



Review of status of the main chemistries for the EV market

EMIRI – Energy Materials Industrial Research Initiative
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www.emiri.eu

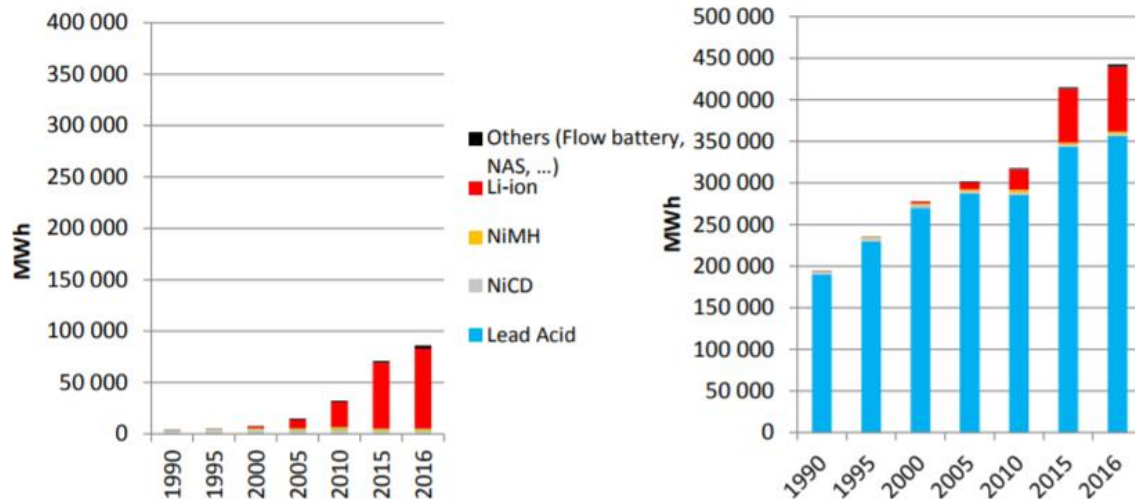
Agenda

- 1. Review of status of **current** main battery chemistries for EV's:
 - Market prospects E-mobility/Li Ion
 - Li Ion battery chemistries ; trends to NMC types
 - Key to succes is cost reduction Li Ion
- 2. Advanced materials pave the way to **new** battery chemistries:
 - EU-SET Plan-10 targets and key actions
 - Roadmap Li Ion 2020->2030 :
 - Advanced Li Ion batteries
 - Solid State Li Ion batteries
 - Beyond 2030: Novel chemistries
- 3. **EMIRI** battery program

1. Market prospects E-mobility/Li Ion (Source Avicenne/Umicore 2017): X9 by 2025



THE WORLDWIDE BATTERY MARKET 1990-2016

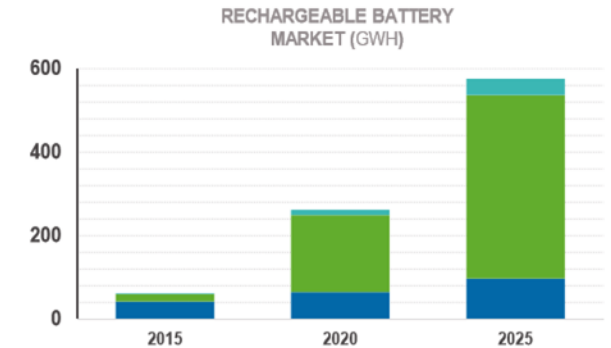
Lithium Ion Battery: Highest growth & major part of the investments
Lead acid batteries: By far the most important market (90% market share)



Exciting market potential

umicore

-  **Portable**
Societal driver
-  **Electrification**
Regulatory driver
-  **Energy Storage System**
Regulatory driver



The main growth driver will be vehicle electrification







European Innovation Summit 2017 November 28th 2017 –European Parliament



Li Ion to remain EV technology of choice

- Traction batteries are considered as a Key Enabling Technology in electric vehicle (EV) drive trains. Current traction batteries are, to a large extent, based on lithium-ion (Li-ion) chemistry which is expected to remain the technology of choice for many years to come (decades). In the longer future, other lithium (Li) and non-Li based chemistries are expected to gain ground.

Li Ion battery chemistries: trends to NMC types

	Energy	Power	Safety	Life	Cost	
LCO lithium cobaltite LiCoO_2	+++	+++	+	++	+	
NCA lithium nickel aluminium cobalt oxide $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	+++	++	-	++	-	
LMO lithium manganese oxide LiMn_2O_4	-	+++	++	-	++	
NMC nickel manganese cobalt $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$	++	++	++	+++	+++	 
LFP lithium iron phosphate LiFePO_4	+	+++	+++	++	++	



Segment	Cathode Material Options		
Portables Premium	HE LCO	✓	NMC/NCA ✓
Portables Standard	NMC	LCO	LMO
Automotive 'Energy'	NMC/NCA ✓		LMO
Automotive 'Power'	NMC/NCA ✓	LMO	LFP
Energy Storage System	LFP	NMC/NCA ✓	LMO

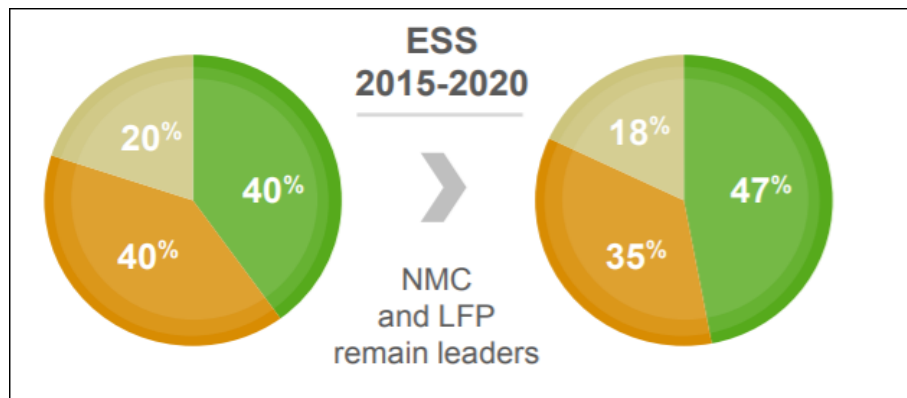
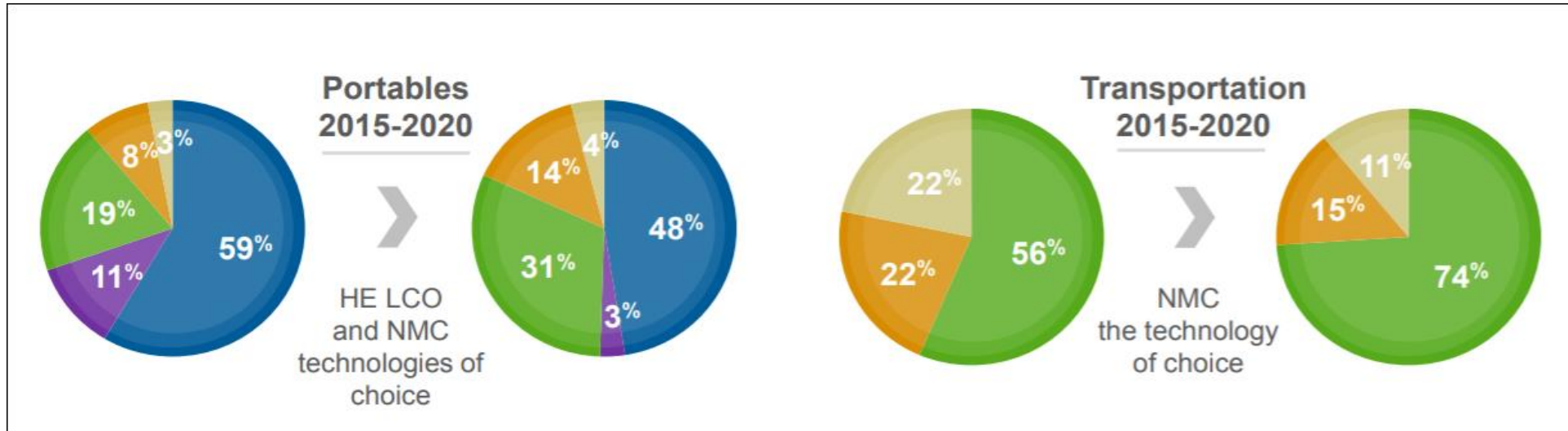
● Umicore present

Umicore's portfolio focuses on **sizeable segments offering significant market growth**

Major types cathode materials for rechargeable Li ion batteries:

- Layered cathodes (incl. LiCoO_2 (LCO), NMC, NCA) : > 90% of market
- Phosphates (LiFePO_4) (LFP)
- LiMn_2O_4 spinel (LMO)

