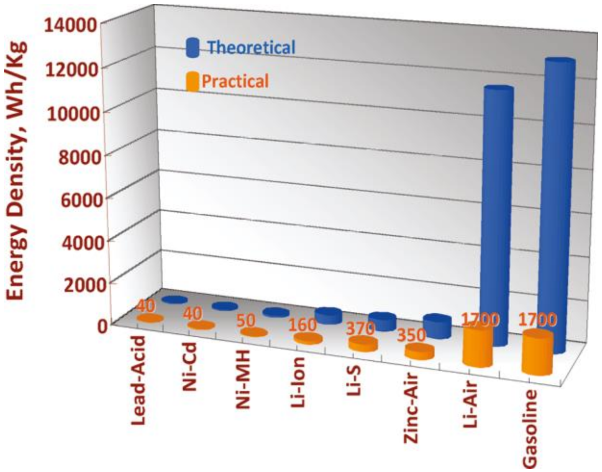
Lithium Air Batteries

Cheap and v. high (gravimetric) energy density

- But far from commercial due to problems with electrolyte degradation, large overpotentials, protection of Li metal etc.

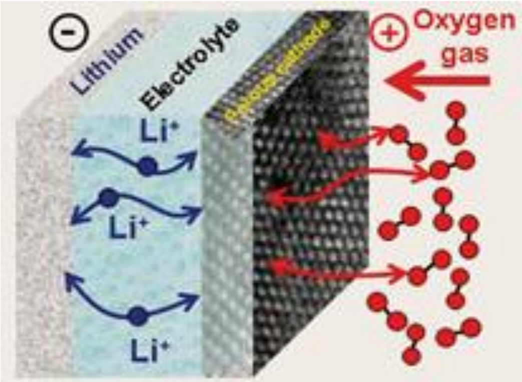
Voltage gap must be reduced





G. Girishkumar et al. *J. Phys. Chem. Lett.* **2010**, *1*, 2193.

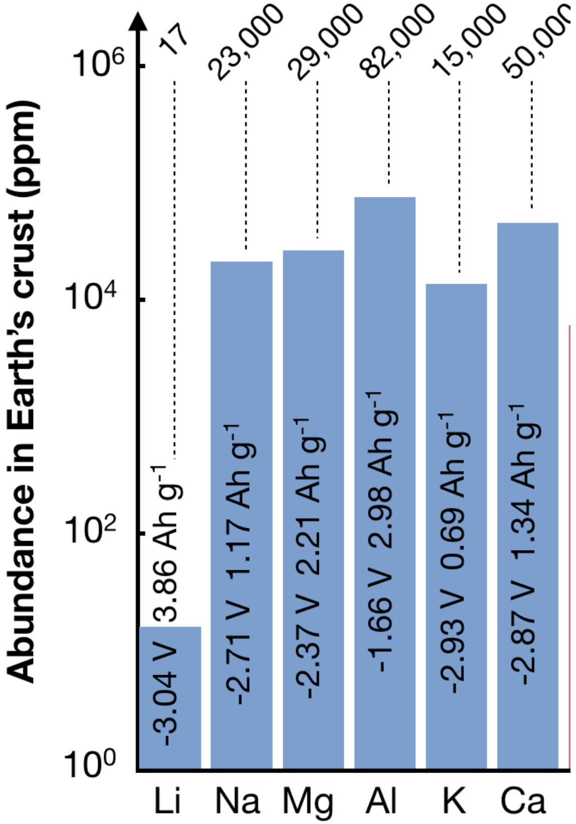
$2Li + O_2 \rightarrow Li_2O_2$



A. Débart et al. *Angew. Chem. Int. Ed.* (2008) 47, 4521.

Some current directions in the battery field

Moving Beyond Li?

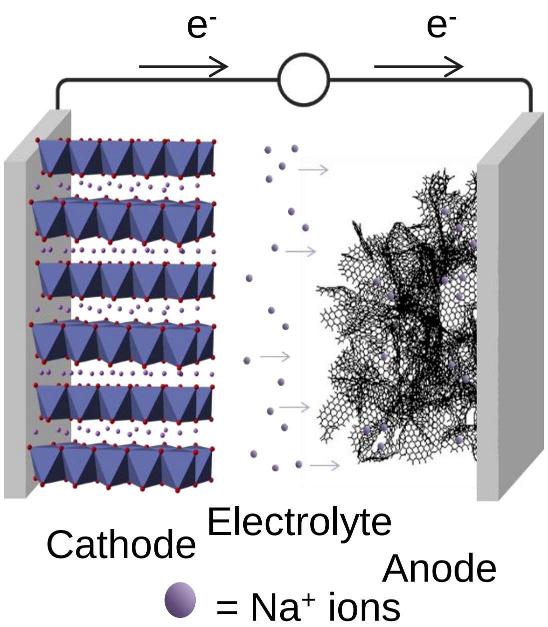


C.P. Grey, J.M. Tarascon, *Nat. Mater.* (2016).

