Battery Materials for Electric Vehicles: Today and Tomorrow

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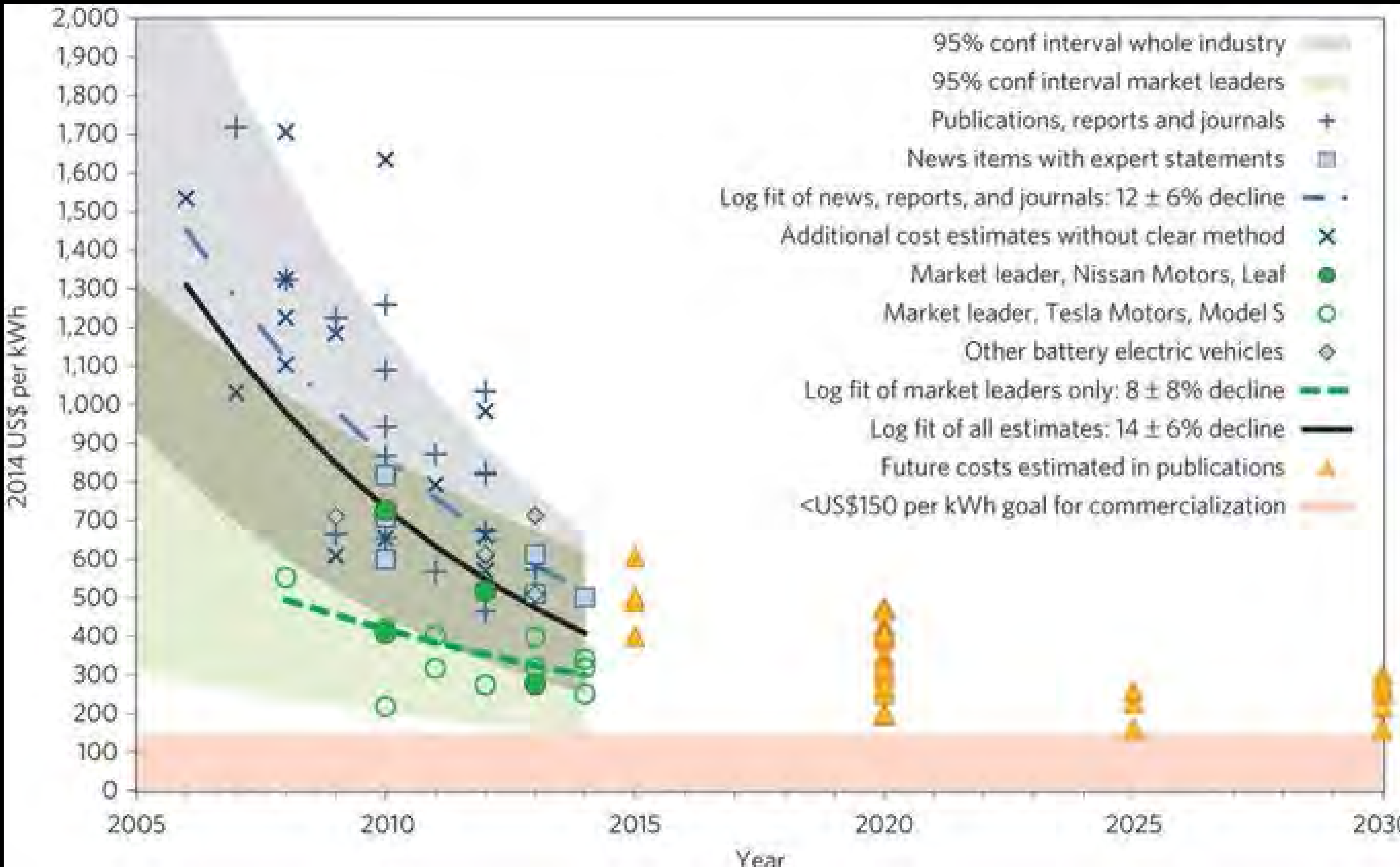
INTRODUCTION

- All EV by 2030: National Mobility Mission; FAME- Rapid scale of commercialization (6-7 million sale by 2020)- April 2015 -2/3/4 Wheelers
- Increase in Fuel Price -daily
- Climate Mitigation- India committed to reduce 25% by 2020 (INDC)
- 175 gW by 2022; 100 - solar, 60 - wind, 10 -small hydro and 5 from biomass – but no storage

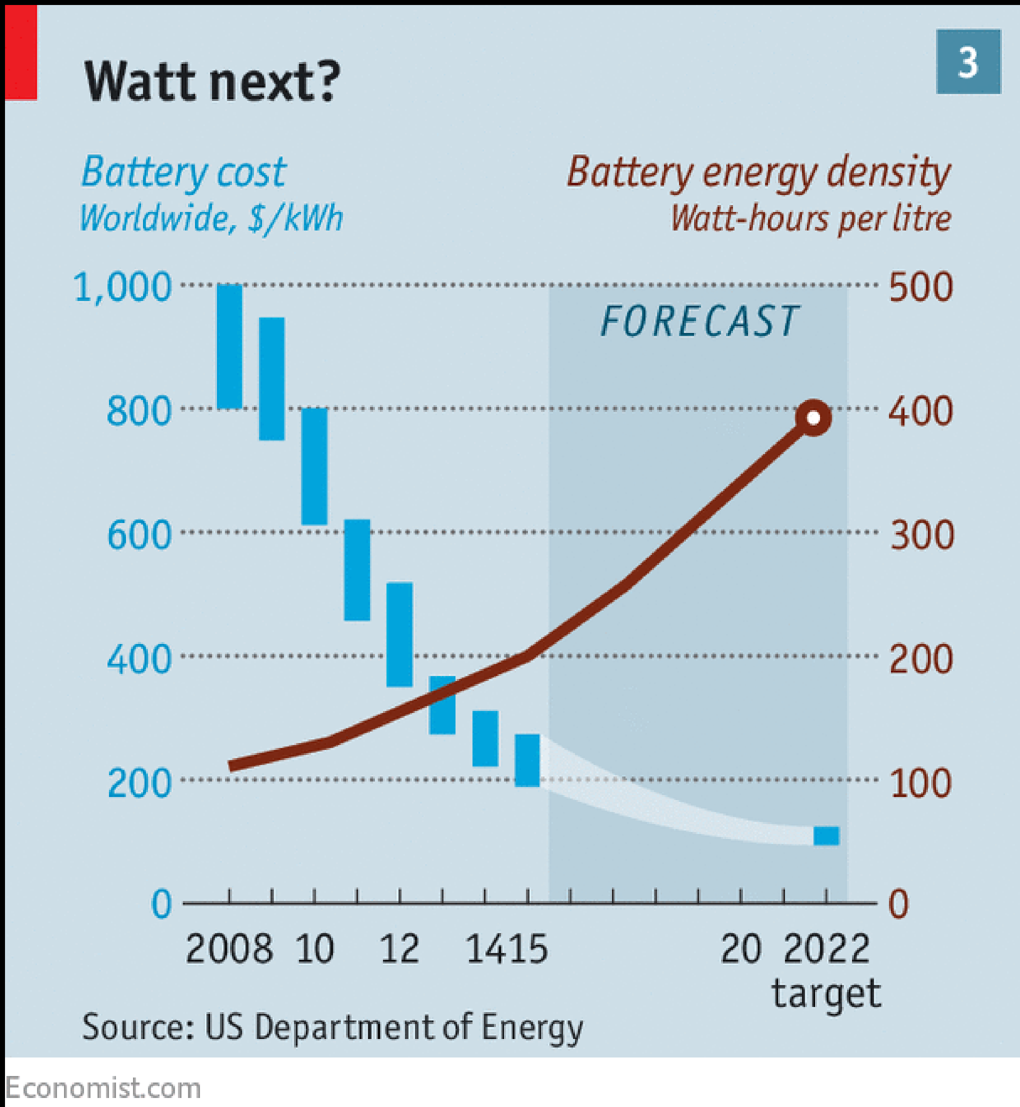
Kyoto Protocol- to expire in 2020
UNFCCC- COP 21 PARIS – ratified by 111
Marrakesh Climate Change Conference COP 22 (190 countries)
US, now Australia - out