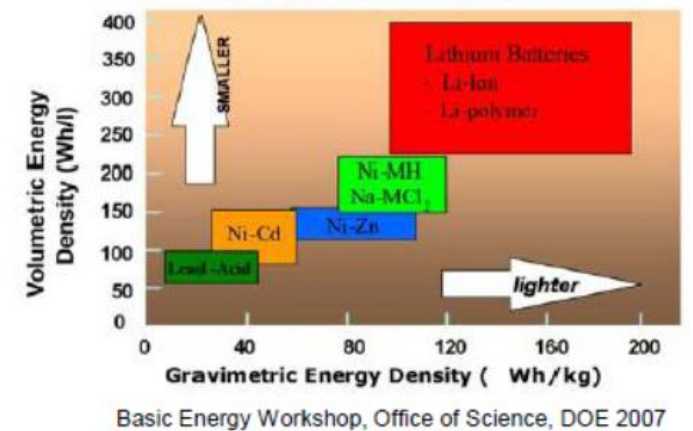
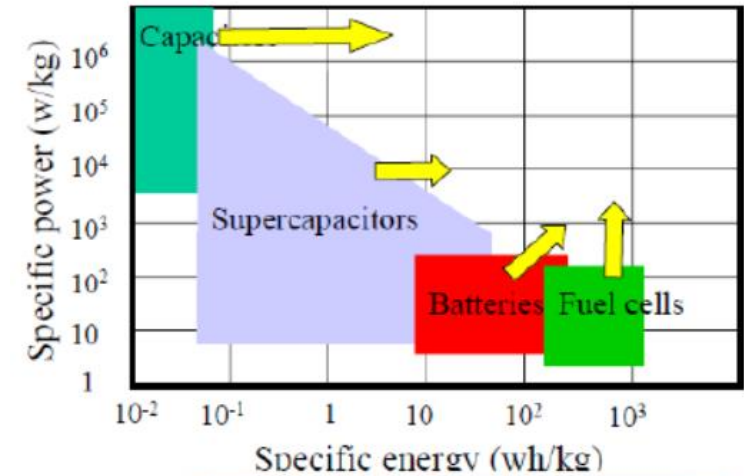
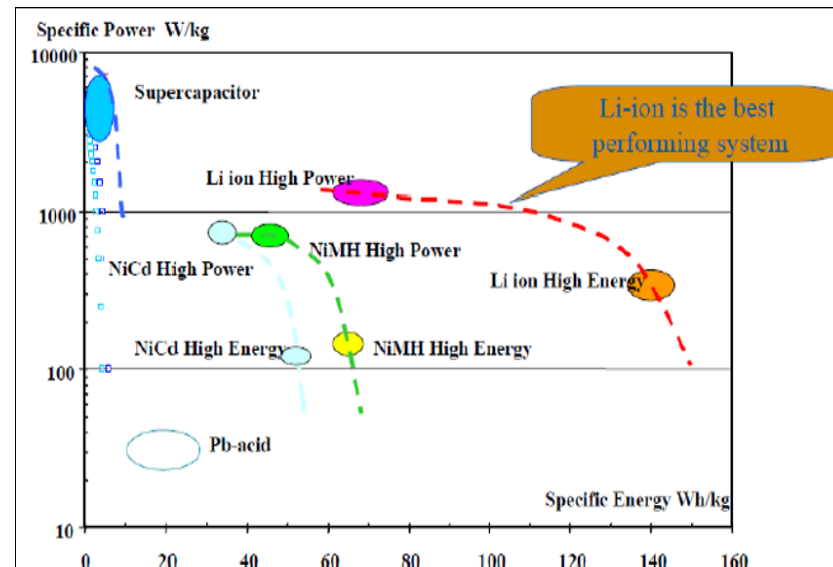
Li Ion battery chemistries: trends to NMC types



Umicore Markets Day Presentations - 03/09/2015

Key parameters

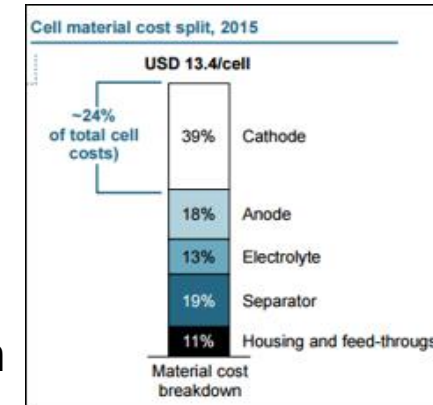
- Energy Density
- Power density
- Cycle life, Lifetime
- Charging rate
- Temperature stability
- Safety, Cost
- Manufacturability



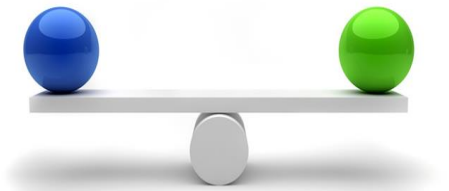
Key to success is cost reduction Li Ion

- Cathode Material = Key cost / performance driver

By 2030, pack cost in € /kWh has to come down to **< 100 €/kWh**
 For stationary applications down to **< 0,05 €/kWh/cycle**

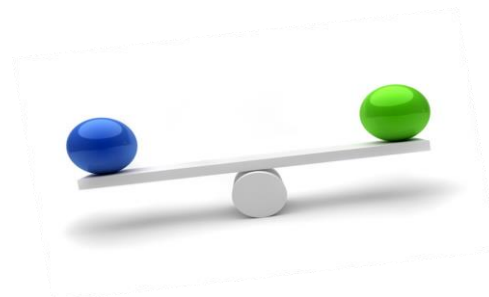


R.Berger



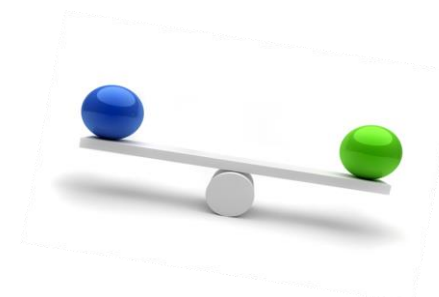
Price: \$/kg

- Cheaper Metal base
- Economies of scale
- Increased yield



Performance: kg/kWh

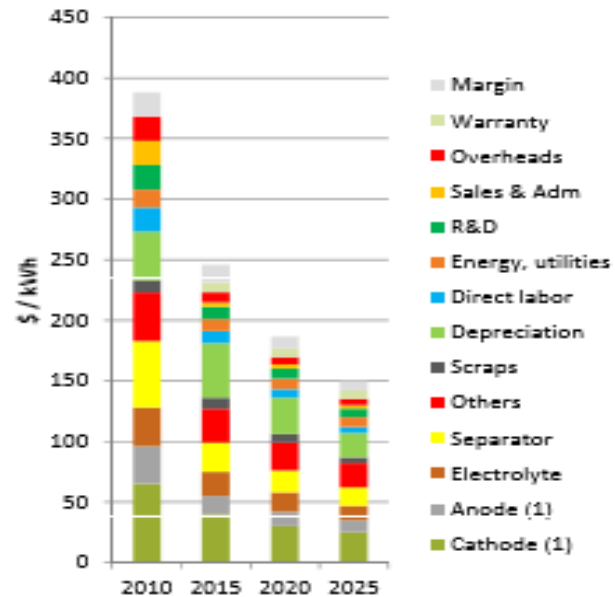
- Higher Energy density
- Higher Voltage
- "Intelligent design"



And cost is evolving to targets

LI-ION BATTERY COST 2015-2025

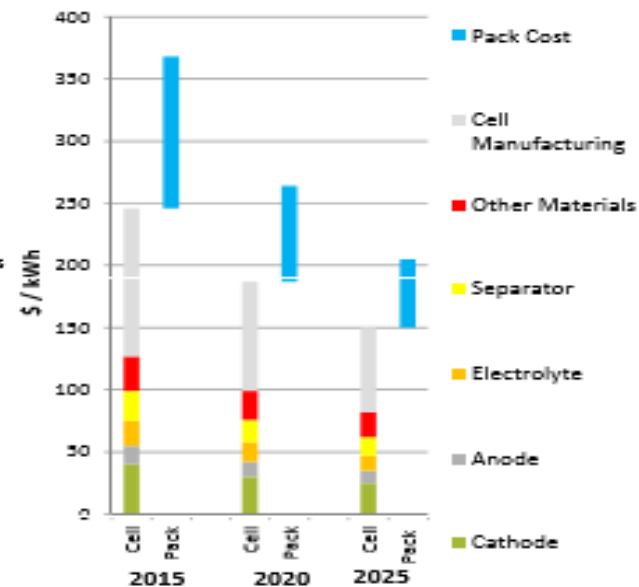
LIB cell average cost (36Ah pouch)
(EV design ; LMO/NMC cathode)



(1) Active materials only

Source: AVICENNE ENERGY 2016

LI-ION BATTERY PACK COST
FOR EV



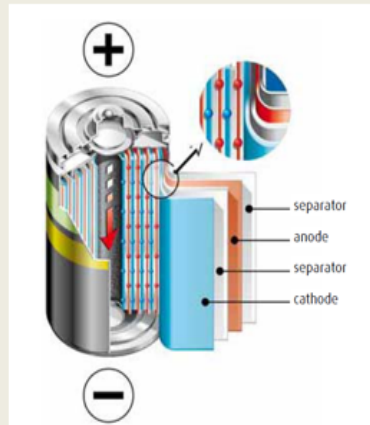
* For Production > 100 000 packs/year

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2. Advanced materials pave the way to **new** battery chemistries



