Skoltech
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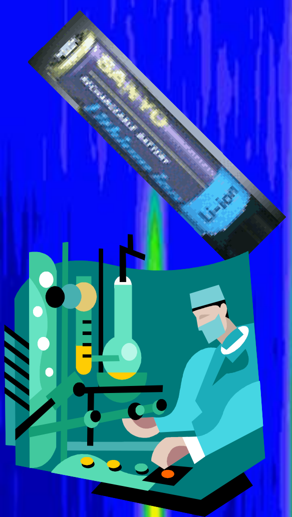
1st International Conference of Young Scientists
"TOPICAL PROBLEMS OF MODERN ELECTROCHEMISTRY AND ELECTROCHEMICAL MATERIALS SCIENCE"
September 18th, 2017



"Solid State batteries are coming back on the scene: is it for good?

J.M. Tarascon

cnrs

COLLÈGE DE FRANCE 1530

http://www.college-de-france.fr/site/en-college/index.htm

ENERGIE RS2E

Contents

Introduction

- ▶ Why all solid state batteries (ASSB) are back ?
- ▶ Recall on ionic conductors: basic principles and their use

All solid state lithium batteries

- ▶ Their evolution and the challenges
- ▶ Family of materials considered (oxides vs sulfides)

Assembling of all solid state batteries

- ▶ Solving the interfaces problems
- ▶ Cell configuration/performances

Conclusions

- ▶ What to expect ?

Why such a regain interest in solid state Li-based batteries ?

Battery research is mainly driven by business

Toyota Announces 4-layer All-solid-state Battery

Nov 22, 2010 19:06
Kouji Kariatsumari, Nikkei Electronics

2010

Toyota Motor Corp unveiled a prototype of its all-solid-state battery Nov 18, 2010, in Japan. It is a laminated cell measuring about 10 x 10cm.

Toyota's new solid-state battery could make its way to cars by 2020

y Darrell Etherington (@etherington)

2017

progress on a new kind of battery technology, which uses a solid
f the conventional semi-liquid version used in today's lithium-ion

Crunchbase

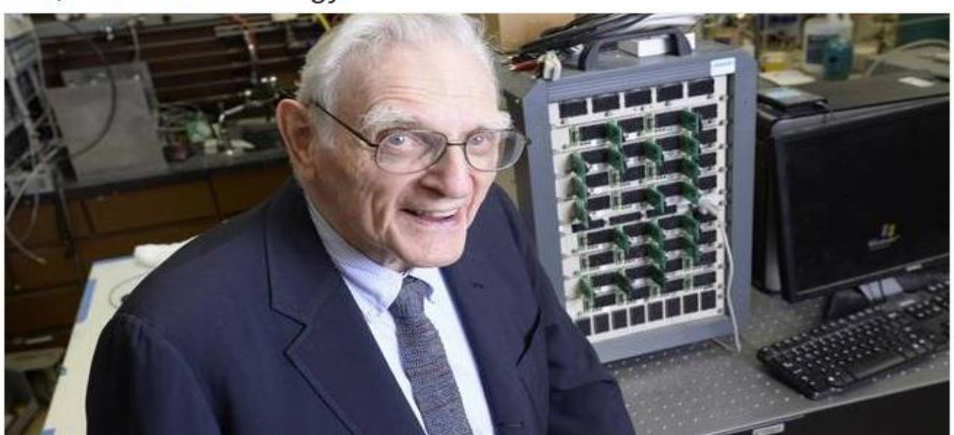
Toyota Motor Corporation

FOUNDED
1937

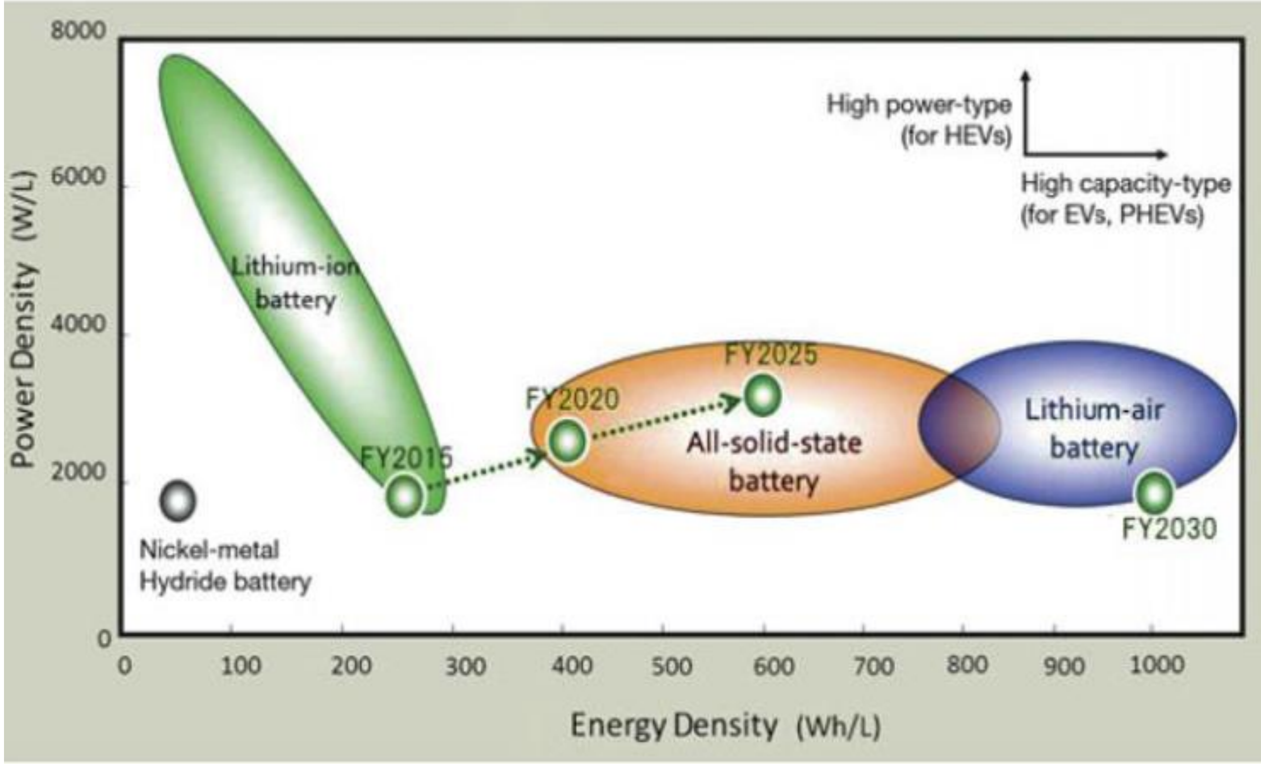
OVERVIEW
Toyota is a company that is operating its business with a focus on vehicle production and sales. Toyota completed its A1 prototype passenger car and G1

Li-ion king Goodenough creates battery he says really is... good enough

Batt inventor John is back – and says his latest design charges fast, holds more energy



All solid state Li-based batteries: Toyota's view of the future ?



Highly anticipated to provide new opportunities for high energy density, safer batteries in the near future

BUT

pose many challenges

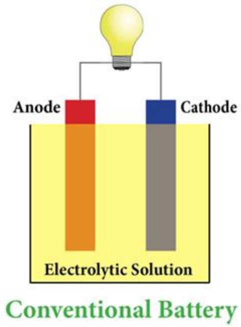
From MRS bulletin, Dec 2014:
Solid State Batteries enter EV fray

Toyota roadmap suggests all solid state batteries are an important step in the evolution of batteries for electric vehicles , but are not the ultimate solution

Figure courtesy of H. Iba (Toyota Motors Corporation)

Advantages of all-solid state batteries

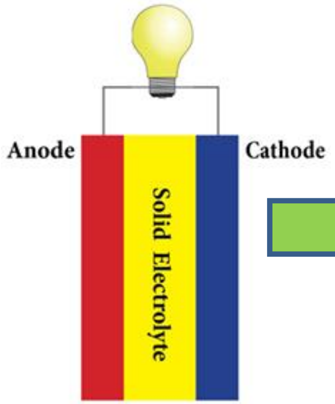
Liquid electrolytes



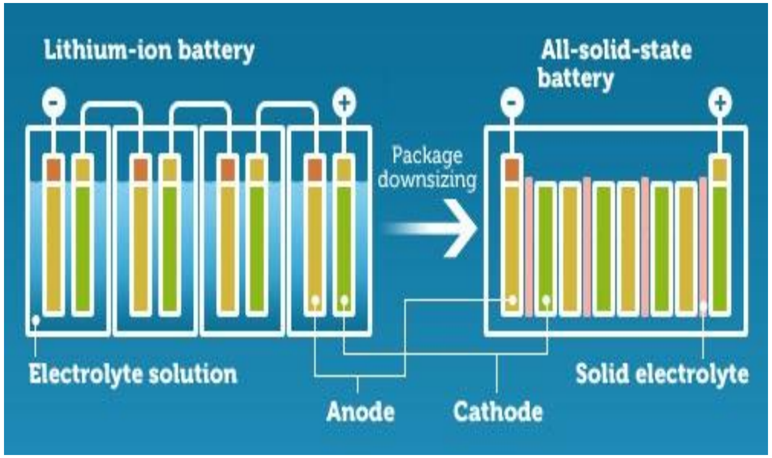
Safety concerns

Voltage limited

Solid electrolytes

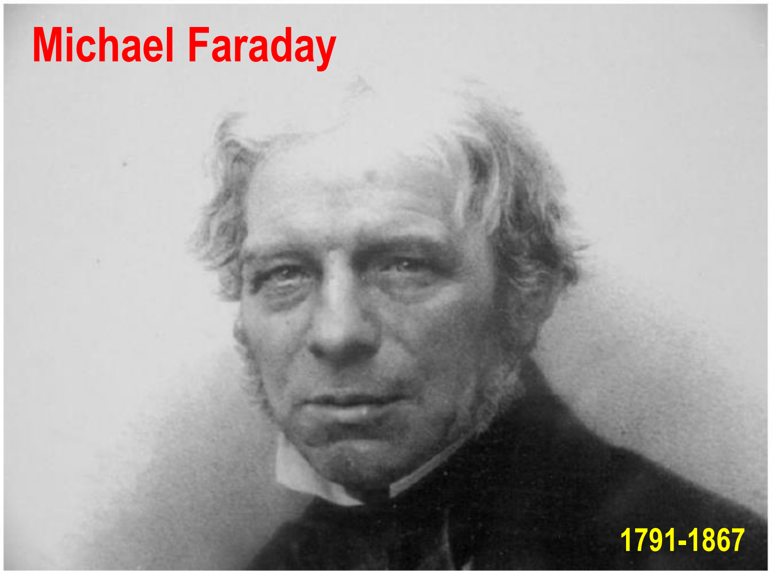


- **Improve safety**
  (Non-flammable solids)
- **Improve energy density**
  (higher voltage, compactness)
- **Could be used with other technologies** (Li-air, Li-S, ..)