Mg batteries – higher capacity due to 2+ charge?

Na ion batteries:

- Replace Cu current collectors by Al
- Higher abundance of Na

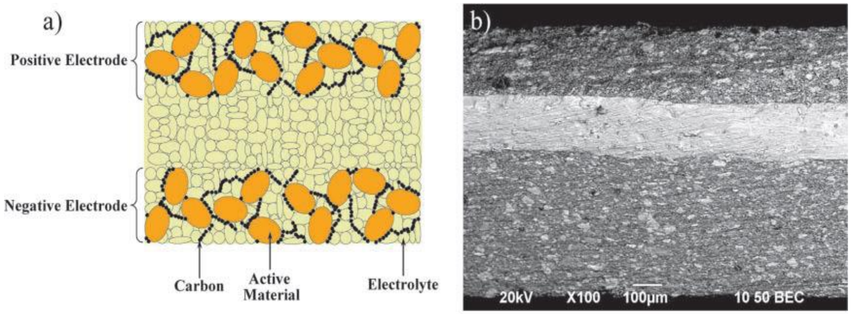


- But energy density is lower than for Li-ion

Some current directions in the battery field

The ultimate in safety?

All-solid state batteries



A. Aboulaich.. Dollé, M. et al. *Adv. Energy Mater.*, 1, 179 (2011).

Challenges:
Conductivity of solid electrolyte; transport of (Li) to active materials
No conductor is stable against Li metal
Dendrites can still push through grain boundaries in ceramics
Volume changes, cracking and mechanical issues
Energy density

Polymer batteries are sometimes (now) being called solids state batteries !

Some current directions in the battery field

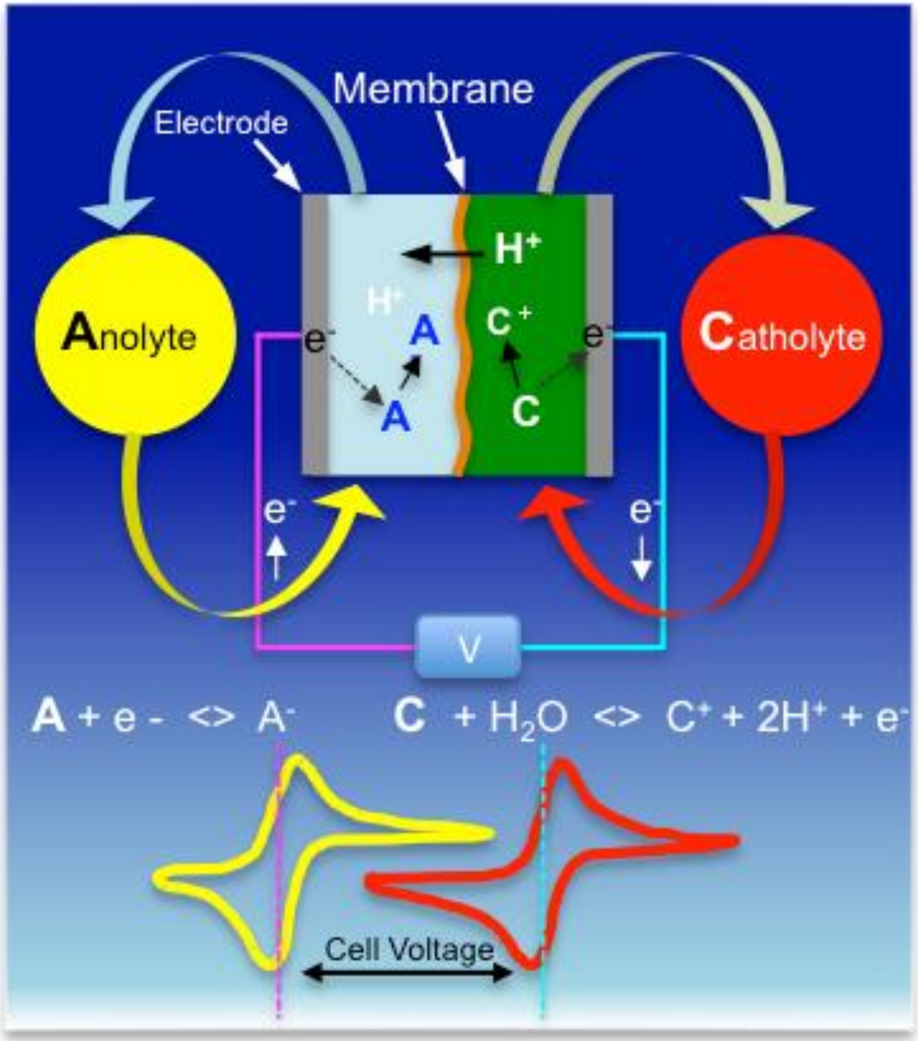
Lifetime cost
Scalability
Power/Energy density
Safety