Current Li-ion battery materials

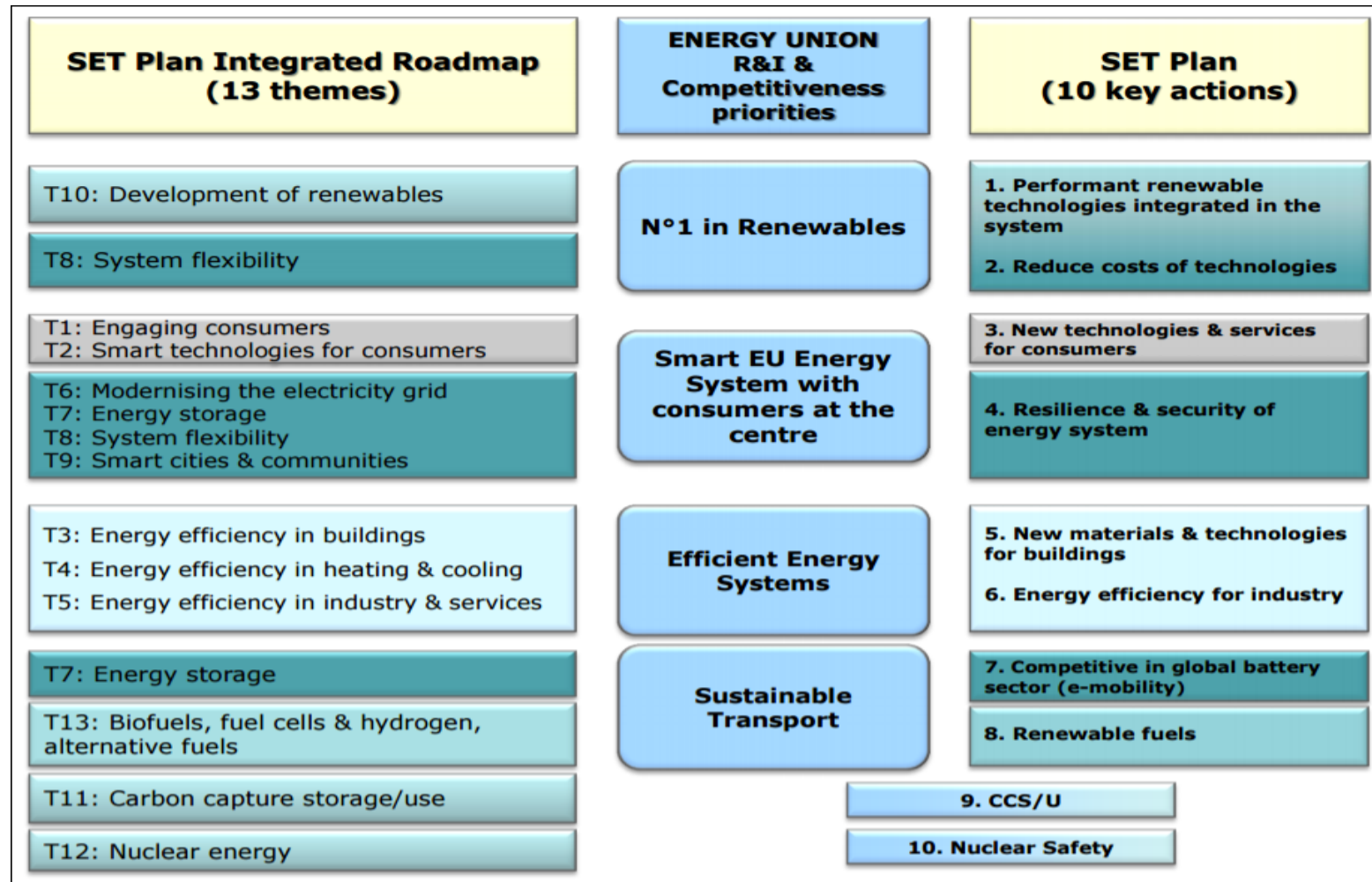


- Anode (= negative)
 - graphite/carbon
- Separator
 - Ion permeable inert membrane
- Cathode (= positive)
 - Lithium cobaltite and new generation materials
- Electrolyte
 - Liquid or gel

Charge: Li-ions from cathode to anode

Discharge: Li-ions from anode to cathode

EU-SET Plan-10 targets and key actions



R&I targets on performance, cost, manufacturing

- **Basis:** as set to the Implementation Plan of **Key Action n°7** of the SET Plan

Table a

		Current (2014/ 2015)	2020	*2030
Performance targets for automotive applications unless otherwise indicated				
1	Gravimetric energy density [Wh/kg]			
	pack level	85-135	235	> 250
	cell level	90-235	350	> 400
2	Volumetric energy density [Wh/l]			
	pack level	95-220	500	> 500
	cell level	200-630	750	> 750
3	Gravimetric power density [W/kg]			
	pack level	330-400	470	> 470
	cell level		700	> 700
4	Volumetric power density [W/l]			
	pack level	350-550	1.000	> 1.000
	**cell level		1.500	> 1.500
5	Fast recharge time [min] (70-80% ΔSOC)	30	22	12
6	Battery life time (at normal ambient temperature)			
	Cycle life for BEV*** to 80% DOD [cycles]		1.000	2000
	Cycle life for Stationary to 80% DOD [cycles]	1000-3000	3000-5000	10000
	Calendar life [years]	8-10	15	20

*: Post-Lithium ion technologies are assumed relevant in this time frame

**: May also be relevant to stationary applications

*** Cycle life for PHEV must be bigger

Table b

	TARGETS	Current (2014/ 2015)	2022	2030
Cost target				
1	Battery pack cost for automotive applications [€/kWh]	180-285	90	75
2	Cost for stationary applications requiring deep discharge cycle [€/kWh/cycle]		0,1	0,05

R&I targets on performance, cost, manufacturing

Table c

TARGETS		Current (2014/ 2015)	2020	2030
Manufacturing targets				
1	Automotive (Li-ion and next generation post-lithium) battery cell production in EU [GWh/year] ¹ (% supporting EU PHEV+BEV production)	0,15 – 0,20	5 (50% of the 0.5 M EVs with 20 kWh)	50 (50% of the 2 M EVs with 50 kWh)
2	*Utility Storage (Li-ion and next generation post-lithium) battery cell production in EU [GWh/year]	0,07 – 0,10	2.2	10
3	Recycling			
	**Battery collection/take back rate	45% (Sept 2016)	70%	85%
	Recycling efficiency (by average weight)	50%	50%	50%
	Economy of recycling	Not economically viable	Break even	Economically viable
4	Second Life	Not developed	Developed	Fully established

Implementation Plan Action 7 SET Plan endorsed and published

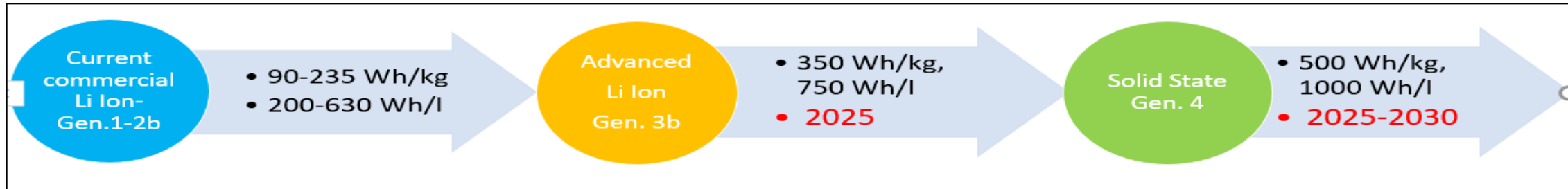


Integrated SET-Plan Action 7

~ Implementation Plan ~

"Become competitive in the global battery sector to drive e-mobility and stationary storage forward"

Roadmap Li Ion 2020->2030



Cell generation	Cell chemistry
Generation 5	<ul style="list-style-type: none"> Li/O₂ (lithium-air)
Generation 4	<ul style="list-style-type: none"> All-solid-state with lithium anode Conversion materials (primarily lithium-sulphur)
Generation 3b	<ul style="list-style-type: none"> Cathode: HE-NCM, HVS (high-voltage spinel) Anode: silicon/carbon
Generation 3a	<ul style="list-style-type: none"> Cathode: NCM622 to NCM811 Anode: carbon (graphite) + silicon component (5-10%)
Generation 2b	<ul style="list-style-type: none"> Cathode: NCM523 to NCM622 Anode: carbon
Generation 2a	<ul style="list-style-type: none"> Cathode: NCM111 Anode: 100% carbon
Generation 1	<ul style="list-style-type: none"> Cathode: LFP, NCA Anode: 100% carbon