Toyotaglobal.com/innovation.environmental technology

Solid state electrolyte: a nearly two centuries story



1834

'I formerly described a substance, sulfuret of silver, whose conducting power was increased by heat; and I have since then met with another as strongly affected in the same way: this is fluoride of lead. When a piece of that substance, which had been fused and cooled, was introduced into the circuit of a voltaic battery, it stopped the current. Being heated, it acquired conducting powers before it was visibly red hot in daylight; and even sparks could be taken against it whilst still solid'.

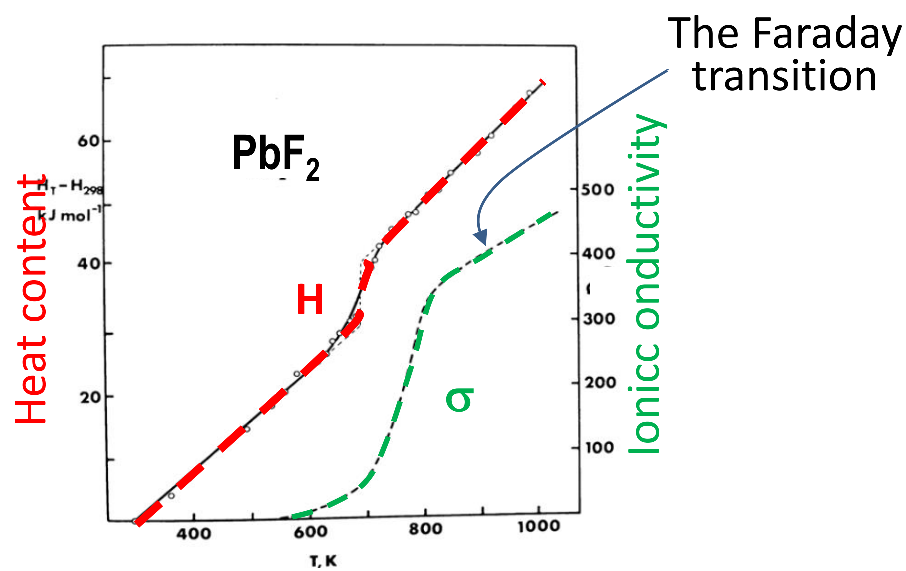
1831-1834: He laid the foundation of electrochemistry and of solid state ionics

→ **Demonstrate electrolysis:**
(ion, cation, anion, electrode, cathode, anode)

→ **Discovered what is known as the faraday's first and second law**

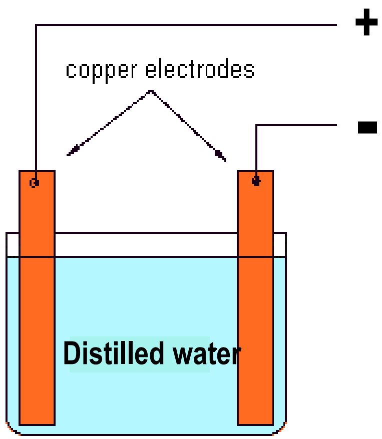
Δm α Δq **Δm α ΔqM/z**

F = (Δq/Δm)(M/z)

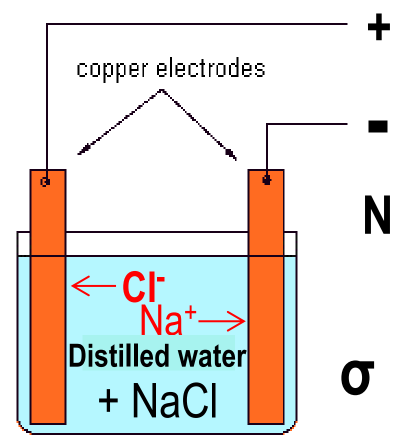


Ionic conduction: Observations/remarks

Distilled water



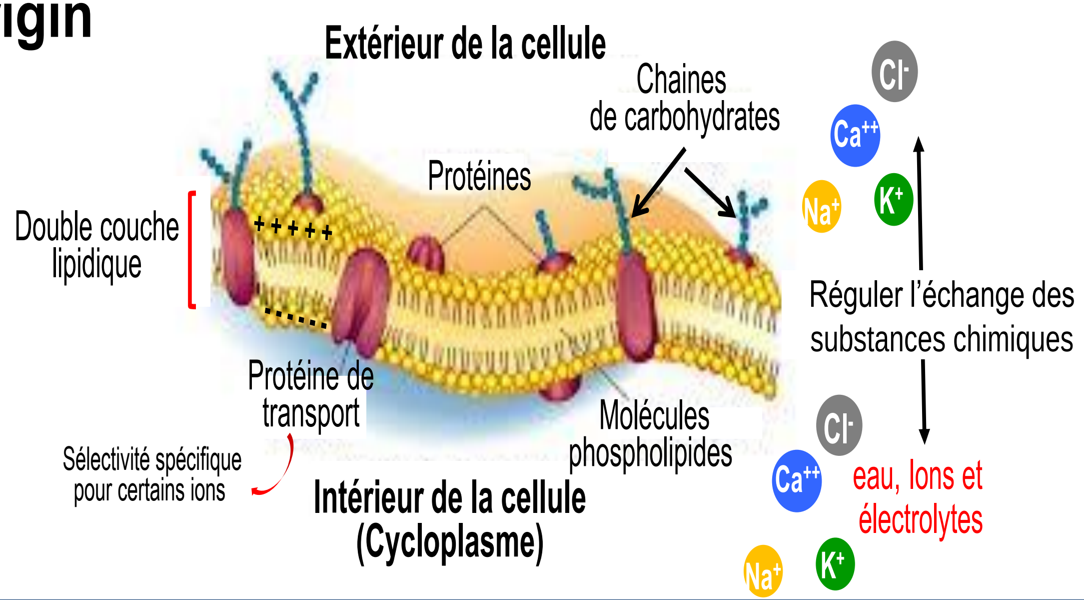
Distilled water + NaCl



NaCl disolved in water

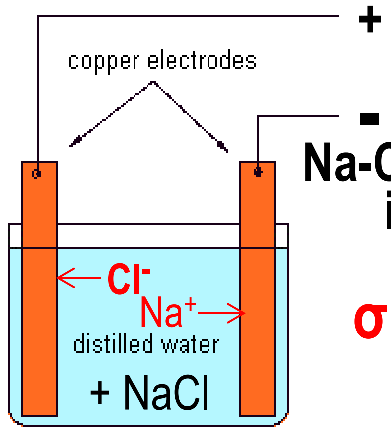
$\sigma \approx 10^{-1}\ Scm^{-1}$

Ionic conduction is at the origin of life processses



Ionic conduction: Difference between Liquid and Solid

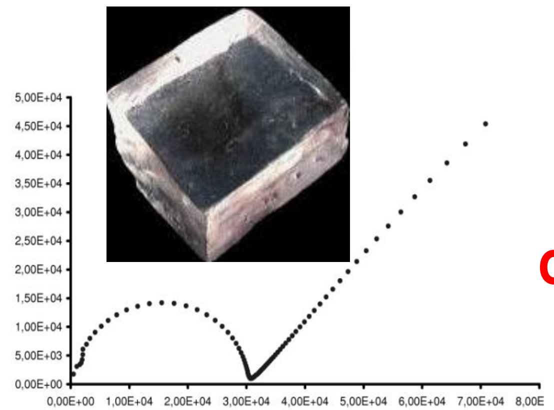
NaCl in aqueous medium

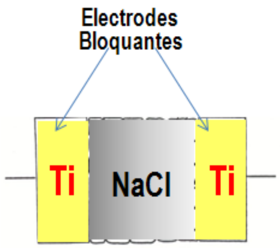


Na-Cl dissolved in water

$\sigma \approx 10^{-1}$ Scm^{-1}

Solid NaCl





$\sigma \approx 10^{-12}$ Scm^{-1}

Devices → **Solid ionic conductors**

Solid-state applications: Ionic conductions at least in the order of $\approx 10^{-3}$ Scm^{-1} at room temperature

How to improve ionic conductivity in solids?