Vanadium ions
Zinc-bromine
Organic molecules
Aqueous systems?

But cost is still no lower than for LIBs

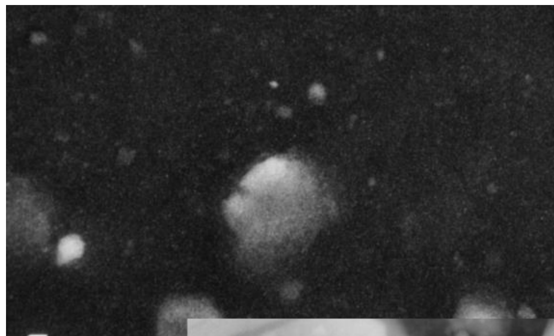
Scalable batteries:

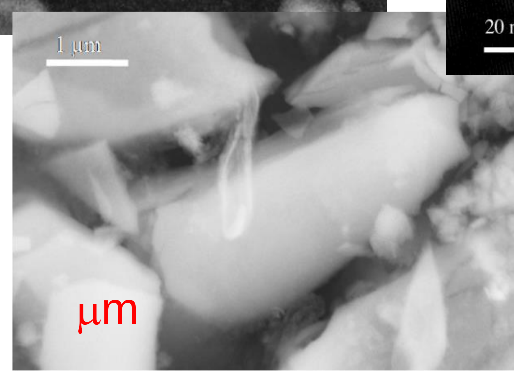
Redox Flow

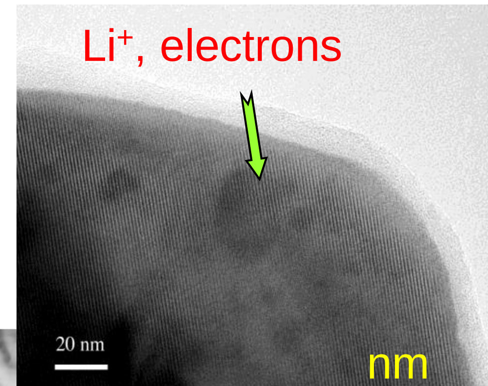


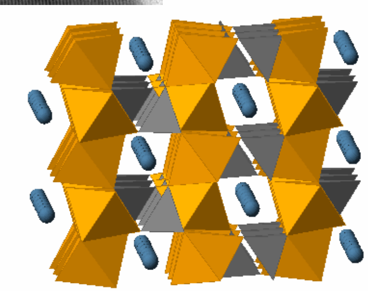
Towards a more sustainable battery chemistry: Battery Degradation and Increased Lifetime

We need to understand how chemical and mechanical processes that occur over extremely wide length and *time scales*