China emits 9 gT CO_2/year - India will follow-
Smart Cities, Smart Grid – Carbon neutral to negative
2015-16 (Rs. 75 & 122.90 crore for 2016-17)
Charging Infrastructure; Recyclability

Exponential Evolution of Li-ion Batteries and Rapid Decline of Cost



KEY BARRIERS FOR LARGE SCALE EV PENETRATION



EVs need powerful, light and affordable batteries – Li-ion compact and stable (last 15–20 years, 3 times longer than the 5–7 years for Pb-acid, but still too bulky and expensive – current cost is 3-5 times higher
Safety – overcharge protection currently expensive

Steady improvement for decades - energy stored in 1 L pack has more than tripled (200 to > 700 Wh/L) and cost has fallen 30 times (US$ 150/kWh) still exceeding $100 goal for affordability by DOE - batteries powerful enough for an electric car (50–100 kWh) still weigh 600 kg with 500 L Scarce and expensive materials like Co and Ni – Co prices surged 4 times in the past two years from 22 to 81 $/kg

Agastya battery: the first?

A Sanskrit verse written by Maharishi Agastya in *Agastya Samhita* (7000 years ago!)

संस्था प्ये मृन्मये पत्रे "तम्रपात्र्न" सुसांकरतम
च्छाड्येत शिखी ग्रिवेनड्रारभिही कस्थापन्सुभिही
दस्तलोष्तो निधताव्याहा पारडच्छादितस्ताटाहा
संयोगात जयते तेजो मित्रावरून संघ्यिटम
अणेन जलभगोस्ती प्रणोदनेशू वायूषू
एवं शतना कुंभना संयोगहा कार्यक्ृटसमृताहा

संस्था प्ये (Take) मृन्मये (soil) पत्रे (patra= container) "तम्रपात्र्न" (cleaned copper plate)
सुसांकरतम च्छाड्येत (covered with) शिखी (Morchud = copper sulphate) ग्रिवेनड्रारभिही कस्थाप

Sansthapya Mrinmaya Patre Tamrapatram Susanskritam
Chhadyechhikhigriven Chardrarbhih Kashthpamsubhih
Dastaloshto Nidhatavyah Pardachhaditastah
Sanyogajjayte Tejo Mitravarunsangyitam
Anen Jalbhangosti Prano Daneshu Vayushu
Evam Shatanam Kumbhanamsanyogkaryakritsmrita

mitra = cathode

varuna = anode

pranavayu = oxygen

udanavayu = hydrogen

ghritachi = earthen ceramic beaker

shata kumbh = 100 cells in series to convert chemical energy

to electrical energy

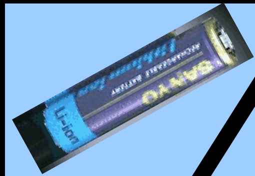
apsara = water tight vessel

A clean copper plate is put in an earthenware vessel. It is covered first by copper sulfate and then moist sawdust. After that put a mercury-amalgamated-zinc sheet on top of an energy known by the twin name of Mitra-Varuna. Water will be split by this current into Pranavayu and Udanavayu. A chain of one hundred jars is used to give a very strong electricity