Solid electrolytes: Numerous ions and numerous materials

- **Ag^+ based ionic conductors**
  - AgI & $RbAg_4I_5$
- **Na^+ based ionic conductors**
  - Sodium β-Alumina (i.e. $NaAl_{11}O_{17}$, $Na_2Al_{16}O_{25}$)
  - NASICON ($Na_3Zr_2PSi_2O_{12}$)
- **Li^+ based ionic conductors**
  - $Li_{10}GePS_{12}$, $Li_{3x}La_{2/3-x}\square_{1/3-2x}TiO_3$, Li_6PS_5X

Cationic

Some fundamentals remarks on Ionic conductivity

Electrical conductivity (Scm^{-1})

$$\sigma = \sum_i Q_i \mu_i [i]$$

- Q_i → Charge in Coulombs
- $[i]$ → Concentration of defects/ions, …(per cm^{-3})
- μ_i → Mobility $cm^2 s^{-1} V^{-1}$

Ionic conductors: ionic species are (H^+, Li^+, Na^+ O^{--}, F^-)

Defects

☞Doping/substitution

→ Addition of cations/anions creates defects $Zr_{1-x}Ca_x\square_x O_{2-x}$

☞Intrinsic disorder

Défauts

→ Disorder created by phase transitions (β/α **AgI**) or **Na β-Alumina**, or by amorphisation (e.g, glasses)

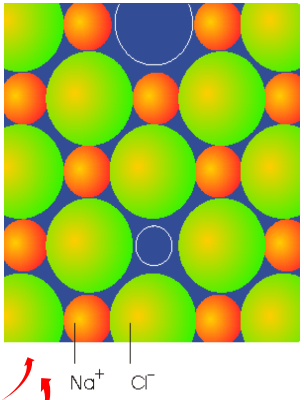
☞Space charges

→ Modification of charges at the interfaces to balance opposite charge planes: formation of a depletion zone which improves conduction

Types of defects in some inorganic systems

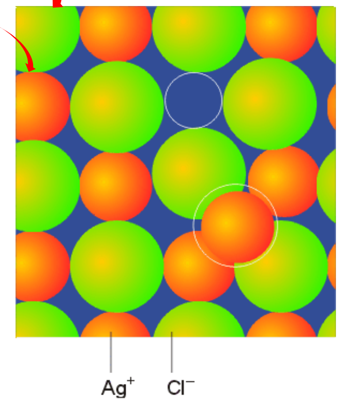
Some examples

Crystal	Crystal structure	Types of defects
Alkali halides (NaCl, LiF, KCl)	Rock salt (NaCl)	Schottky
Alkaline Earth Oxides (MgO)	Rock salt	Schottky
AgCl, AgBr	Rock salt	Frenkel (cation)
BeO	Wurtzite (Hexag)	Schottky
Alkaline earth fluorides CeO_2, ThO_2	CaF_2	Frenkel (anion)



Schottky (1886-1976)

Ions with opposite charges leave the lattice, so as to maintain electroneutrality



Frenkel

One atom leaves the lattice, thus creating a vacancy and occupying an interstitial site

Some fundamentals remarks on Ionic conductivity

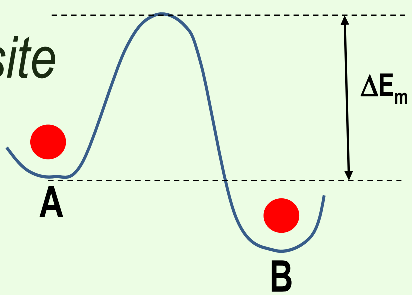
Electrical conductivity (Scm^{-1})

$$\sigma = \sum_i Q_i \mu_i [i]$$

- Q_i → Charge in Coulombs
- $[i]$ → Concentration of defects/ions, …(per cm^{-3})
- μ_i → Mobility $cm^2s^{-1}V^{-1}$

Mobility

☞ *Nature/amplitude of the energy barrier to shift from one site to the other*



→ **Structural:** Geometry constraint to enter the site

→**Electrostatic**: Interaction with neighbouring ions

→**Free volume**, ion **size**

→**Polarisability** of the lattice, **charge** of the ion ($Na^+ > Ca^{2+}$)

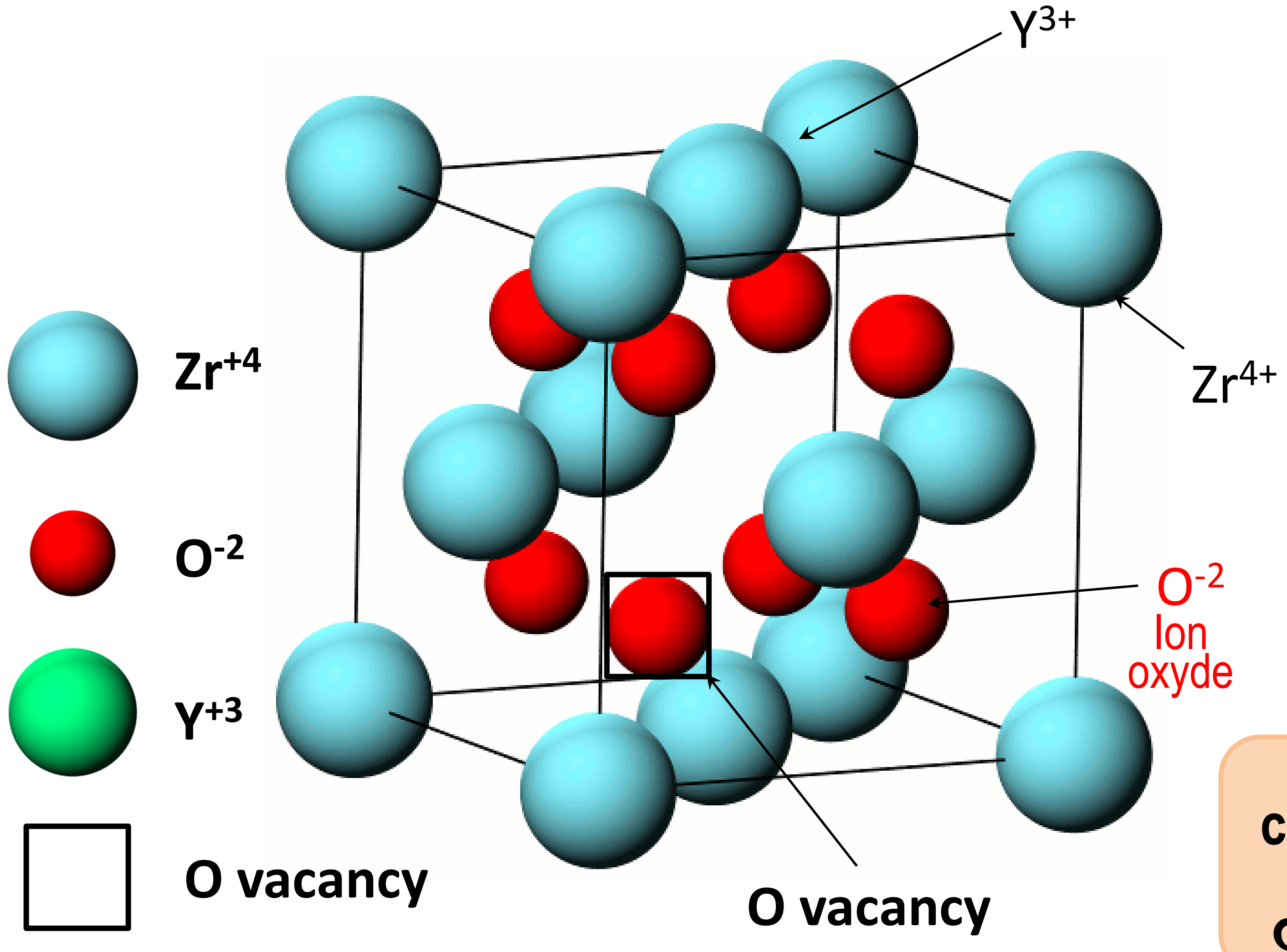
→Advantage of less polarizing ions (Cu+, Ag+)