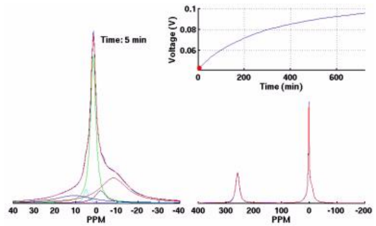
10^{-2} centimeters Pack level

10^{-6} microns electrode level

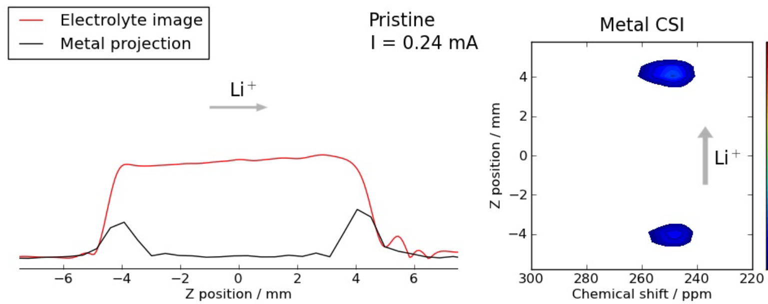
nanometers particle level

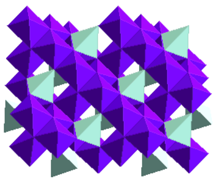
10^{-10} Ångstoms atom level

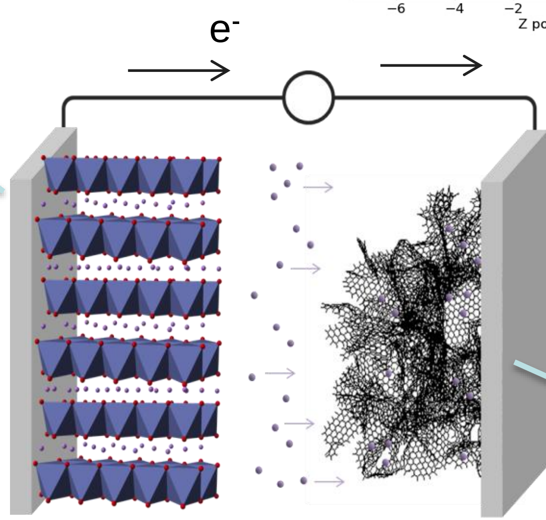
My group has developed the use of NMR and MRI in the *in situ* study of batteries



Metastable electrode phases



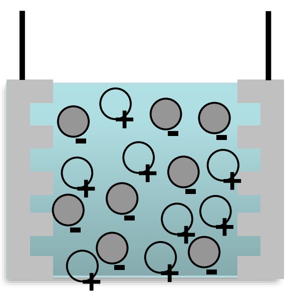


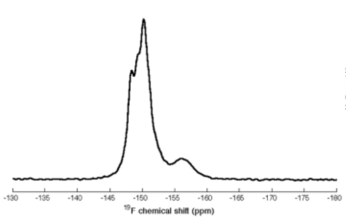


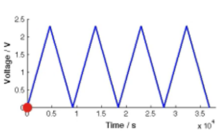
Mechanisms for dendrite formation

Development of *in-situ* methods to probe Li dynamics in spinel cathodes

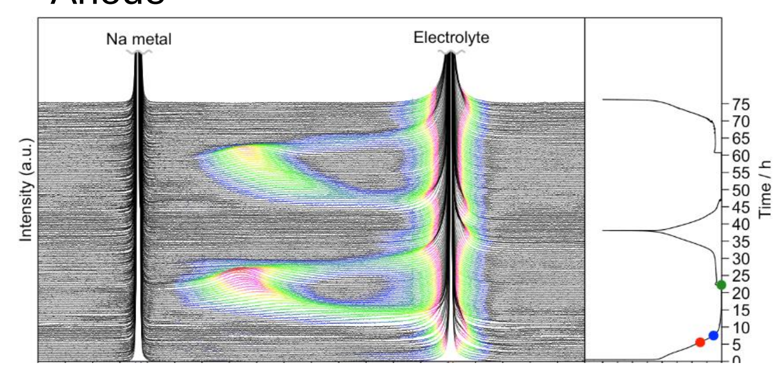
Solving the structures of amorphous anode materials



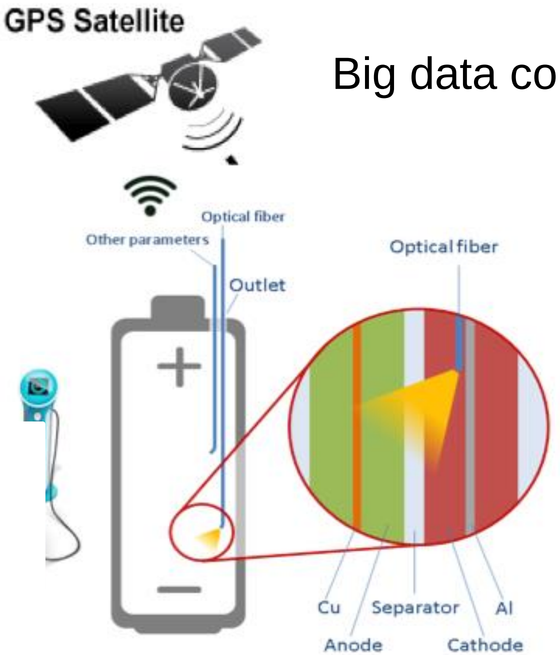




Charging mechanisms in supercapacitors



Where will we be in 5-10 years?



Big data collection

- **New Chemistries** coupled with responsive BMS systems
- New sensors; SoH measurements
- Fundamental insight: new degradation mechanisms
- (On the fly/responsive) mitigation strategies

- Generalize approach to other (electrochemical) technologies
  - Redox flow batteries