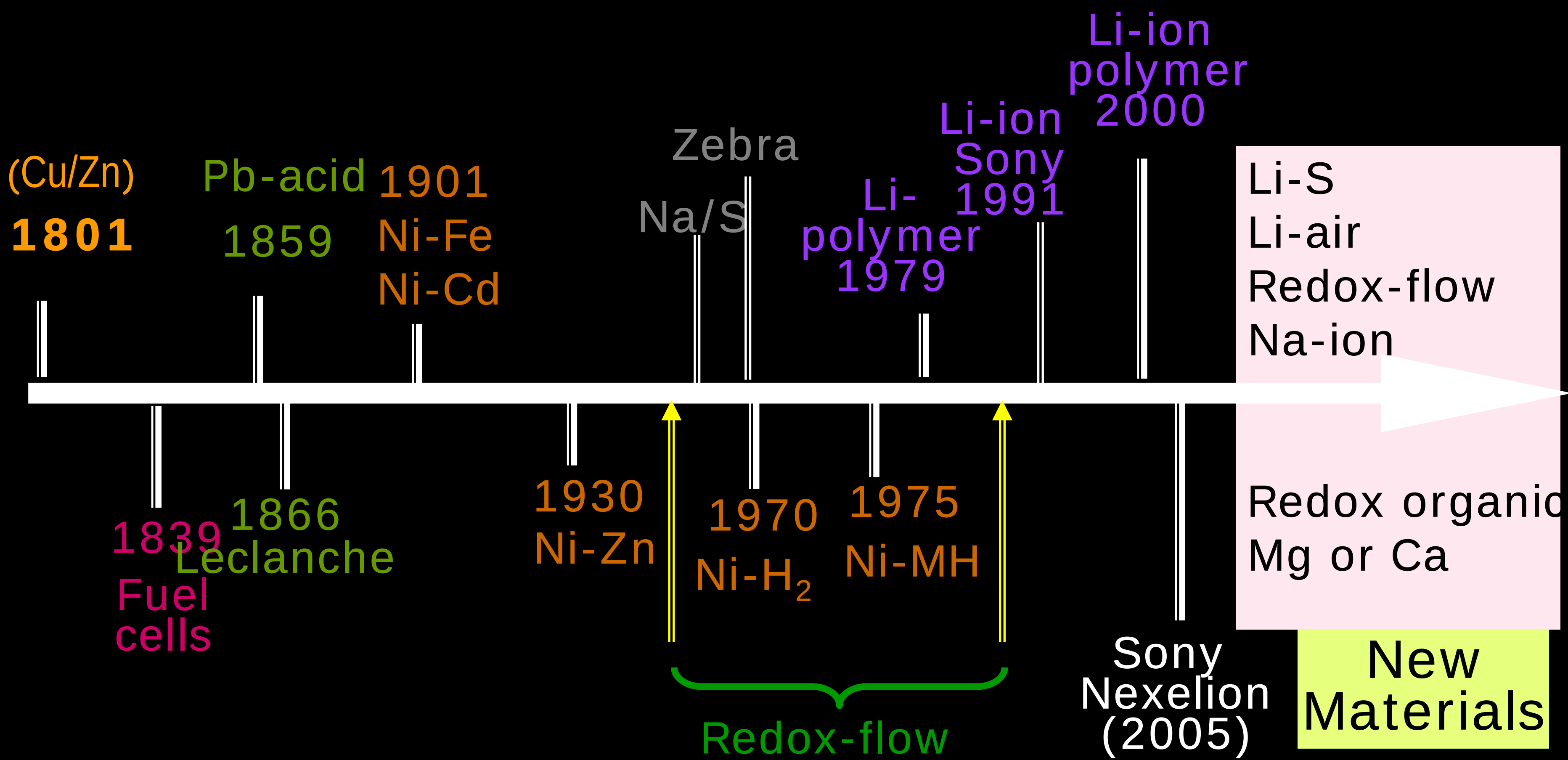
Baghdad batteries (*ca.* 2000 years ago)

container: terracotta jar
cathode: copper cylinder
anode: iron rod
electrolyte: vinegar
separator: non-conducting stopper
debated uses: electroplating;
experiencing god!

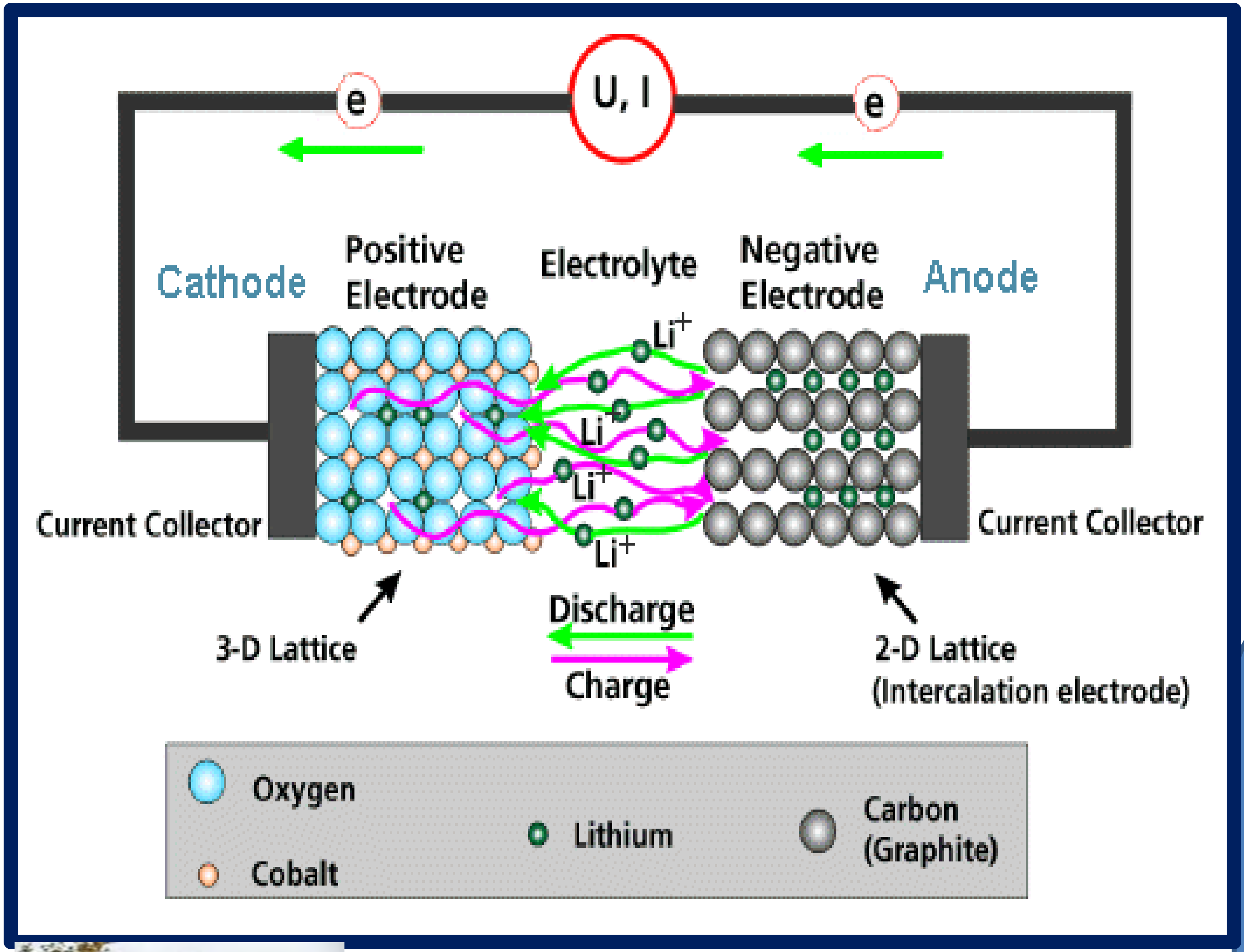
Sumerian batteries (2500 BC)



Evolution of batteries



LITHIUM BATTERY : WORKING PRINCIPLE



OTHER NAMES:

SHUTTLE- COCK BATTERY

SWING BATTERY

ROCKING CHAIR BATTERY

Essential Components

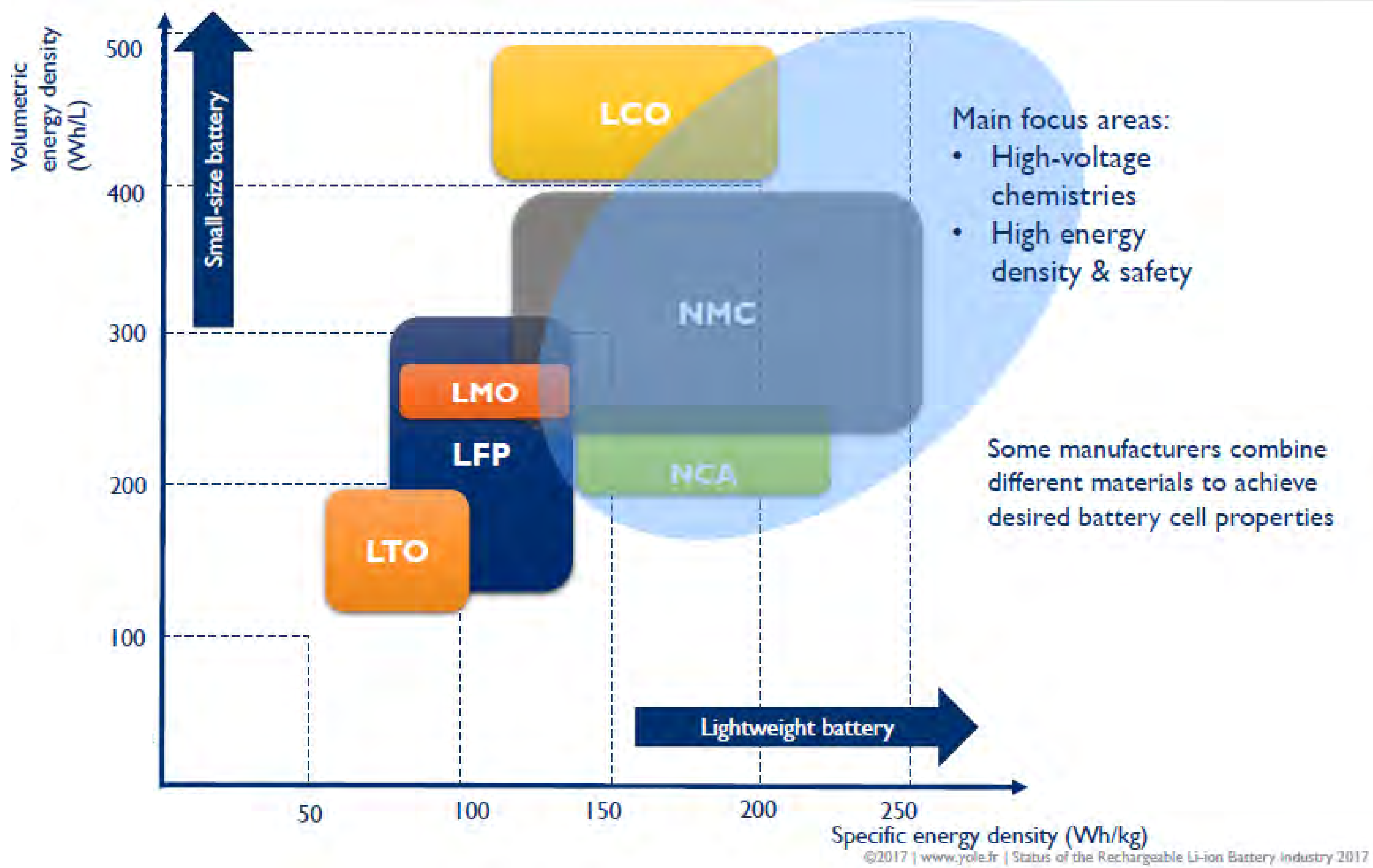
Anode

Cathode

Electrolyte

Separator / Container

Technology Trends –Cell Type

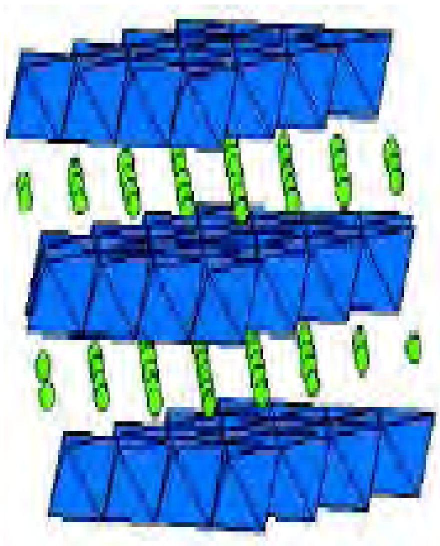


Trend Towards higher energy density (and to a lesser extent , safety) will drive the Li-ion cell type and market share

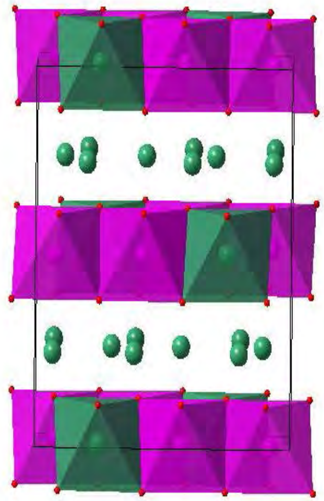
Characteristics of POPULAR cathode materials

Crystal Structure	Compound	Specific capacity mAh/g (theoreticl/experimental/typical commercial cells)	Volumetric capacity (mAh cm^{-3}) (theoretical/ typical in commercial cells)	Average Voltage (V)	Level of Development
Layered	$LiTiS_2$	225/210	697	1.9	Commercialized
	$LiCoO_2$	277/148/145	1363/550	3.8	Commercialized
	$LiNiO_2$	275/150	1280	3.8	Research
	$LiMnO_2$	285/140	1148	3.3	Research
	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$	280/160/170	1333/600	3.7	Commercialized
	$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	279/199/200	1284/700	3.7	Commercialized
	Li_2MnO_3	458/180	1708	3.8	Research
Spinel	$LiMn_2O_4$	148/120	596	4.1	Commercialized
	$LiCo_2O_4$	142/84	704	4.0	Research
Olivine	$LiFePO_4$	170/165	589	3.4	Commercialized
	$LiMnPO_4$	171/168	567	3.8	Research
	$LiCoPO_4$	167/125	510	4.2	Research
Tavorite	$LiFeSO_4F$	152/120	487	3.7	Research
	$LiVPO_4F$	156/129	484	4.2	Research