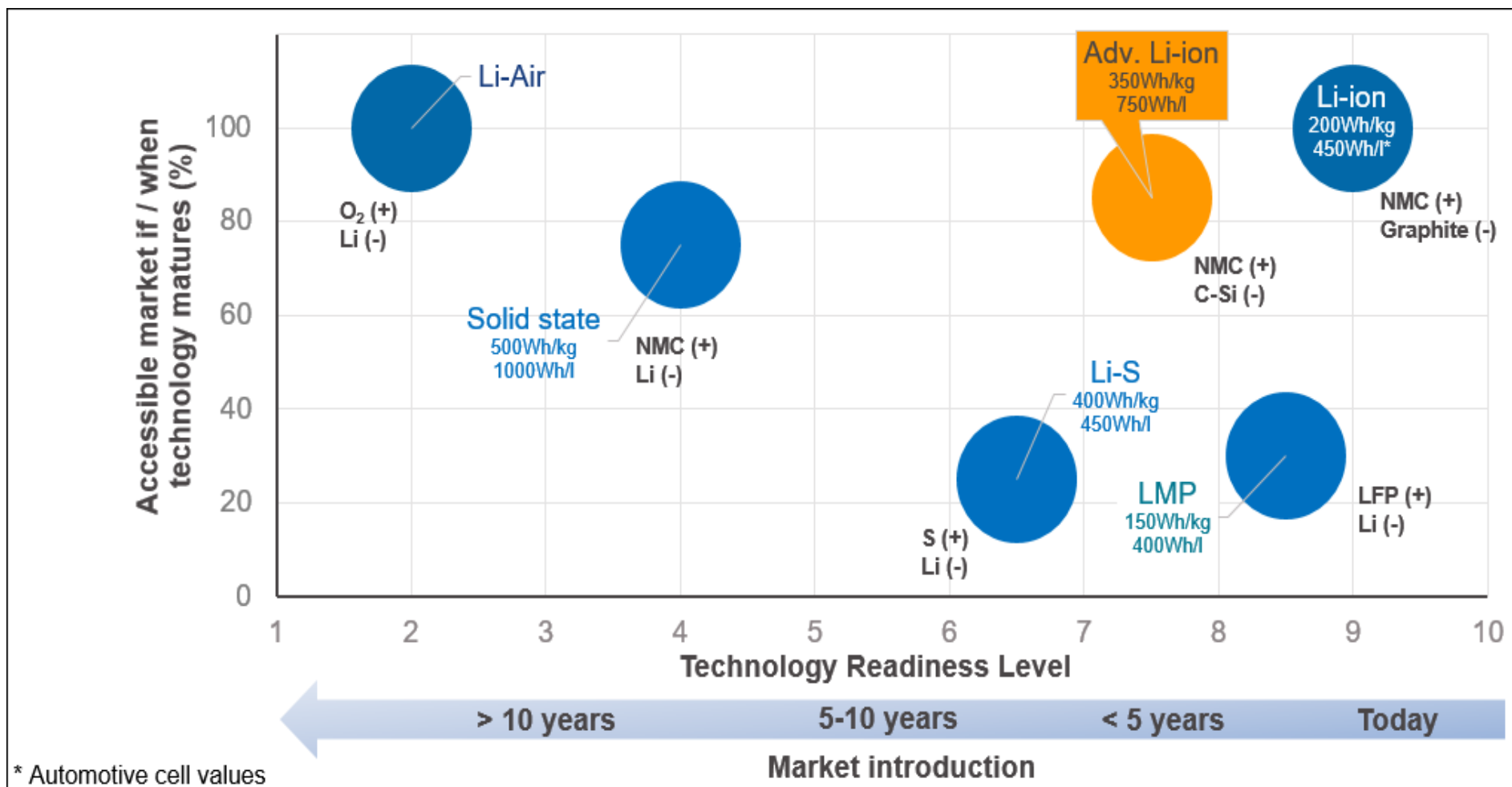
Timeline markers for the table:

- > 2025 ? (for Generation 5)
- ~ 2025 (for Generation 4)
- ~ 2020 (for Generations 3a and 3b)
- current (for Generations 1, 2a, and 2b)

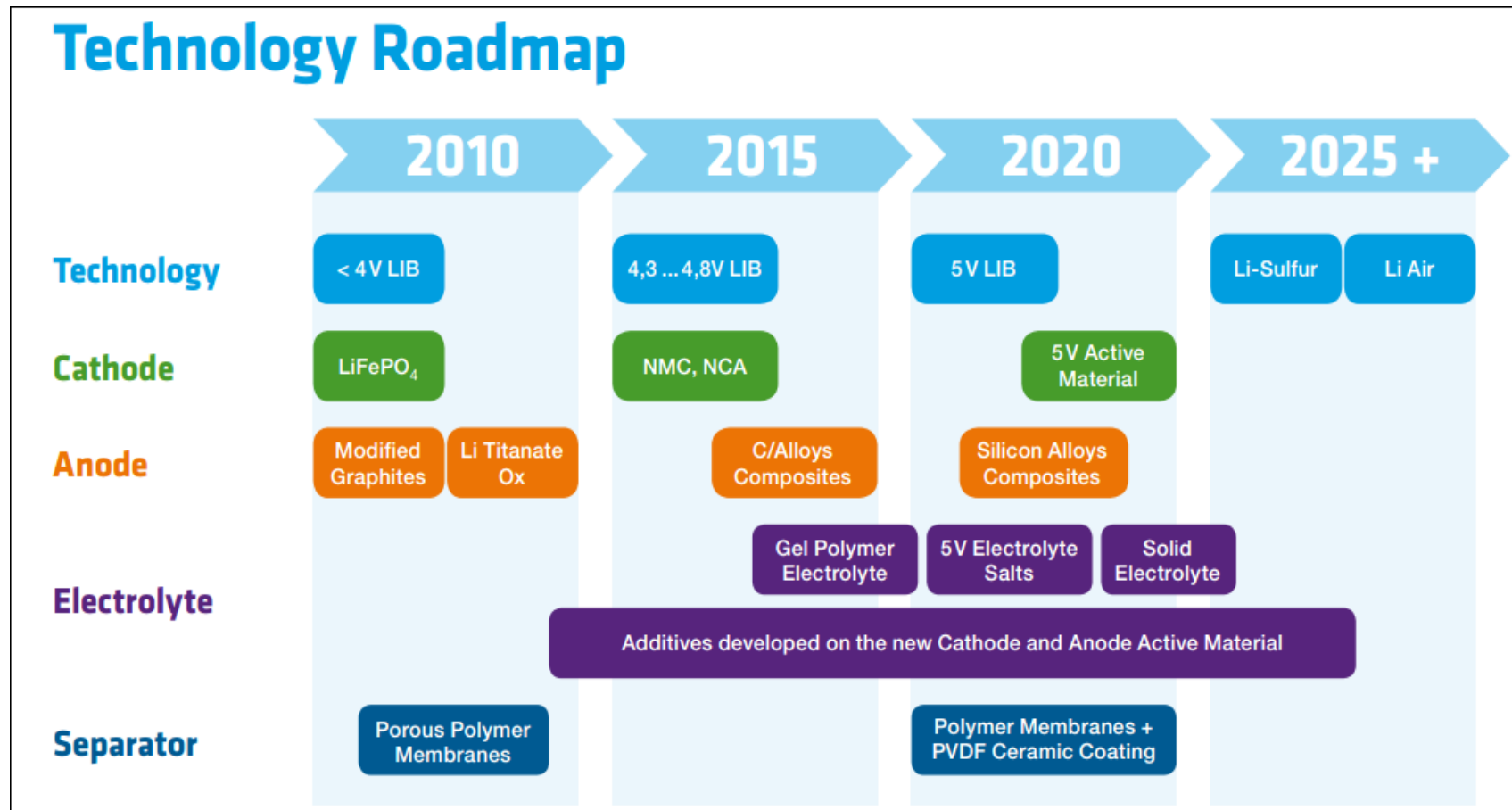
Discussion paper EU
Workshops Jan.18

Nationale Plattform Elektromobilität: Roadmap integrierte Zell-
und Batterieproduktion Deutschland, Jan. 2016