$$\sigma_{ion} = \frac{\sigma_0}{T}\exp\left(-\frac{\Delta_{act}H}{kT}\right)$$

$$\Delta_{act} = \Delta_{defects\ creation} + \Delta_{migration}$$

Fundamentals on ionic conduction in solids: extrinsic defects

- **Ionic conductors: Y^{+3}-doped ZrO_2 ($Zr^{+4} \rightarrow Y^{3+}$)**

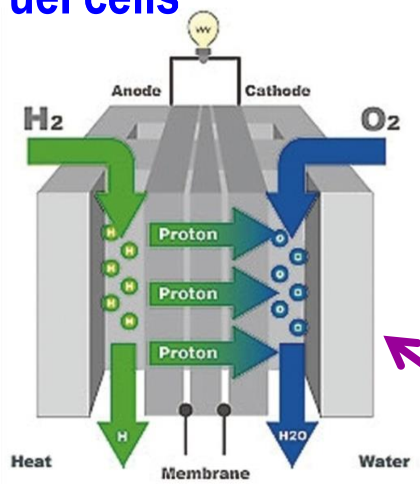


Oxygen conductivity

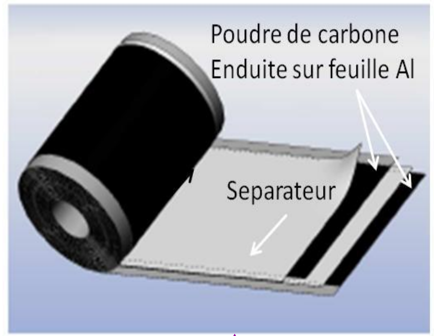
$\sigma_{RT} = 10^{-4}$ S/cm²

Ionic conducting membranes: A large scope of applications

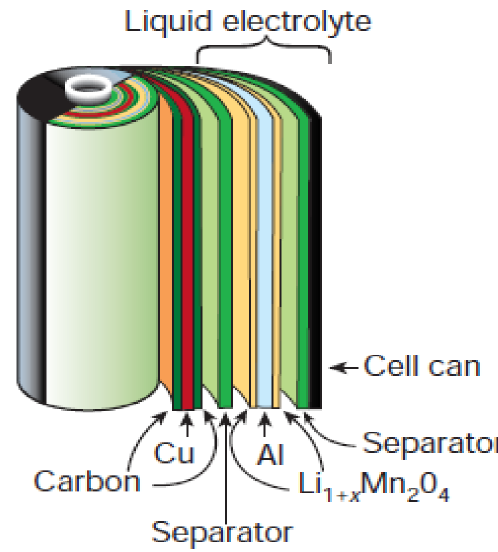
Fuel cells



Capacitors

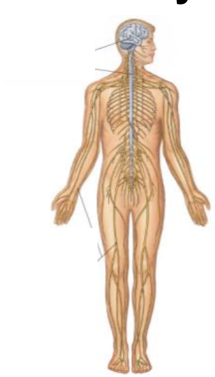


Batteries



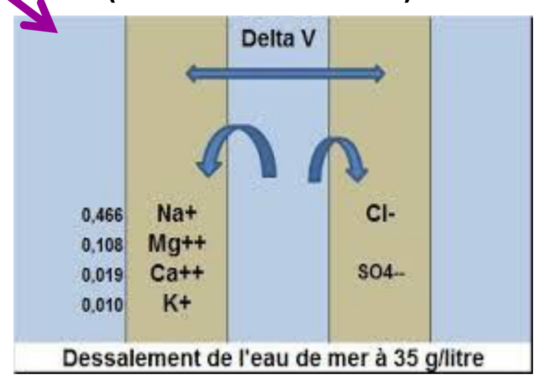
Ionic conductors

Our body



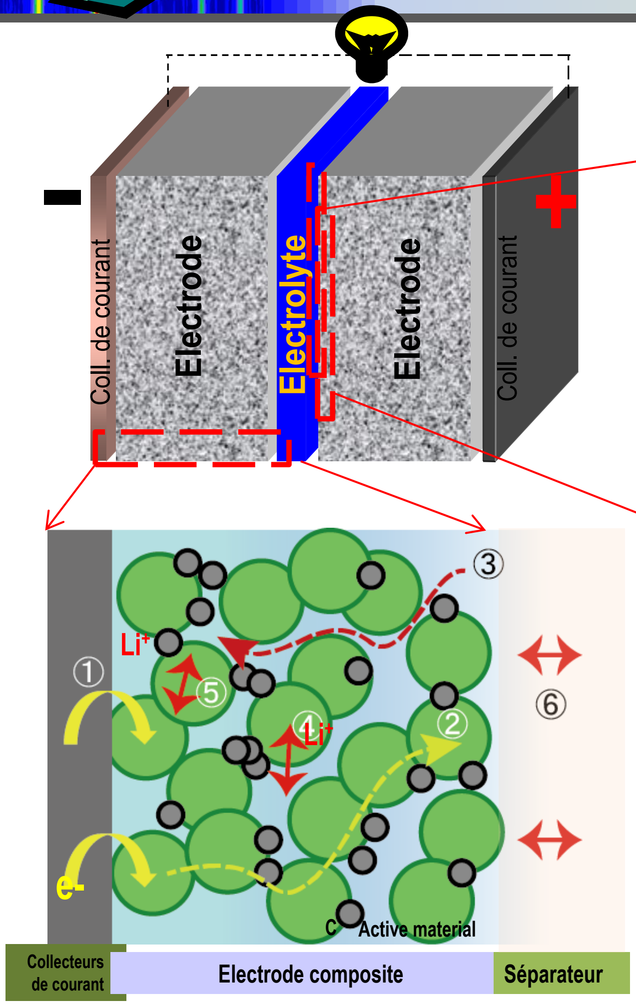
Ionic detectors

Water desalination
(Ionic membranes)

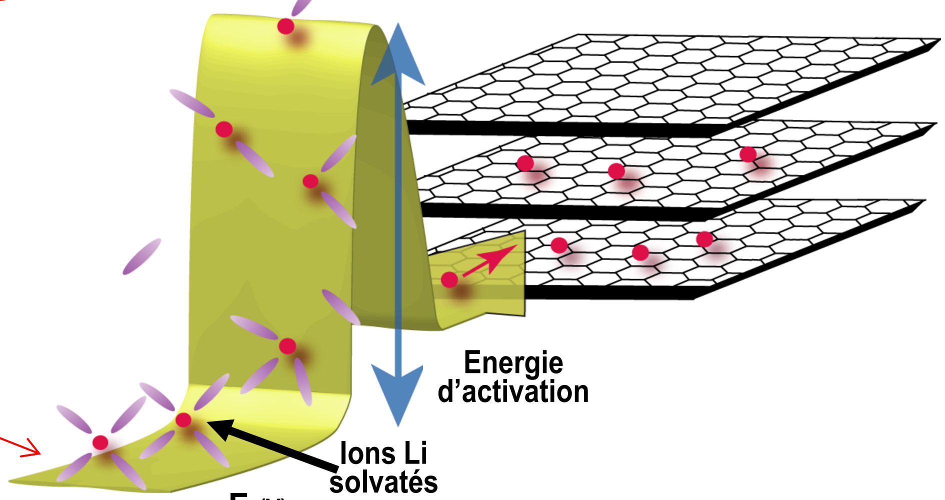


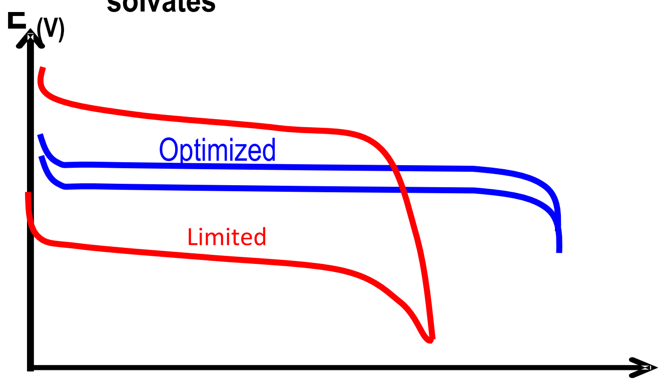
Li-based batteries
ionic conduction/transport

Lithium-ion batteries: Importance of ion transport



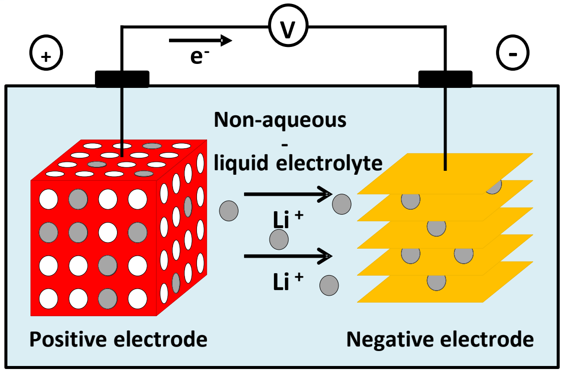
$$1/R_{ct} \propto A.\exp(-Ea/RT)$$



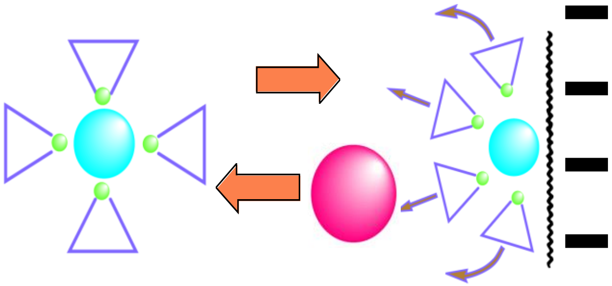


Batteries potential/ capacity = ∑ [Ionic conductivity at the membranes + Ionic conductivity In the electrodes + Ion transport at the interfaces]

Liquid Li-ion technology



Liquid electrolytes: Transport of solvated species



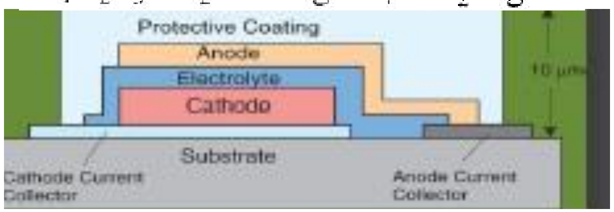
From liquid to plastic and finally inorganic electrolytes

All solid state batteries

All-solid-state batteries: a long story that resurfaces???

Thin
film solid-state batteries

$Li/P_2S_5-Li_2S-LiI$ glass/TiS_2 + glass



J.R.Akridge (1986)

TOYOTA announced the
solid-state batteries
No 22, 2010
Nikkei Electronics

Kanno
Nature Materials
Vol. 10 - (2011)

$Li_{10}GeP_2S_{12}$
$1.2*10^{-2}$ Scm^{-1}

1980

1990

2000

2010

Strong interest
for Li-based
fluoride/sulfide glasses
in France
(Bordeaux-Montpellier)
and worldwide

Na-based electrolytes

LISICON
$Li_{2+2x}Zn_{1-x}GeO_4$

NASICON
$Na_3Zr_2(XO_4)_3$

Thio-LISICON
Li_4GeS_4

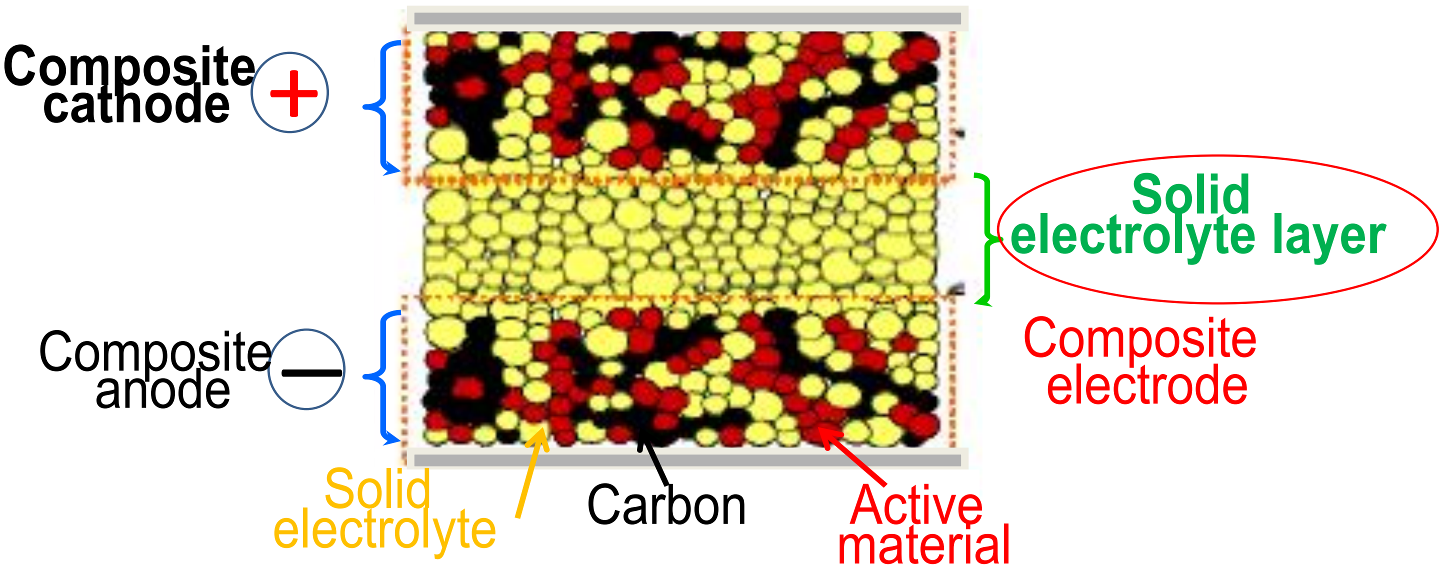
Search for ionic conductors

$Li_3(NH_2)_2I$ (2010)
$Li_2Ti_6O_{13}$ (2011)
$Li_{1.2}Zr_{1.9}Ca_{0.1}(PO_4)_3$ (2011)
$Li_2ZnGe_3O_8$ (2011)
$LaLi_{0.5}Fe_{0.2}O_{2.1}$ (2011)