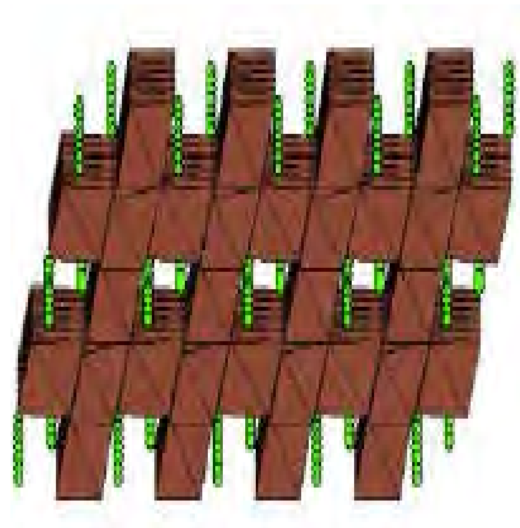
Well-known Cathode Materials for Li-ion Batteries



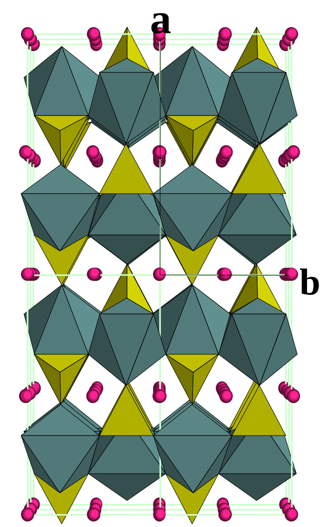
$LiCoO_2$
(layered)



Li_2MnO_3
Li-rich
layered



$LiMn_2O_4$
(Spinel)



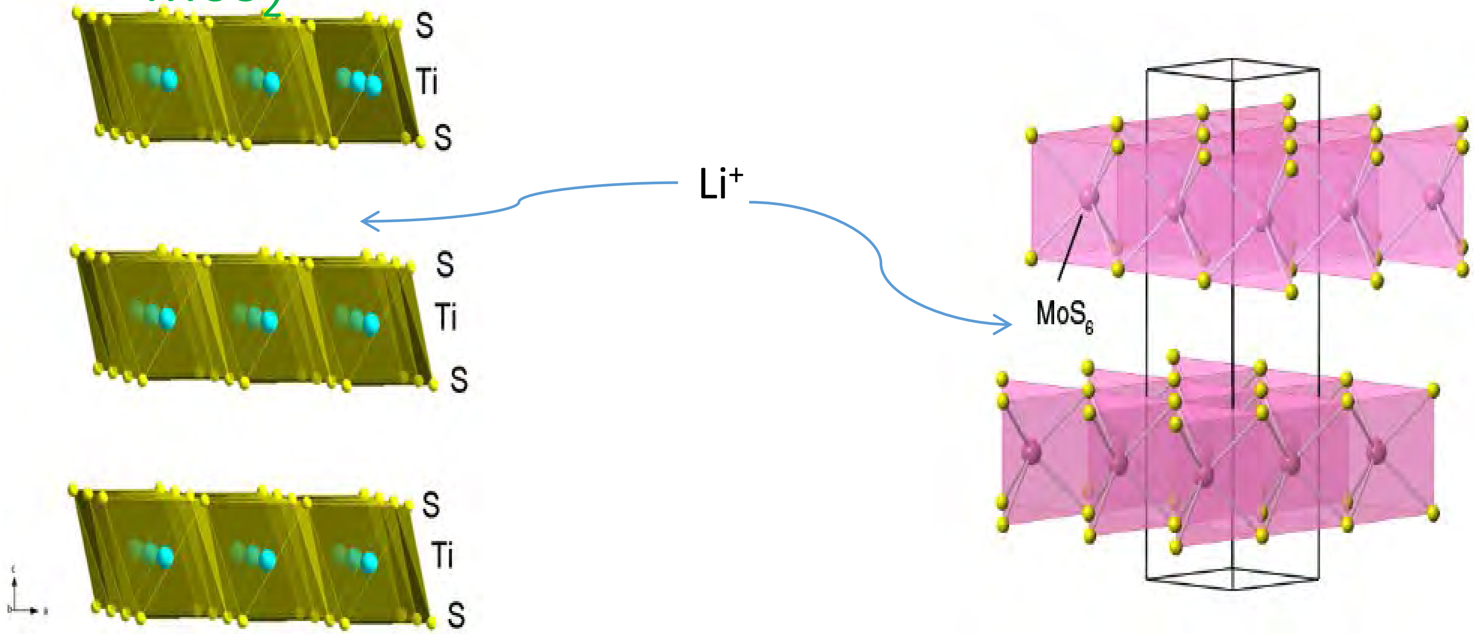
$LiFePO_4$
(Olivine)

Mechanism: Li deintercalation-reintercalation during charge-discharge process

Metal dichalogenides: The early known Li^+ intercalation layered compounds

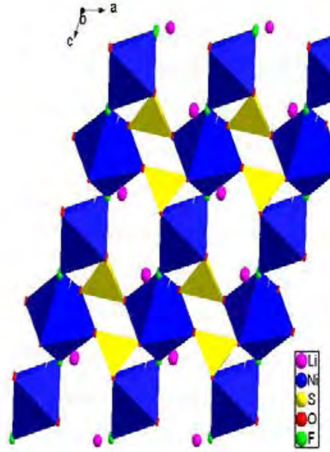
TiS_2

MoS_2

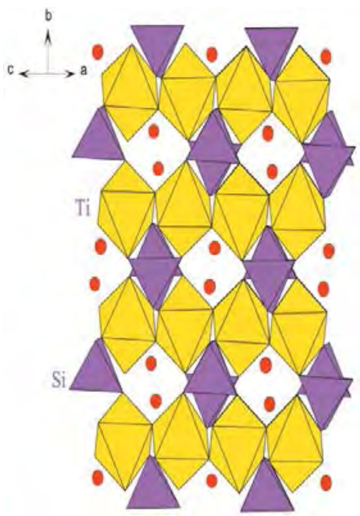


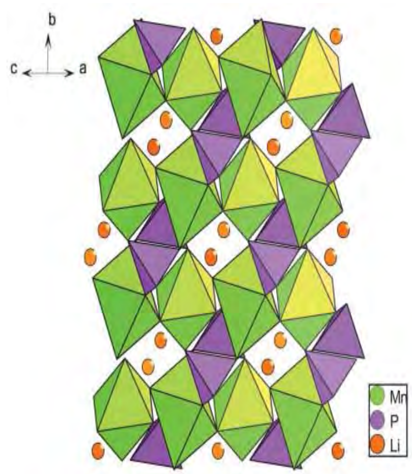
Whittingham, Science. **192**, 1126 (1976).