Advanced Li Ion batteries

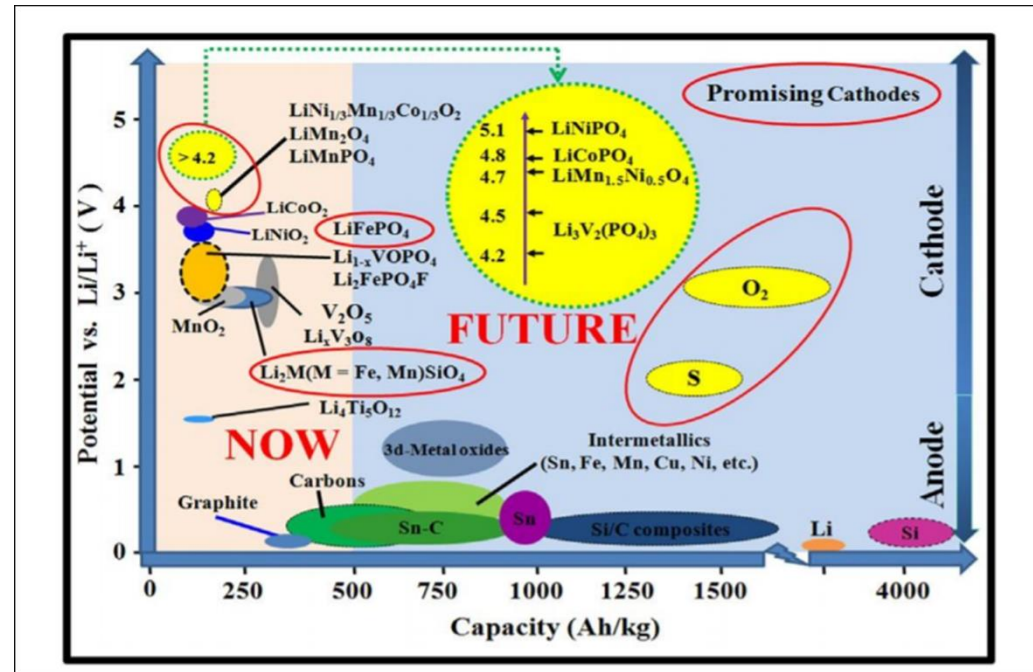
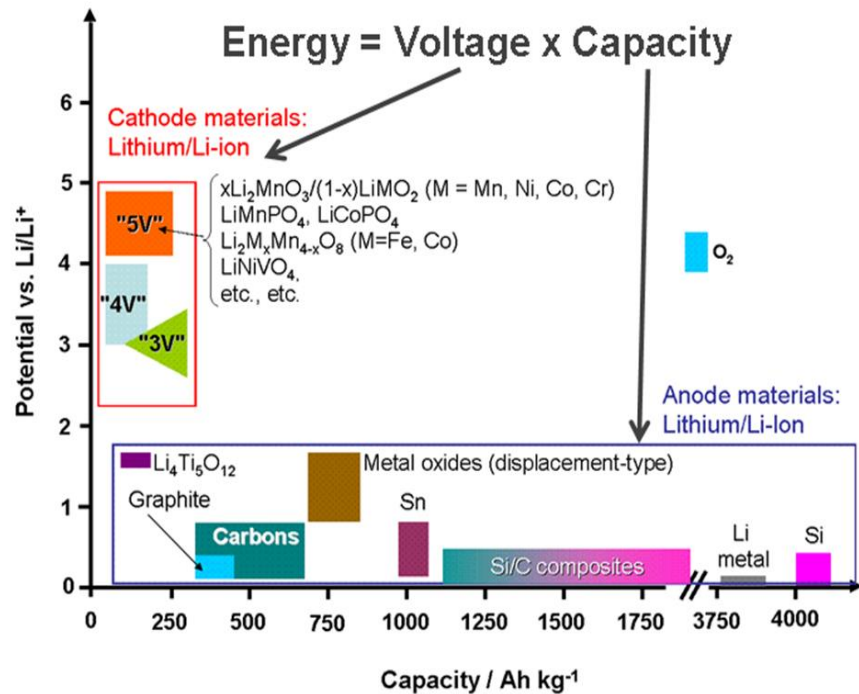


Future evolution to higher voltage battery systems



Solvay R&I

Developments 5V cathode materials: www.fivevb.eu



Xu, J. T.; Dou, S. X.; Liu, H. K.; Dai, L. M. Nano Energy 2013, 2, 439

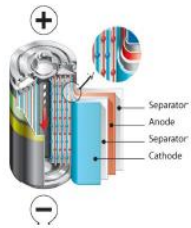
Paired with high capacity novel anode materials

www.spicy-project.eu
www.sintbat.eu

■ Si/C composites



High capacity anode materials for Li-ion batteries

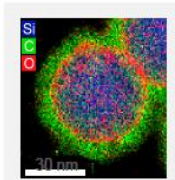


New high capacity anodes are mandatory to achieve the energy targets of portable and automotive applications

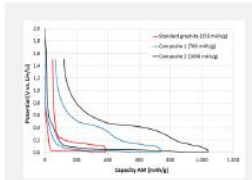
Silicon technology is the preferred solution but faces technological challenges

Umicore's core competences enable development of functionalized silicon compounds for high-capacity advanced anodes

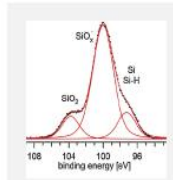
Functionalized silicon



Anode capacity



Silicon surface

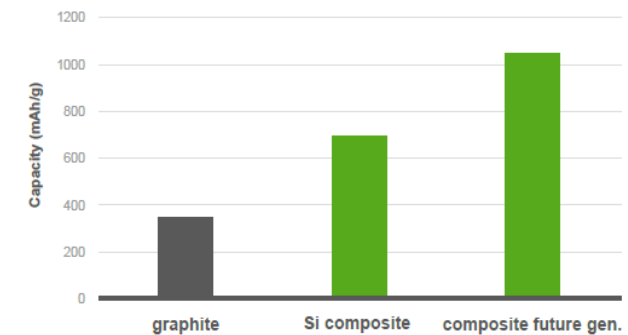


Step change improvement in performance



Silicon technology has 2-10 times higher capacity than current graphite technology

Energy density of batteries will potentially be increased by 50% or more compared to current state-of-the-art technology



Electrolyte modifications

Requirements for electrolytes:

A classical electrolyte is composed of a conductive salt, organic solvents and additives

Possible Li Salts

LiPF_6 (commercial)
 LiAsF_6
 $\text{LiN}(\text{SO}_2\text{CF}_3)_2$
 LiClO_4
 LiBOB (commercial)
 LiBF_4
 LiSO_3CF_3

Mixture of 2 or more solvents

Cyclic esters: Ethylene carbonate (EC)
Propylene carbonate (PC)

Acyclic esters: such as dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethylmethyl carbonate (EMC)

Requirements are:

- ionic conductivity/solubility/dissociation
- electrochemical stability window
- corrosion resistance of cell components
- stability at high temperatures and cell safety
- non-toxicity

4.3 – 4.6 V

- Use of fluorinated esters and fluorinated carbonates as co-solvents (e.g. F1 EC Solvay)
- Use of novel SEI promoting and thermal stabilizing additives
- Mixtures LiPF_6 + LiBOB
- Studies of non-fluorinated anions as replacement for PF_6^-
- Flame retardant additives
- Redox shuttle additives
- etc...

5.0 V

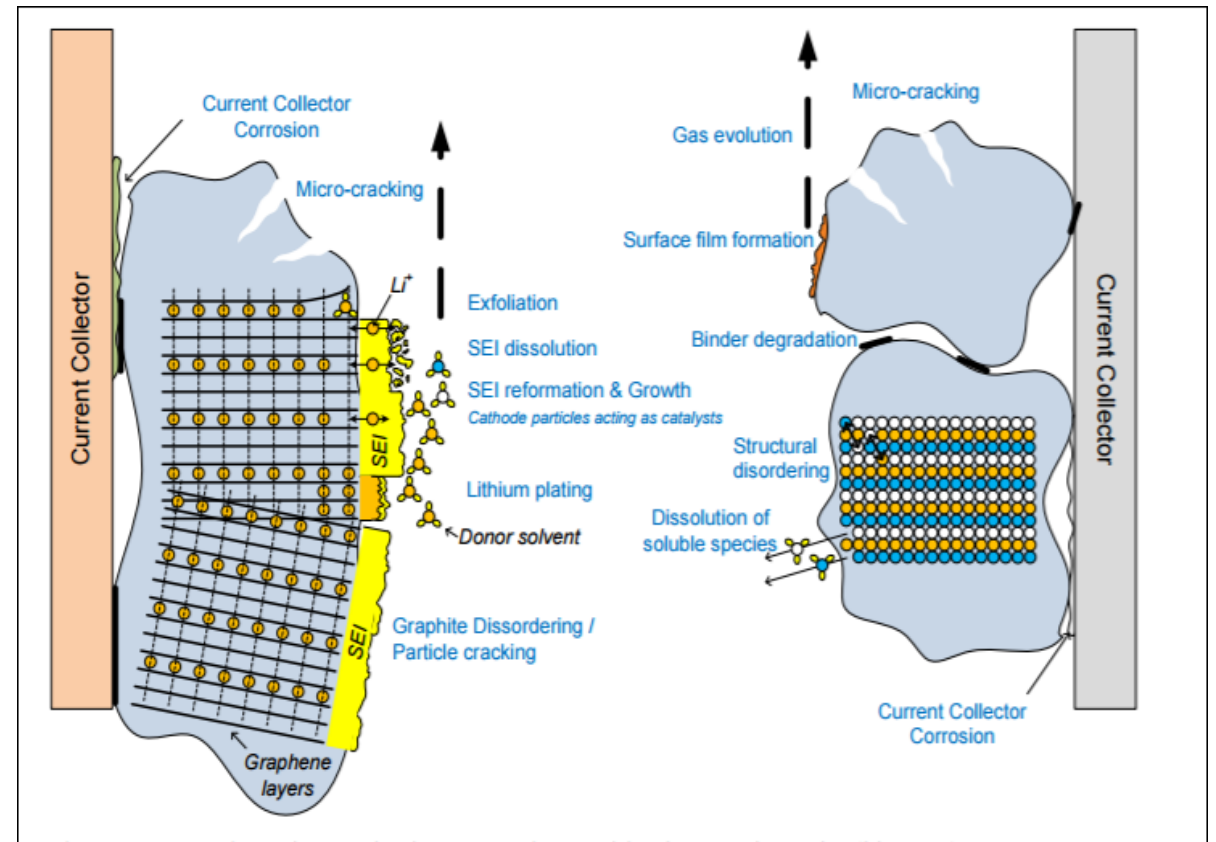
- Sulfone based solvents (up to 5.8V) current work at Argonne ...
- Ionic liquids
- Solid electrolytes
- etc...