Low interest

Crazyness

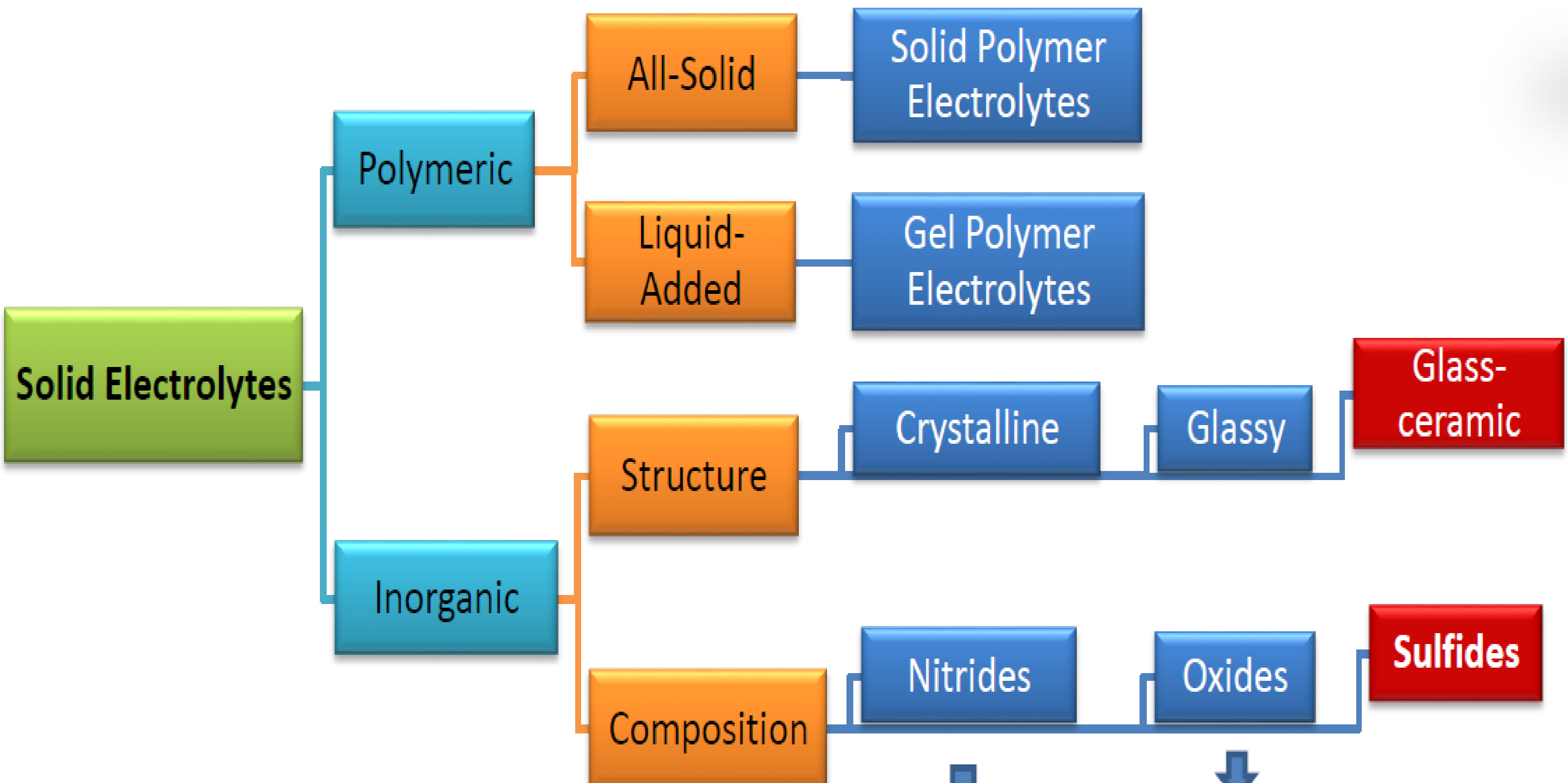
Concept and design of All solid state batteries



Specifications of the solid electrolyte

- High ionic conductivity (at least 10^{-3}S/cm à RT)
- Negligible electronic conductivity to prevent short-circuits
- Compatibility interfaces - electrodes (avoid delamination)
- Chemical and electrochemical stability to avoid redox reactions
- Mechanically stable, low dilatation with temperature
- High defect concentration

Materials discovery: Solid state electrolytes



$Li_7La_3Zr_2O_{12}$ (J. Sakamoto et al., *Solid State Ionics*, 28-32, 206 (2012)

LIPON (N. Dudney *et al.*, *Solid State Ionics*, 53-56, 647 (1992)

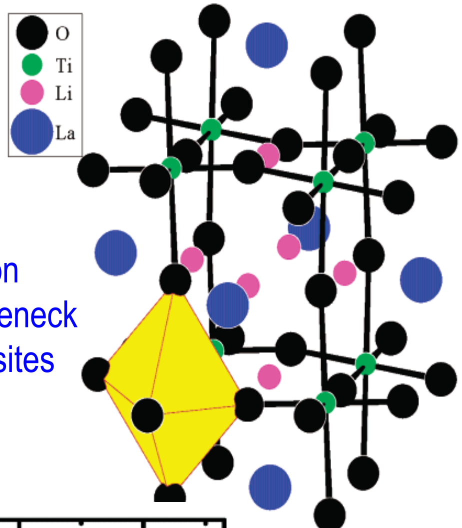
Ionic Conducting Ceramics Based on Li^+ - perovskite Type

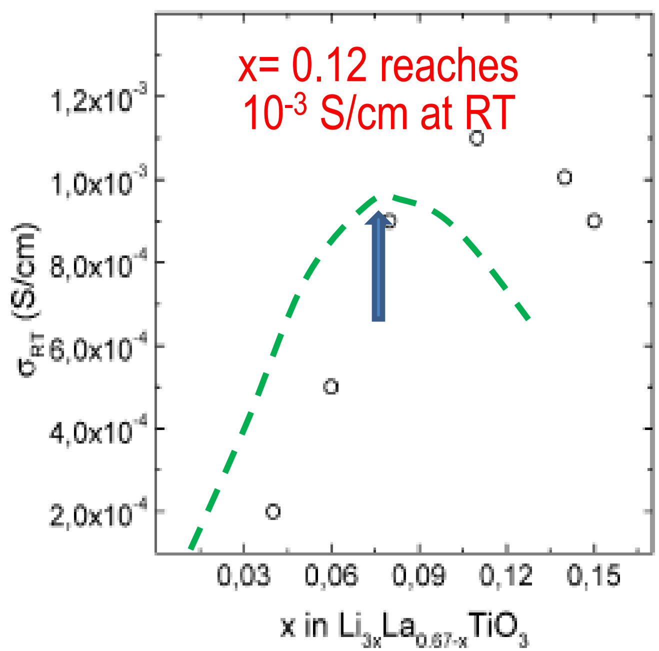
Perovskite (ABO_3) materials: LLTO

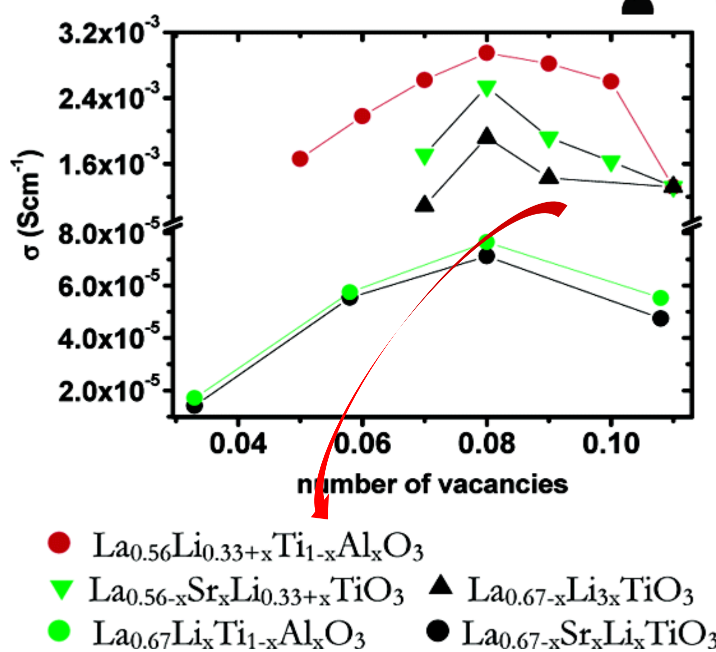
$$Li_{3x}La_{(2/3)-x}\square_{(1/3)-2x}TiO_3$$