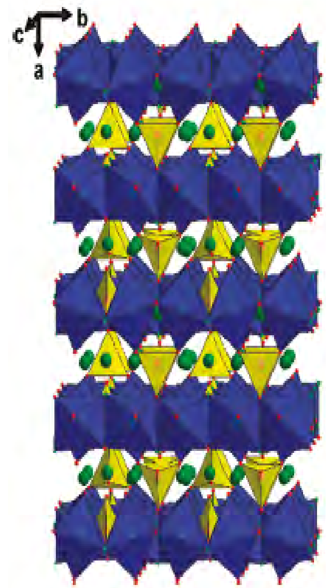
Whittingham, Mater. Res. Bull. **10**, 363 (1975).



$LiMSO_4F$ (M = Fe, Co, Ni)
– Keiserite like structure
($LiMgSO_4F$)







$CaTiOSiO_4$ (sphene)
$Li_2CoPO_4(OH)$

$LiMnPO_4(OH)$

J. Gopalakrishnan, J. Mater. Chem. **13**, 433 (2003)

Cathodes: Comparison of Oxide *vs.* Phosphate

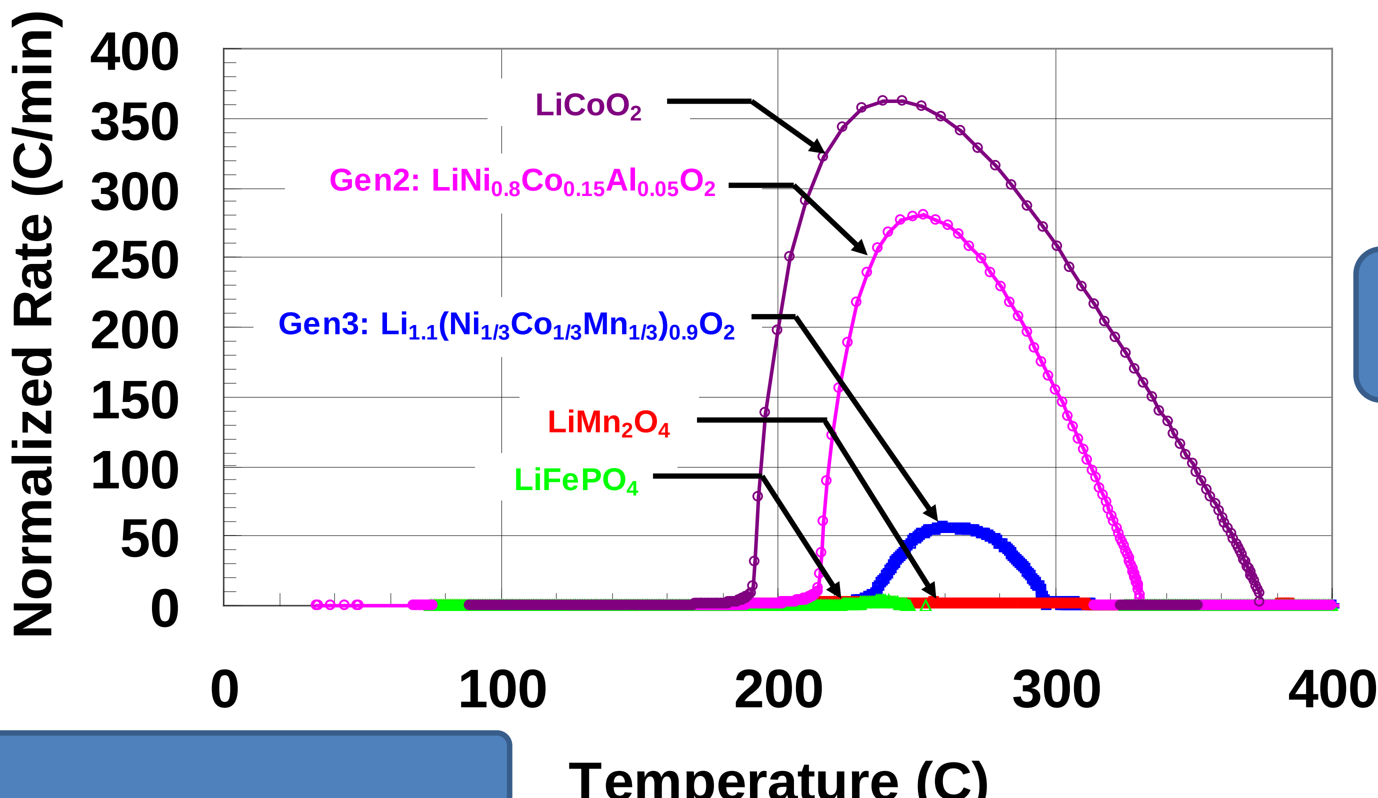
Oxide Cathodes :: (+) High Capacity, Cycleability, Proven cathode candidates

$Li_xMO_2^{-n}$ (-) Chemical instability, Off-stoichiometry and Poor safety

Polyanionic Cathodes:: (+) Inherent safety and High voltage possibilities

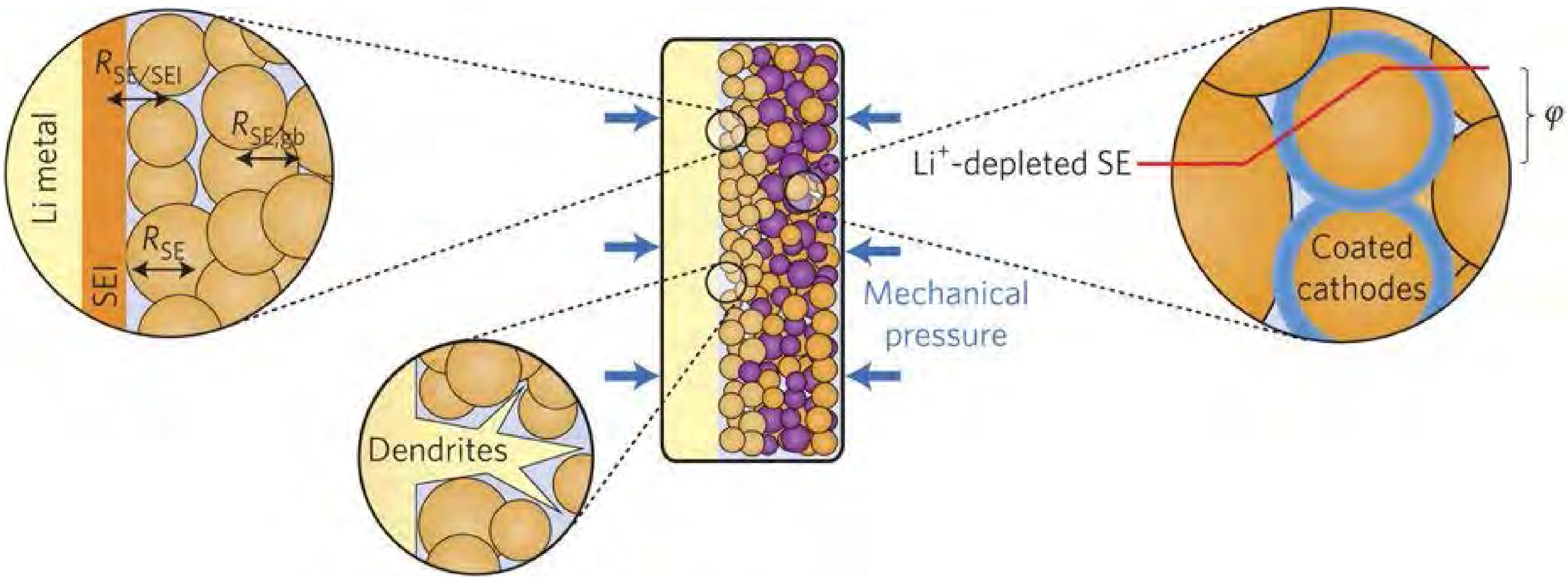
$Li_xM(XO_4)^{-n}$ (-) Poor electronic conductivity, Inferior capacity