Ageing to be controlled and prevented

Generally, the capacity fade of Li-ion cells is due to a combination of three main processes

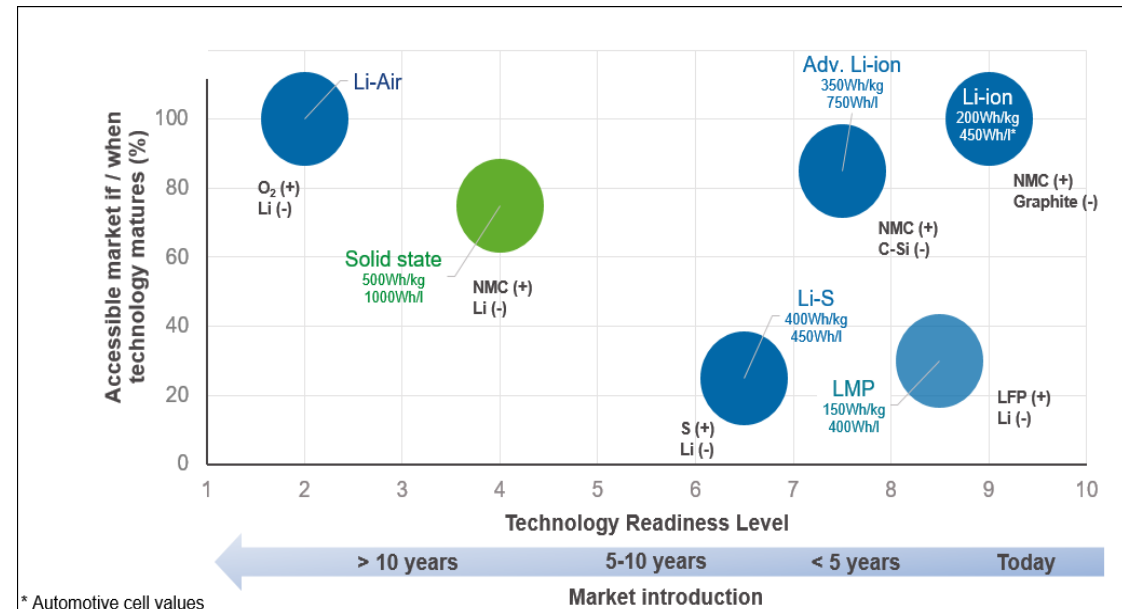
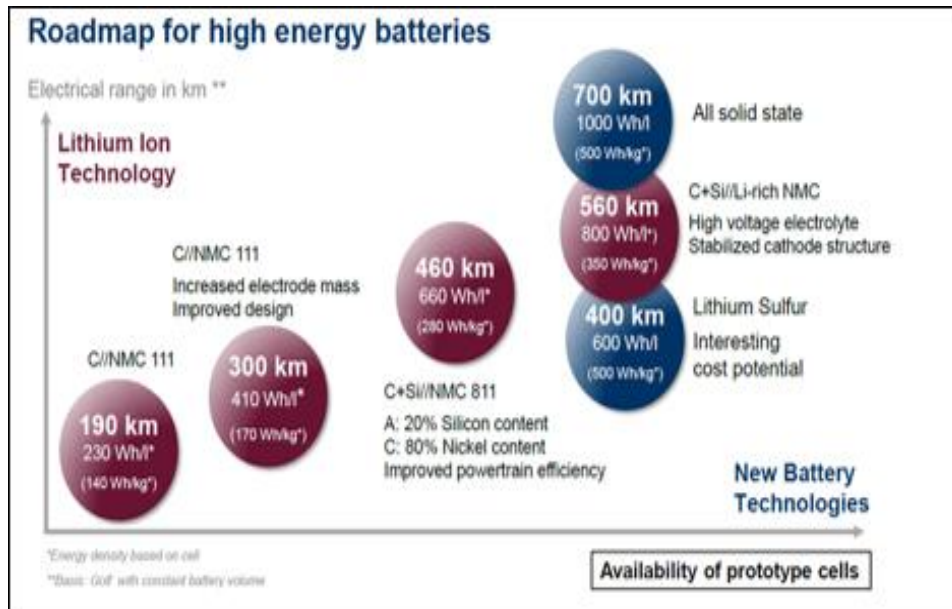
- Loss of Li / loss of balance between electrodes
- Loss of electrode area
- Loss of electrode material / conductivity

Thesis State-of-Health Estimation of Li-ion Batteries:
Cycle Life Test Methods: Jens Groot 2012



Solid State Li Ion batteries

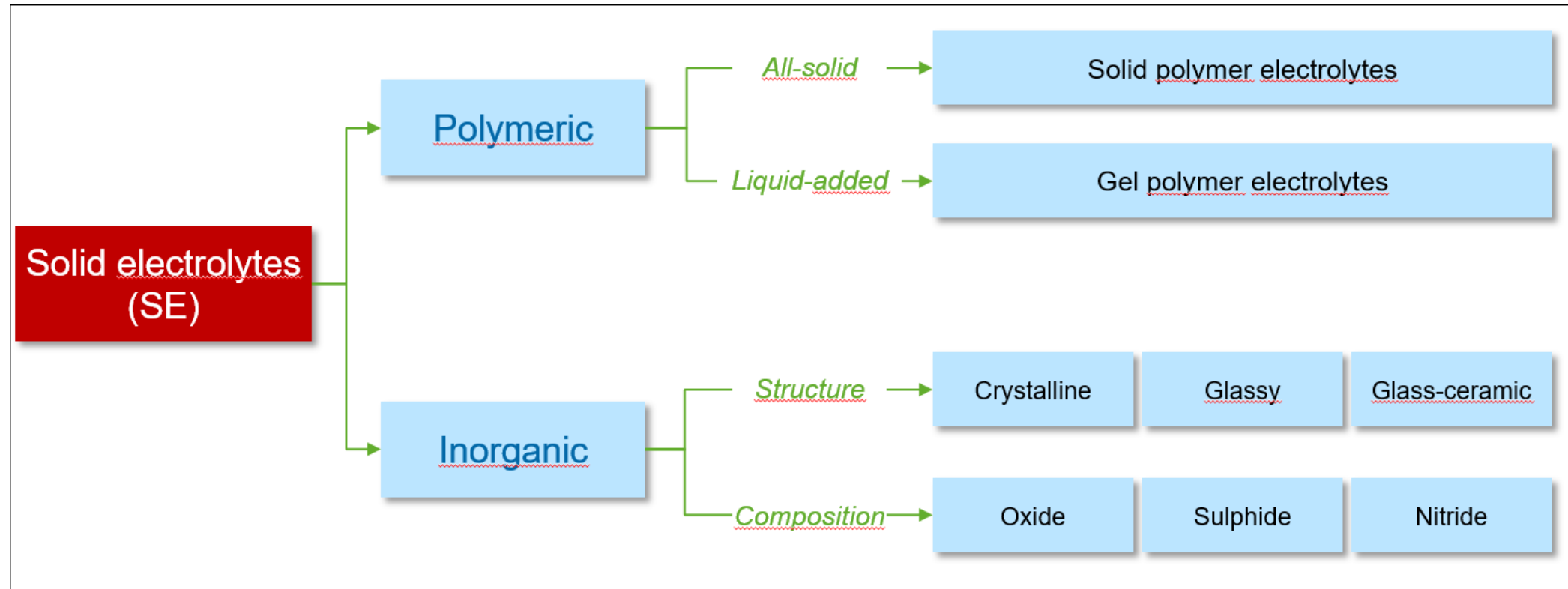
- Solid-state batteries are the next step on major OEM's roadmaps (see e.g. example Volkswagen), they are an enabler for doubling the driving range, they would have better safety and would be denser thus allow potential reductions in the amount of passive components.



Advantages vs Inconvenients - summary

SOLID STATE BATTERIES	
Advantages vs Liquid	Inconvenients vs Liquid
Safety:would eliminate thermal runaway	Lower ionic conductivity: especially at lower temperature
High energy density: less inactive materials higher voltages possible	Poor interfacial contacts Combined with Li metal anode: risk for dendrite formation
Less SEI formation: longer cycle life	More expensive to manufacture?

Key is the solid electrolyte



*Wide variety of SE-types under investigation and competing versus each other
 ... BUT ... huge improvements to be made*

Inorganic solid electrolytes : target > 10^{-2} S/cm ionic conductivity at room t°

Li based glassy solid electrolytes: examples

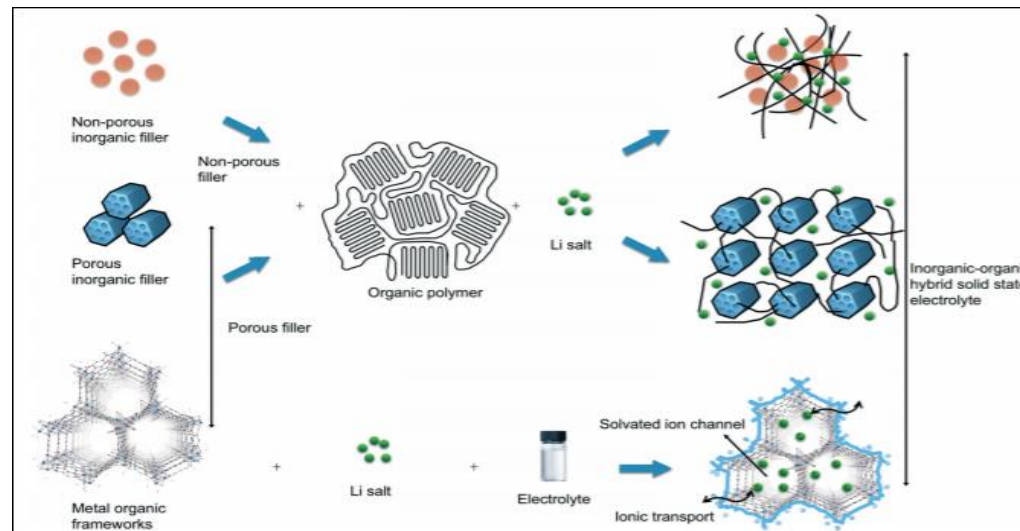
- 1) Oxide electrolytes : Perovskite type structure e.g. $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ with 10^{-3} S/cm
- 2) LISICON type structure : $\text{LiM}_2(\text{PO}_4)_3$ (M=Ge,Ti,Zr), e.g. $\text{LiTi}_2(\text{PO}_4)_3$
- 3) Garnet type structure : LLZO e.g. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
- 4) Sulfide solid electrolytes : e.g. $\text{Li}_2\text{S}-\text{SiS}_2$, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$