- → **Li and La on A-sites; Ti on B-site**
- → **Conductivity arises from high concentration of A-site vacancies and Li+ motion via vacancy**
- → Perovskite phase stable from x = 0.04 to x = 0.16

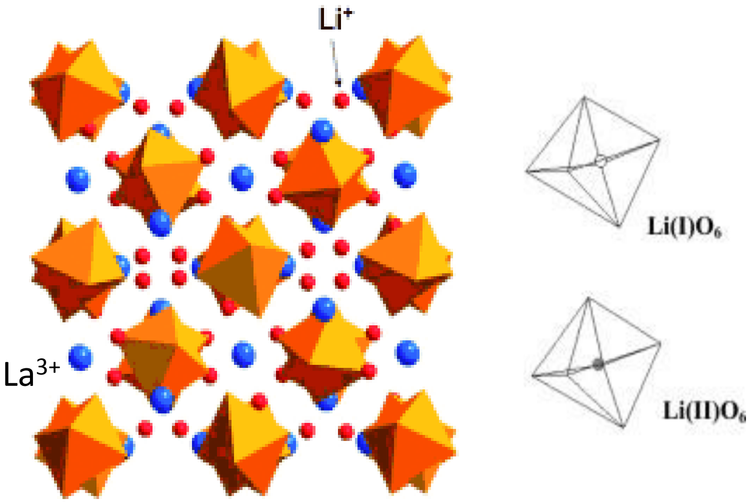
Li^+ motion Through bottleneck between A-sites







Ionic Conducting Ceramics Based on Li^+ - Garnet Structure



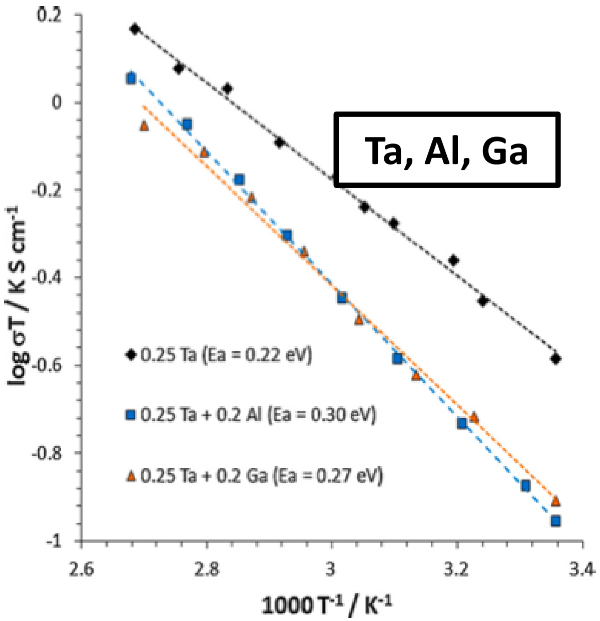
Garnets: $Li_5La_3M_2O_{12}$ (M = Nb, Ta, Sb)

► **La and M in 8- and 6- fold coordinated sites**
Li in highly distorted octahedral sites: Li(I)O_6
MO_6 octahedra surrounded by 6 Li and 2 Li vacancies

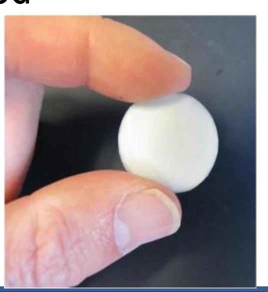
► Substitute with alkaline earth:
Li_5La_3 **A** M_2O_{12} (A = Mg, Ca, Sr, Ba)
Reaches conductivity of 4 x 10^{-5} S/cm

► New composition: **$Li_7La_3Zr_2O_{12}$** **(LLZO)**
Higher Li concentration, larger lattice constant (cubic)
Reach conductivity of **3 x 10^{-4} S/cm**

► Various substitutions (Ta, Al, Ga) have enabled
Systems to reach **1 x 10^{-3} S/cm**

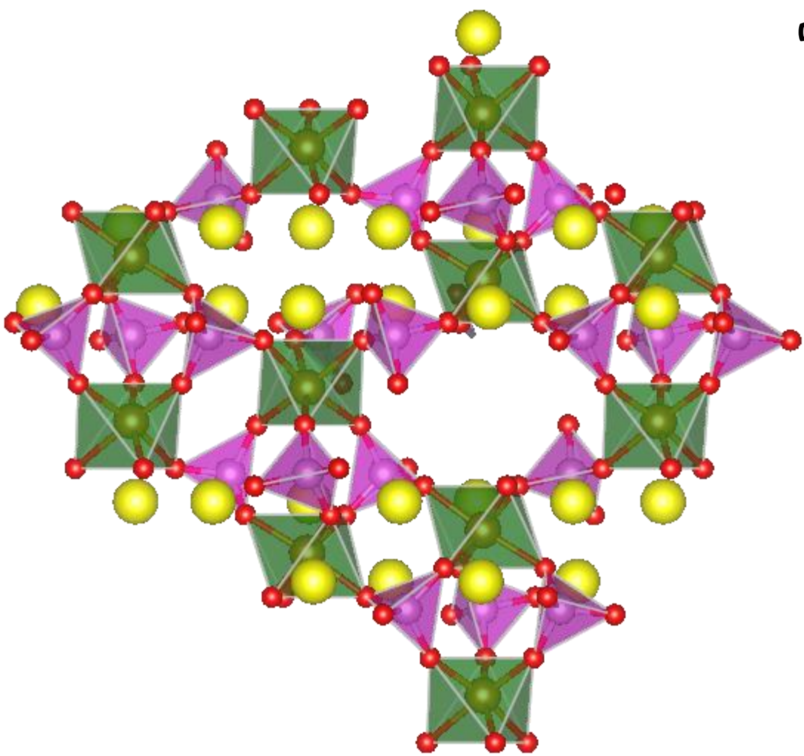


Stable, safe and low cost



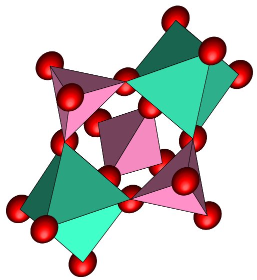
Another family of ionic Conductors: NASICON Structure

$Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$ $(0 \leq x \leq 3)$



- Na^+ occupy trigonal prismatic or octahedral sites, ¼ of the Na^+ are empty

☞ $AM'(XO_4)_3$ In this structure, 3 (Si,P) O_4 tetrahedra are connected to 2 ZrO_6 octahedra in a “lantern” group



☞ **Framework** is able to accommodate many substitutions for A^{n+}, $M^{n'+}$ or $X^{n''+}$ sites

☞ **Very good ionic conductor** with little electronic conduction because of delocalization; octahedra are isolated by tetrahedra of XO_4

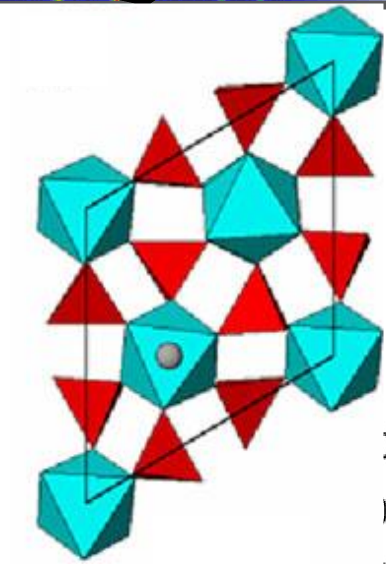
x= 2 → $Na_3Zr_2PSi_2O_{12}$

$E_A \approx 0.3$ eV

$\sigma = 1.2 \times 10^{-4}$ Scm^{-1}

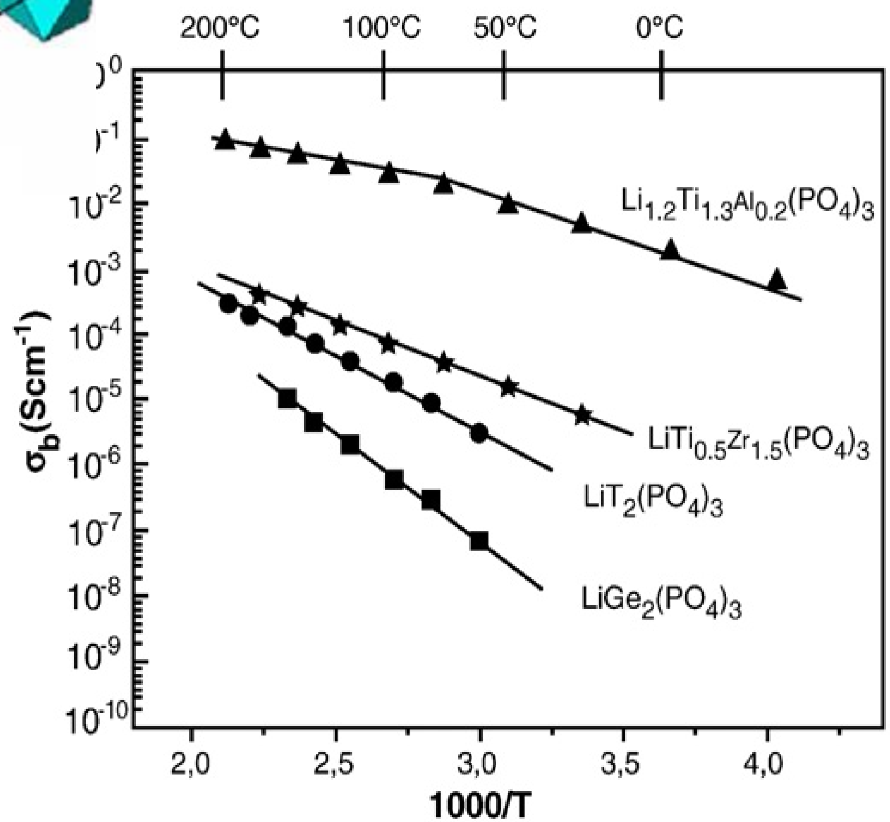
Goodenough 1984

Ionic Conducting Ceramics based on Li^+ - NASICON Structure



Li^+ conductors derived from the NASICON structure: $NaA_2(PO_4)_3$

AO_6 octahedra and PO_4 tetrahedra form 3D interconnected channels with two types of interstitial spaces for Li^+



Starting with $LiGe_2(PO_4)_3$, substitute trivalent (Al, Cr, Ga, ….) and increase Li content.