Thermal stability of Oxide vs. Phosphate cathodes



Phosphates are better than oxides

Major challenges in developing solid-state batteries



Li metal gives 500 Wh/kg but a resistive SEI between anode and electrolyte (RSE/SEI) complicates; the grains and grain boundaries also (RSE,gb) adds and dendrite formation due to highly inhomogeneous lithium metal deposition - serious risk of short-circuiting. Most SEs react with cathode active materials and need to be protected by coating the active material. Potential Li depletion at the cathode (space charge with rectifying effect) to be avoided by a coating. The red curve indicates the drop of potential φ across the space charge; blue arrows- mechanical pressure required to avoid contact loss due to local volume changes upon lithiation/delithiation .

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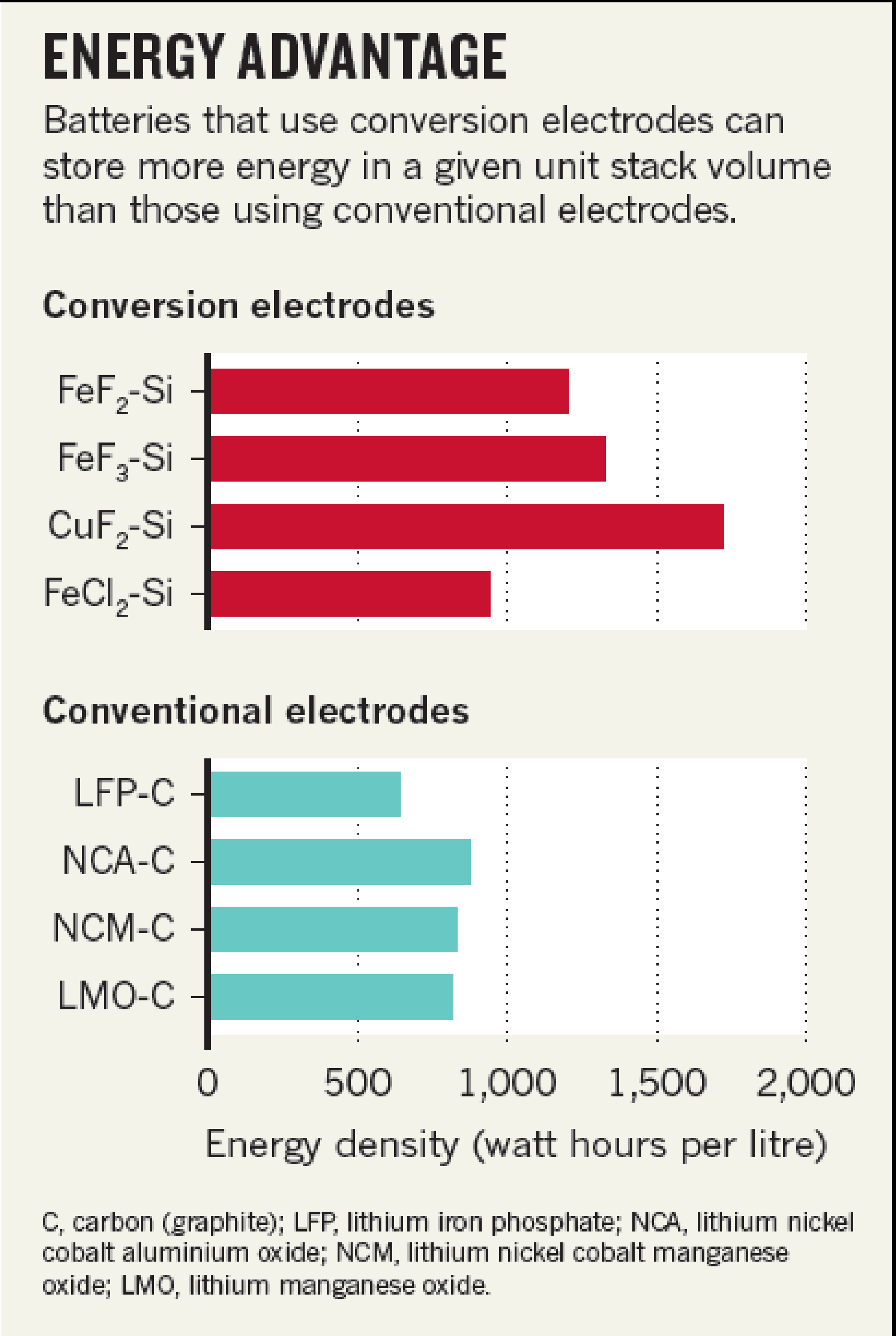

FLUORINATED SOLVENTS AS POTENTIAL ELECTROLYTES FOR HIGH VOLTAGE CATHODES

- Fluoro-EC
- Fluorinated Alkyl EC
- Fluorinated Ether EC
- Fluorinated Linear Carbonate
- Fluorinated Ether
- Fluorinated Linear Sulfone
- Fluorinated Sulfone
- DFT calculations of Redox potential or conductivity
- Leakage current measurements

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Road to Super-Batteries for Tomorrow

CURRENT	FUTURE 425 km range; Functional, Green & Cool
250 Wh/kg ; 650 Wh/L  	500 Wh/kg: 1500 Wh/L Solid-state Li batteries: smaller, cheaper and higher capacity: could potentially charge faster, last longer, and better overall performance for safer EVs
L[illegible] Si, Sn) Li_xMO_2, LiM_2O_4, $LiMPO_4$ Li or Na ion glass electrolyte $\sigma_i > 10^{-2}$ S/cm at 25 °C	Li Metal Anode; Na or Mg Air or Oxygen; Sulphur
Liquid Electrolyte Polymeric Separator	Polymer/Ceramic Electrolytes Smart Composite Separator