J.G. Kim et al. / Journal of Power Sources 282(2015)

Li based solid state electrolytes, their stoichiometries, crystal structure, and repeat units; and optimum conductivity values.			
Electrolyte	Crystal nature	Stoichiometry	Ionic conductivity at room temperature (S cm^{-1})
Lithium lanthanum titanate (LLTO)	Crystalline	$\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$	10^{-3}
Lithium based superionic conductor (LISICON)	Crystalline	$\text{Li}_{14}\text{ZnGe}_4\text{O}_{16}$	10^{-6}
Sulfur doped lithium based superionic conductor (thio-LISICON)	Crystalline	$\text{Li}_{3.4}\text{Si}_{0.4}\text{P}_{0.6}\text{S}_{0.4}$	$6.4 \cdot 10^{-4}$
Lithium lanthanum barium tantalum oxide	Crystalline	$\text{Li}_6\text{La}_2\text{BaTa}_2\text{O}_{12}$	$4 \cdot 10^{-5}$
Li ion conducting mesoporous oxide	Composite	$\text{LiI}-\text{Al}_2\text{O}_3$	$2.6 \cdot 10^{-4}$
Sulfide glass	Amorphous	$\text{Li}_2\text{S} + \text{LiI} + \text{GeS}_2 + \text{Ga}_2\text{S}_3$	10^{-3}
LIPON	Amorphous	$\text{Li}_{2.88}\text{PO}_{3.73}\text{N}_{0.14}$	$3.3 \cdot 10^{-6}$

Organic solid electrolytes : target $> 10^{-2}$ à 10^{-3} S/cm ionic conductivity at room t°

- Polymer electrolytes are investigated as solid electrolytes, the most prominent example being polyethylene oxide (PEO). Others PAN, PEG... Polymers have obvious advantages in cost, production and processing (shaping, patterning and integration). Their low elastic moduli are especially favourable in flexible battery designs. In an ideal solvent-free polymer electrolyte, lithium salts are dissolved and solvated by the polymer chains.
- One possible strategy to improve the conductivity is to form a composite polymer gel by adding a solvent (organic or ionic liquids) as a plasticizer.
- Another strategy is the incorporation of inorganic fillers (Al_2O_3 , TiO_2 , CuO ...) into the polymer to form a composite polymer electrolyte.



Inorganic and organic
hybrid solid electrolytes
for lithium-ion batteries
Xiaotao Fu,

www.rsc.org/crystengcomm

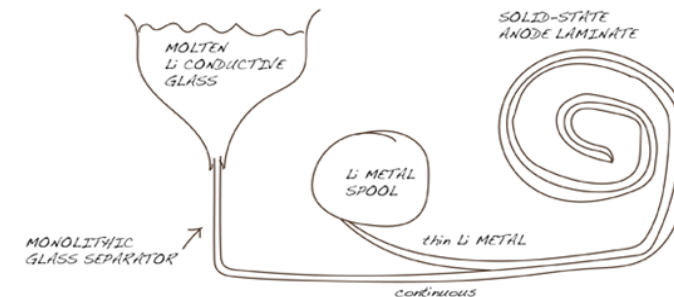
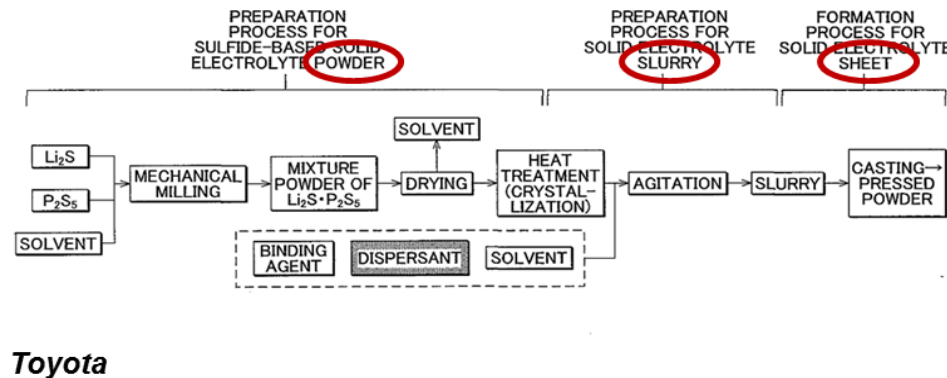
Manufacturing still an issue

Manufacturing of solid electrolytes

Typically two different manufacturing routes are followed for solid electrolytes:

- High energy milling, followed by an appropriate heat treatment (solid-state reaction) → can result in low purity of SSE
- Melting process followed by cooling/quenching step (synthesis of glasses) → high purity, but cost of upscaled process can be an issue

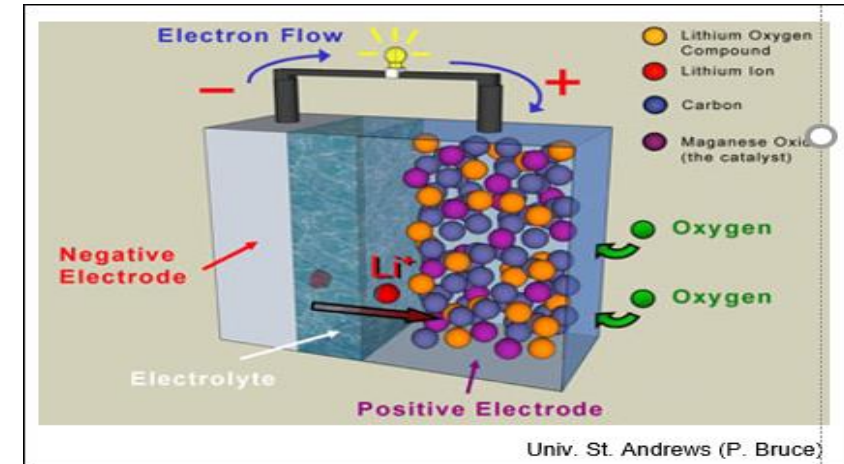
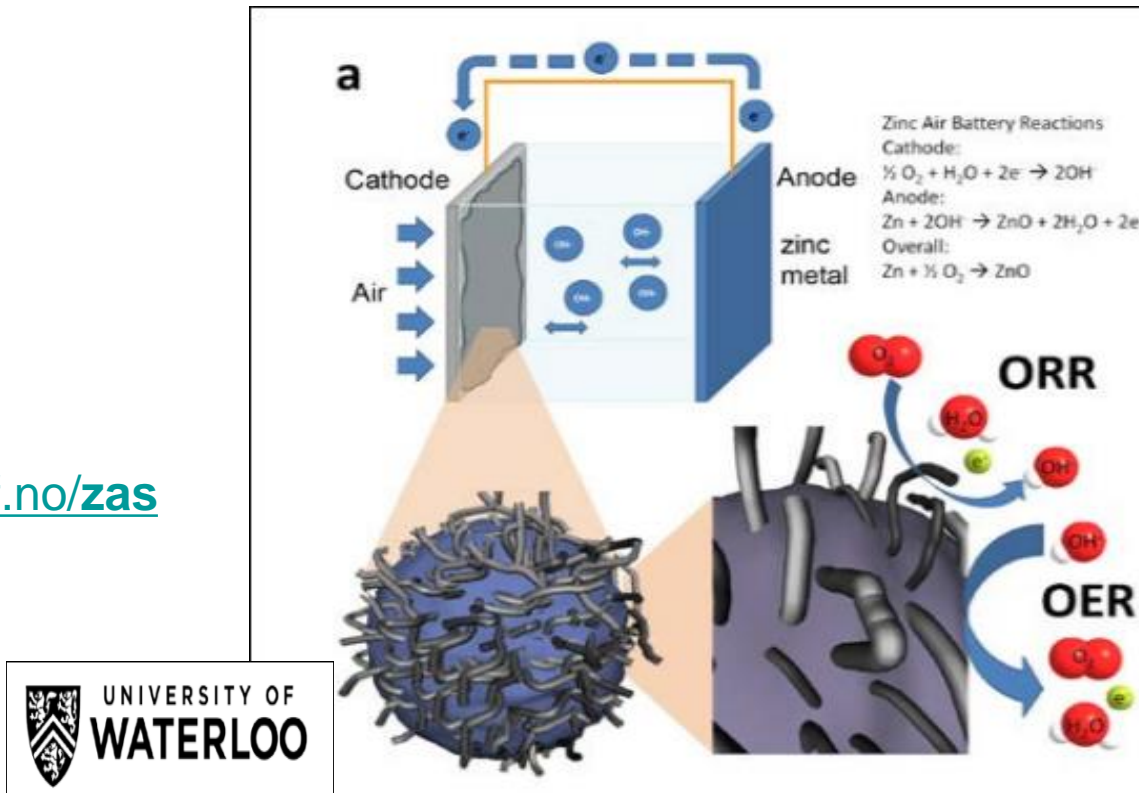
Important to note is that the final application requires a thin layer, so further processing steps (e.g. tape casting, PVD) are needed in case of a powder solid electrolyte