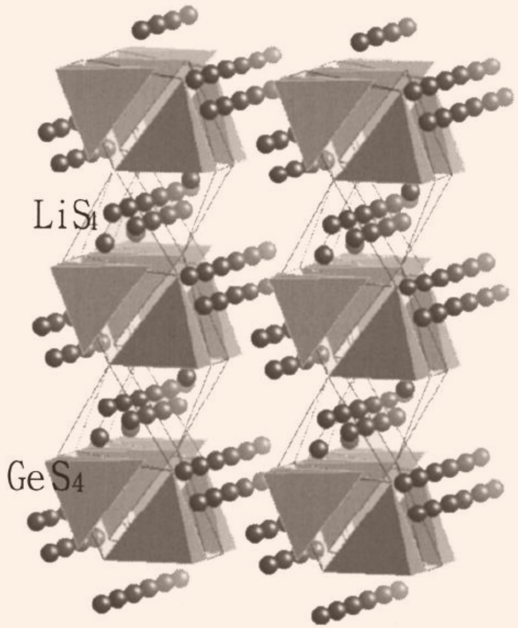
$Li_{1.3}Ti_{1.3}Al_{0.3}(PO_4)_3$ (LATP) has $\sigma = 3x10^{-3}$ S/cm

(Ohara glass)

Li-based ionic conducting ceramics among sulfides

Thio-LISICONS

$Li_{4-x}Ge_{1-y}P_yS_4$



→ Large domain of compositions

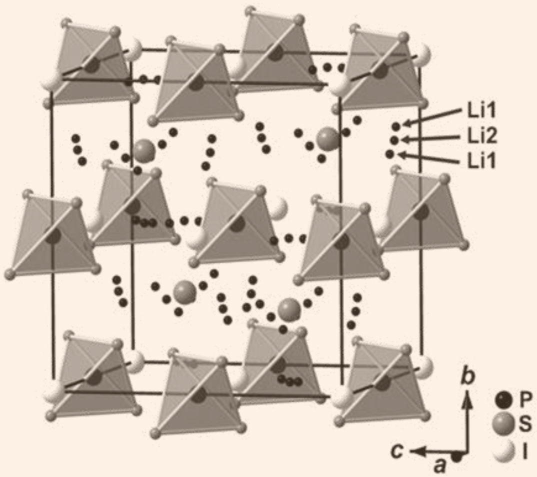
→ Best conductivity for

$Li_{3.25}Ge_{0.25}P_{0.75}S_4$,

$\sigma = 5 \times 10^{-3}$ Scm^{-1}

Argyrodite: Li_6PS_5X

(X= Cl, Br ou I)



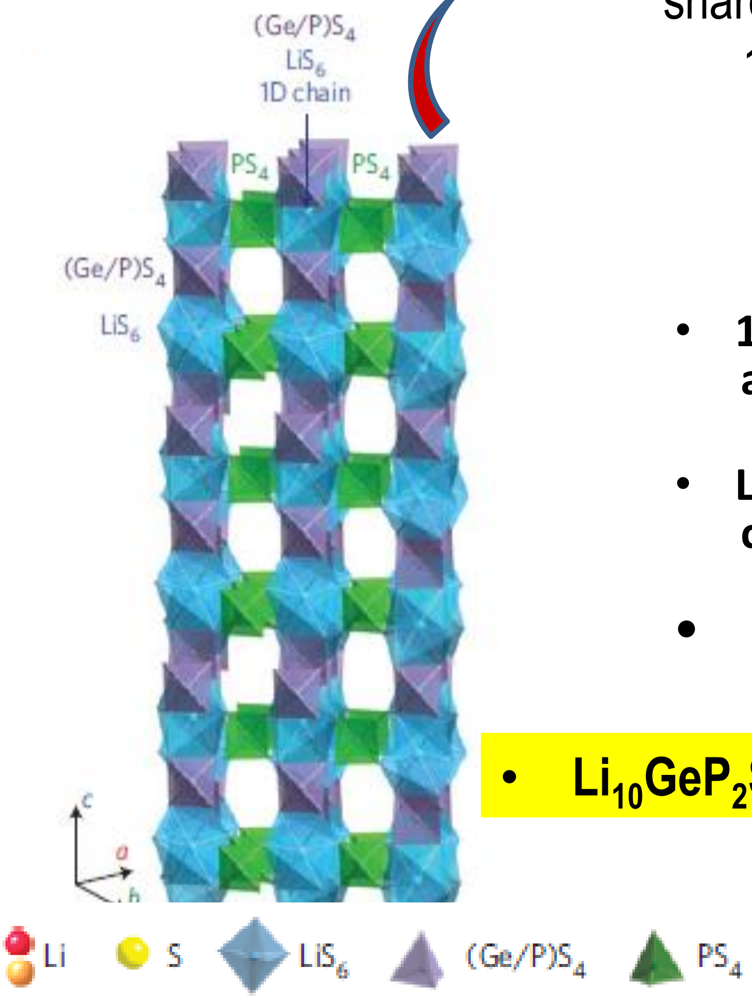
Li_6PS_5Br: $\sigma_{Li} = 1 \times 10^{-4}$ Scm^{-1}

Li_6PS_5Cl: $\sigma_{Li} = 3 \times 10^{-4}$ Scm^{-1}

$Li_{10}GeP_2S_{12}$ - A higher conductivity than liquid systems

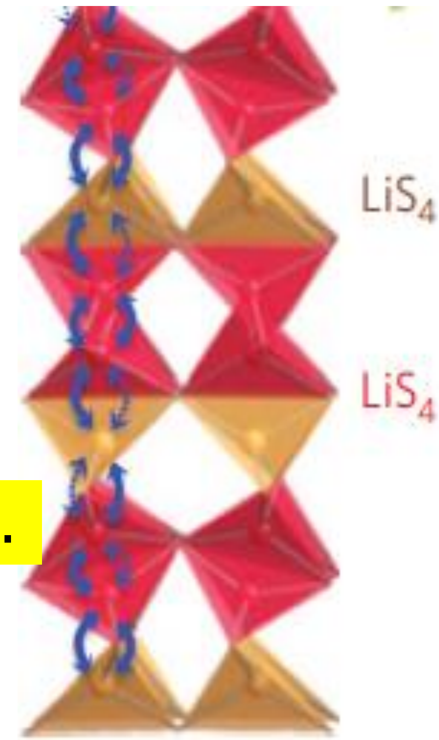
The structure

Framework: $(Ge_{0.5}P_{0.5})S_4$ tetrahedra and LiS_6 oct. share common edge and form 1-D chain along *c-axis;* 1-D chains connected through PS_4 tetrahedra



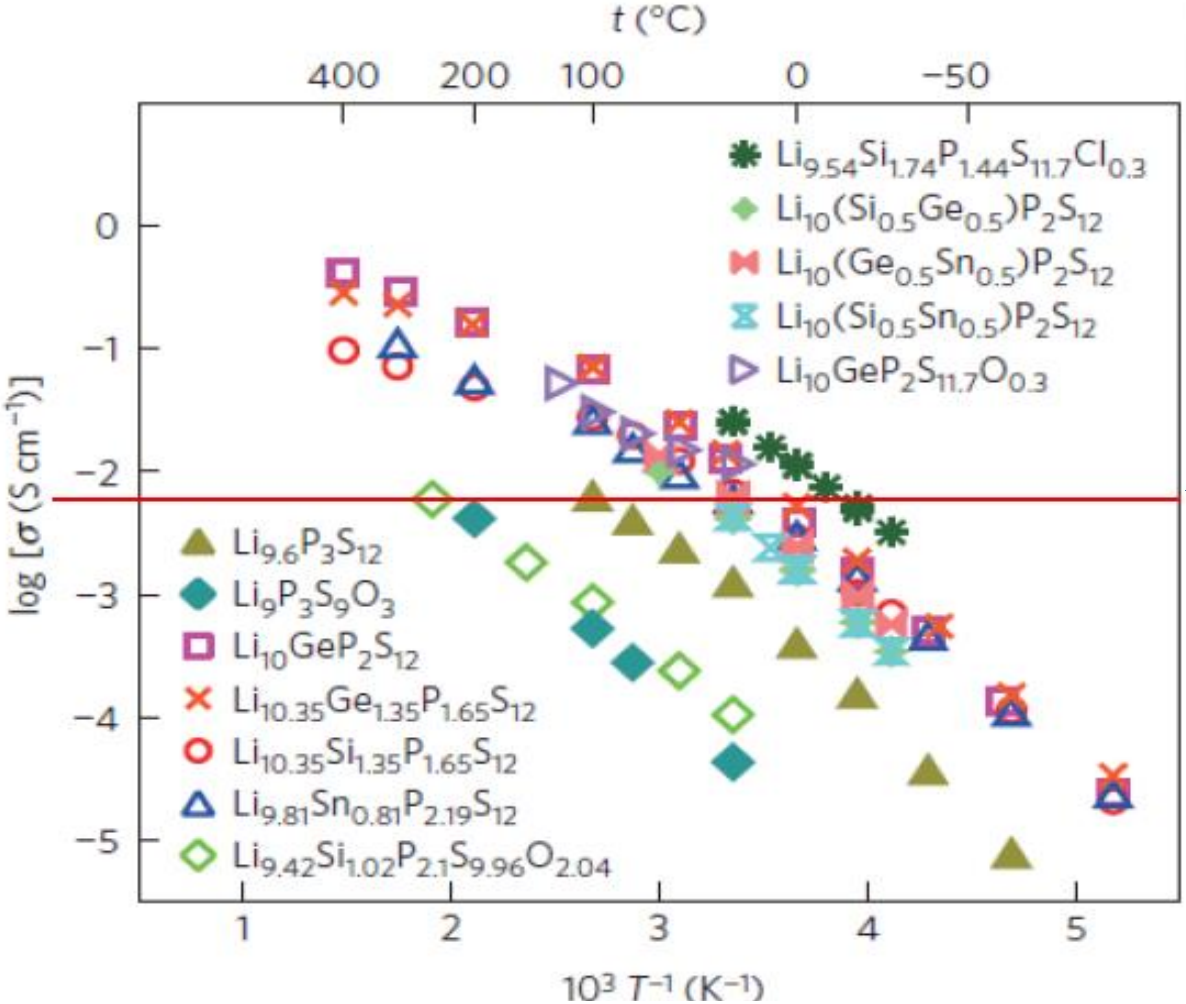
Conductivity

- **1-D lithium conduction along *c-axis***
- **Li^+ in LiS_4 tetraedral sites give conduction;**
- **Site occupancy is 0.7 and 0.65**



- $Li_{10}GeP_2S_{12}$: 1 x 10^{-2} S cm^{-1} at room temp.