$ 100/kWh
Roll-to-roll Process
3-D Printing
AI-enabled BMS software
Layer-by-Layer – paint or skin

Sakti3 24M
Amprius SeeO
SiNode Systems Graphenenano
SiLa Nano Grabat Energy
Blue Current Envia (123)
Nexelon Axion (LLZO)
NanoExa (Sujit Kumar & Sinkula)

Cell generation	Cell chemistry
Generation 5	• Li/O_2 (lithium-air)
Generation 4	• All-solid-state with lithium anode • Conversion materials (primarily lithium-sulphur)
Generation 3b	• Cathode: HE-NCM, HVS (high-voltage spinel) • Anode: silicon/carbon
Generation 3a	• Cathode: NCM622 to NCM811 • Anode: carbon (graphite) + silicon component (5-10%)
Generation 2b	• Cathode: NCM523 to NCM622 • Anode: carbon
Generation 2a	• Cathode: NCM111 • Anode: 100% carbon
Generation 1	• Cathode: LFP, NCA • Anode: 100% carbon

> 2025 ?

~ 2025

~ 2020

current

BATTLE AT THE UNIVERSITY OF TEXAS

1992 - Akshaya Padi - Olivine compounds
Shigeto Okada arrived in 1993 from NTT
– tinked spinel formulation with Co, V, Mn
Developed a secret formulation and in 1995 filed a patent with NTT for LFP -   UT filed a 500 million patent suit against but eventually settled for 30 million from NTT

An MIT professor   Yet-Ming Chiang   tweaked Goodenough's idea and filed   patents for improved material, in a company called A123 & this company persuaded a European tribunal to strike down the old man's patents, which it eventually did in 2008.
The result was a free-for-all, one that reached an apex late in 2008 when Warren Buffett spent $230 million to buy 10 percent of BYD, a Chinese car company used a new LFP powered EV. In 2009, A123 sold shares Chiang's company raised $587 million, Except, again, Goodenough. In the end, the UT settled with NTT. The payoff to the school was $30 million along with a share of any profit from its Japanese patents, recognition that Goodenough had been infringed

BE THE FIRST TO PARK ONE IN YOUR DRIVEWAY: Introducing the Tucson Fuel Cell, Hyundai's first-ever, hydrogen-powered vehicle with zero-emissions. ..And it can be yours.

2007 - Honda FCX Clarity - hydrogen fuel cell; 2010 - Mercedes-Benz F-Cell; 2014 - Hyundai Tucson FCEV; 2015 - Toyota Mirai - production version of the FCV concept car; 2016 - Riversimple Rasa; 2016 - Honda Clarity Fuel Cell; 2018 - Hyundai Nexo

BATTLE AT THE UNIVERSITY OF TEXAS

1992 - Akshaya Padi - Olivine compounds

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– tinkered spinel formulation with Co, V, Mn
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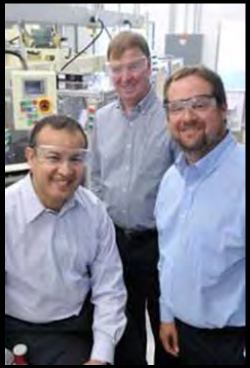

MIT - Yet-Ming Chiang tweaked patents for
improved material,(A123) persuaded a European
tribunal to strike down patents, (2008)
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The fierce war between Start-ups and Venture capital firms
for the most promising ideas.

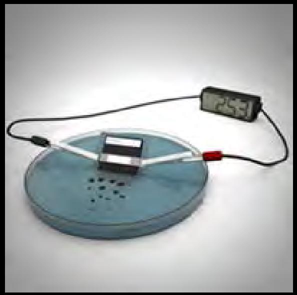
TESLA – GM BATTLE

Toward the end of 2014, - rivalry Tesla with GM to produce the 200 mile electric for mass-market in 2017 - the Model III @ $35,000. The top electrics—the Volt, the Leaf, and Musk's Model S— 2,000 to 3,000 vehicles a month each, but 40,000 for BMW 3-Series, the entry-level gasoline-driven luxury. Musk promised 500,000 electrics a year by 2020.

"GM has observed a significant and very large disparity between the data obtained from Arpa-E cells and proof of concept cells based on 400 wh/kg technology we sent them for testing

Just a year after losing the GM contract, Envia was awarded two grants totaling $7.2 million aimed at making NMC 2.0 work. One of the grants from a government backed consortium (GM, Ford, and Chrysler) - gamble on Envia

ALL SOLID STATE LITHIUM



Edible Battery Could Enable Future Medical Devices!

Self-destructing Li-ion battery propels promise of transient electronics

Li-ion Batteries: Indian Technologies

ISRO	CSIR Technology	ARCI Technology
PRISMATIC CELLS NCA CHEMISTRY ROBUST ENGINEERING TESTED AND VALIDATED AS BATTERY PACKS TESTED FOR ROCKETS THERMAL MANAGEMENT HIGHER TRL? INTERFACE WITH BMS SUPERIOR SAFTY FEATURES COST? FREEDOM TO PRACTICE? IP RIGHTS?	18650 AND POUCH CELLS TRL-5/6 OWNS IP RIGHTS IN KOREA, JAPAN, CHINA, US …….. SYNERGY FROM LABS (NPL, CGCRI, CECRI, IICT?) FLEXIBLE : NMC,LCO,LTO <5 Ah LINK WITH SUPPLY CHAIN STRENGTH WITH ELECTROCHEMISTRY BATTERY PACK NOT VALIDATED FOR EV? SEMIAUTOMATIC? COST? SCALE-UP?	PRISMATIC CELLS LFP CHEMISTRY *TRL-5/6* *BETTER CREDIBITY AND INDUSTRIAL TRACK RECORD* *STRENGTH IN SCALE-UP* *STRONG MATERIALS ENGINEERING GROUP* *FREEDOM TO PRACTICE* *40 Ah* *COST?* *PART IP?* *HOW MUCH INDIGENEOUS?*

IIT-Mumbai, - Cell Fabrication Facility & Strenghth in Materials

"The storage battery is, in my opinion, a catchpenny, a sensation, a mechanism for swindling the public by stock companies. The storage battery is one of those peculiar things which appeals to the imagination, and no more perfect thing could be desired by stock swindlers than that very selfsame thing. . . . Just as soon as a man gets working on the secondary battery it brings out his latent capacity for lying"

Thank You

1883

Thomas Alva Edison