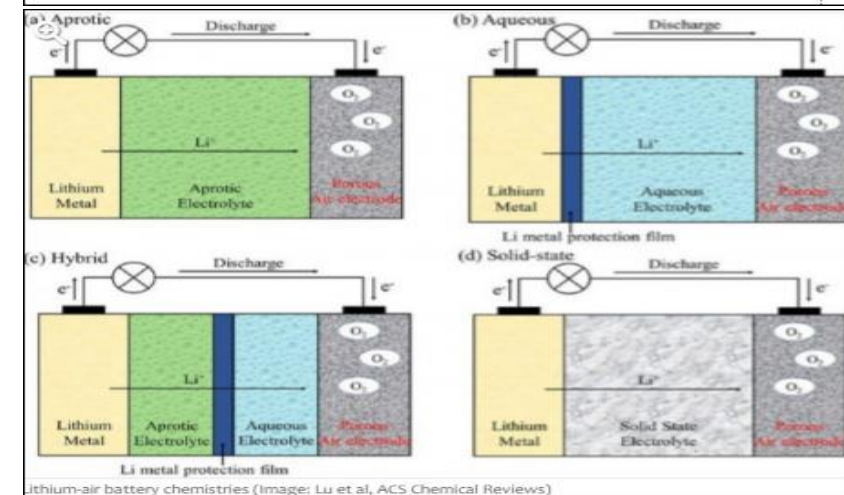
Beyond 2030 novel chemistries: ex. Metal (Zn,Li) - Air (TRL 2 today)

Issues: dendrites, rechargeability, bi-functional air catalysts, electrolyte choice...

sintef.no/zas



Univ. St. Andrews (P. Bruce)

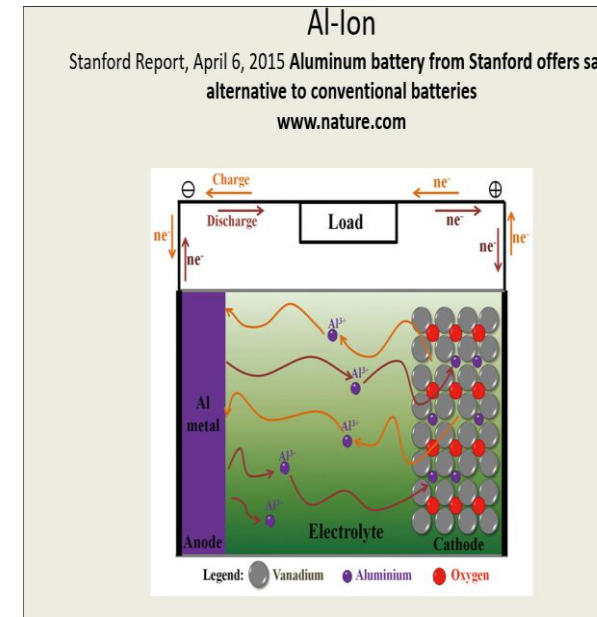
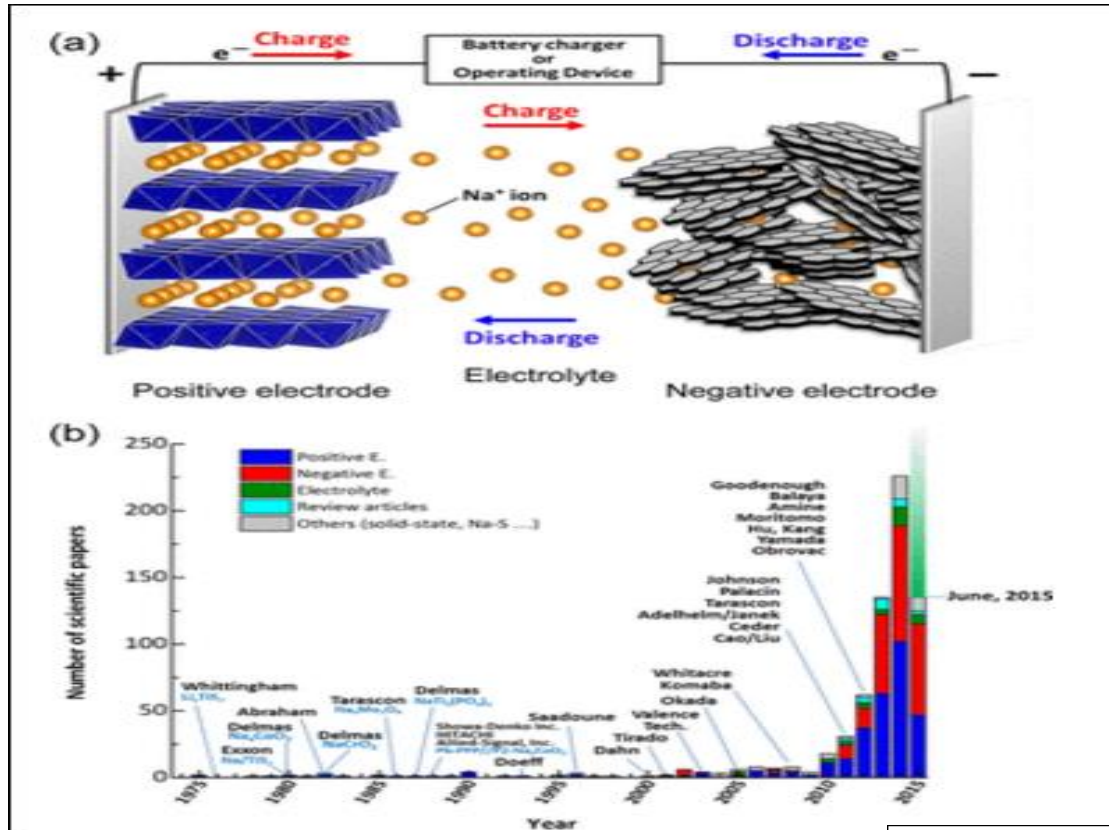


Lithium-air battery chemistries (Image: Lu et al, ACS Chemical Reviews)

Ex. Alternative Metal-Ion systems: Na-ion, Al-ion(TRL 2 today)

www.alionproject.eu

www.naiadesproject.eu



Review—Practical Issues and Future Perspective for Na-Ion Batteries

Kei Kubota^{a, b} and Shinichi Komaba^{a, b, *, z}

3. EMIRI battery program



EMIRI
Bridging the Innovation Gap

EMIRI works for the future of Advanced Materials * for low carbon energy (LCE) technologies in Europe

EMIRI is an Industry Community coming together ...




* Founding / current members

Supported by Research & Technology Organizations



With key Associations bringing in their expertise



Spanning Innovation & Manufacturing



- PV & CSP
- Energy Storage
- Wind & Marine
- Energy Efficiency
- CCS & CCU

3 technologies on average per EMIRI member

- Presence in 19 EU countries
- Over 80 innovation centers
- Over 50 manufacturing sites

* Advanced Materials such as steel, non-ferrous metals, alloys, glass, ceramics, polymers, composites ...

Among 23 topics promoted by EMIRIT IDI, 9 EV/ESS related topics are of interest to support Action 4 and 7 of Integrated SET Plan- Energy Union

Key Component 3			Research & Innovation Actions	Innovation Actions
Advanced Materials to enable energy system integration, E-mobility and lightweight EV's			TRL 4 - 6	TRL 5 - 7
K3-I1	Innovation Topic #1	Advanced Materials for lower cost, high safety, long cycle life & environmentally friendly electrochemical batteries for stationary energy storage - Li- ion batteries		
K3-I2	Innovation Topic #2	Advanced Materials for lower cost, high safety, long cycle life & environmentally friendly electrochemical batteries for stationary energy storage- Next generation batteries		
K3-I3	Innovation Topic #3	Advanced Materials for lower cost, high safety, long cycle life & environmentally friendly electrochemical batteries for E-Mobility- Li Ion batteries		
K3-I4	Innovation Topic #4	Advanced Materials for lower cost, high safety, long cycle life & environmentally friendly electrochemical batteries for E-Mobility- Next generation batteries		
K3-I5	Innovation Topic #5	Lightweight materials for Battery packaging and Powertrain		
K3-I6	Innovation Topic #6	Lightweight materials for EV passenger cars and EV Heavy duty		
K3-I7	Innovation Topic #7	Advanced Materials for lower cost storage of energy in the form of hydrogen or other chemicals (power to gas, power to liquid technologies)		
K3-I8	Innovation Topic #8	Advanced Materials to facilitate the integration of storage technologies in the grid		
K1-I5	Innovation Topic #5	Advanced Materials for thermal energy storage (TES) - Next generation thermal energy storage technologies		

Thank you for your kind attention