Many chemical substitutions on $Li_{10}GeP_2S_{12}$



Ge by Si, Sn
S by Cl or by O

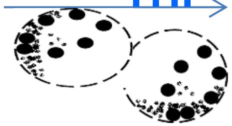
Organic electrolytes:
σ in the range of 10^{-3}-10^{-2} cm^{-1} at RT

LGPS family of solid electrolytes have high ionic conductivity comparable to traditional liquid organic electrolytes

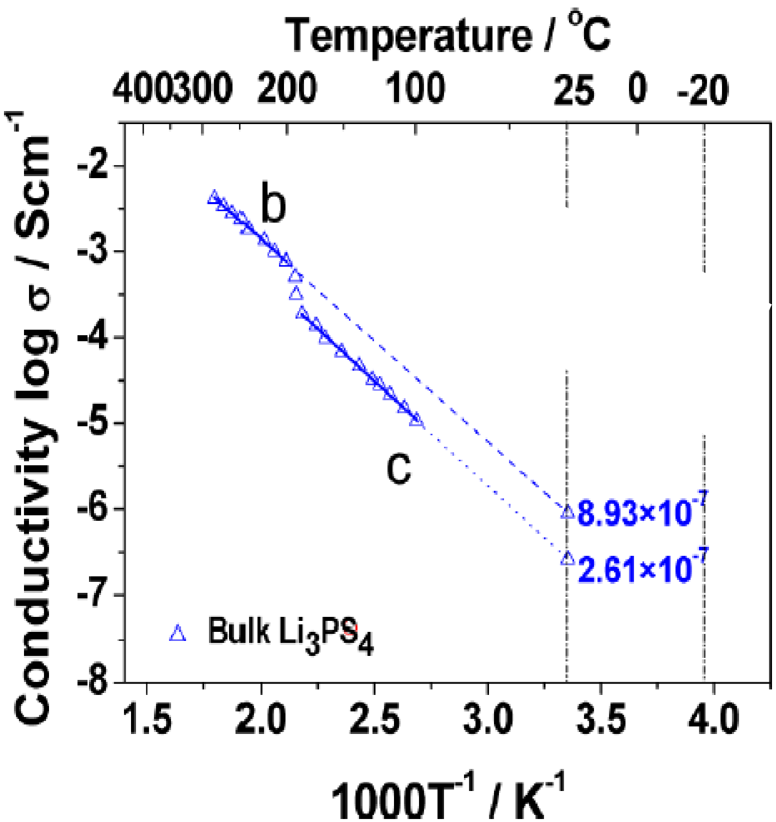
Anomalous High Ionic Conductivity in nanoporous β-Li_3PS_4

- A promising new direction: Solution mediated synthesis

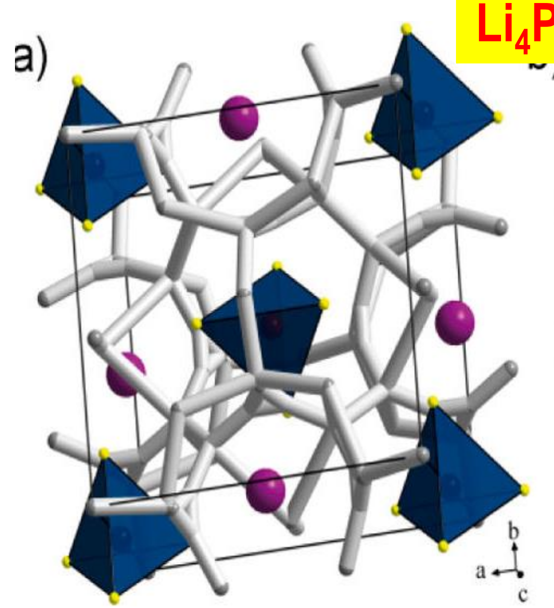
Li_2S + P_2S_5 —THF→ Li_3PS_4.3THF —ΔT→ Nanoporous **β-Li_3PS_4**

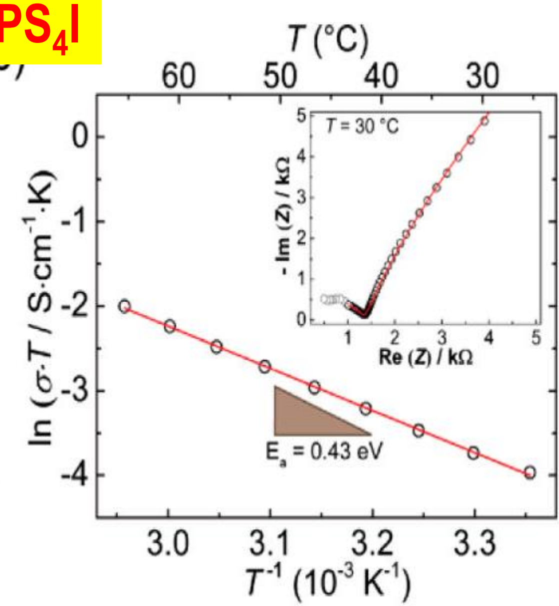


Ball milling



Li_4PS_4I



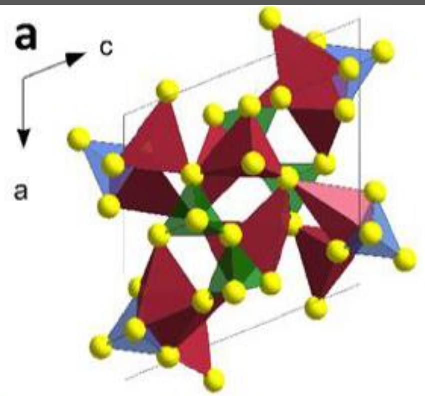


σ= 1.2 10^{-4} S/cm

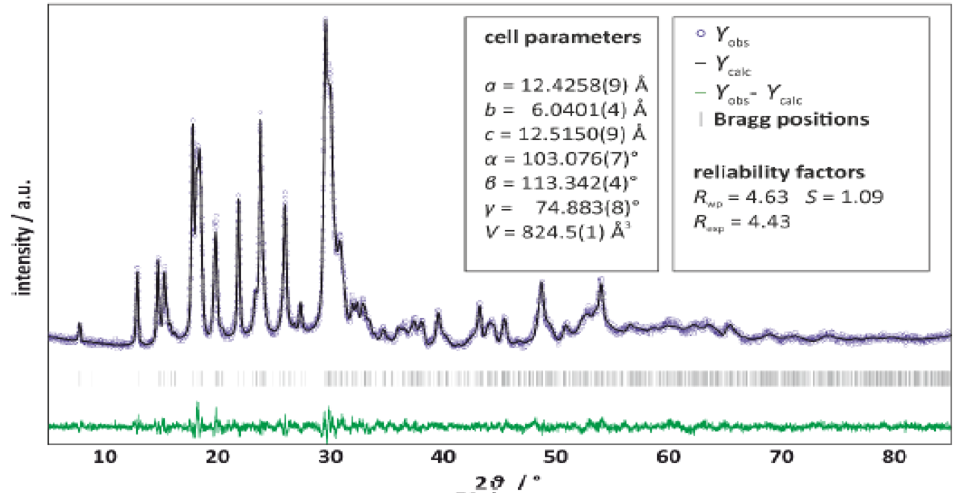
$$3Li_2S + P_2S_5 \xrightarrow[RT]{DME} 2Li_3PS_4\cdot DME$$

$$Li_3PS_4\cdot DME + LiI \xrightarrow[RT]{DEM} Li_3PS_4\cdot DME\cdot LiI \xrightarrow[-DME]{200°C} Li_4PS_4I$$

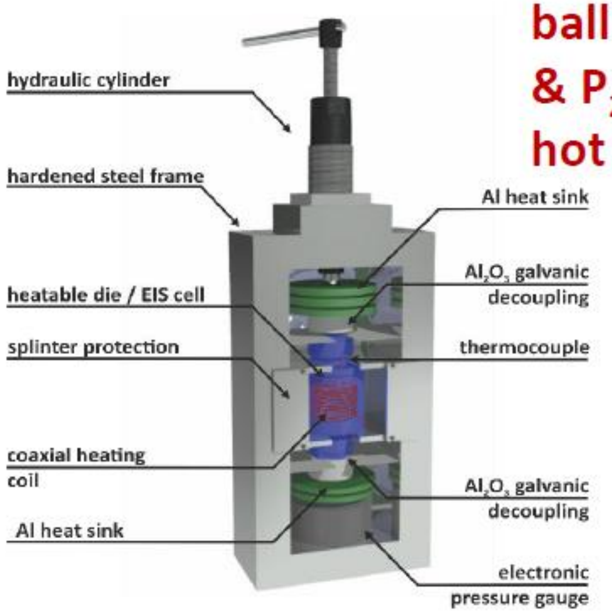
Others interesting phases among the Li_2S-P_2S_5 system



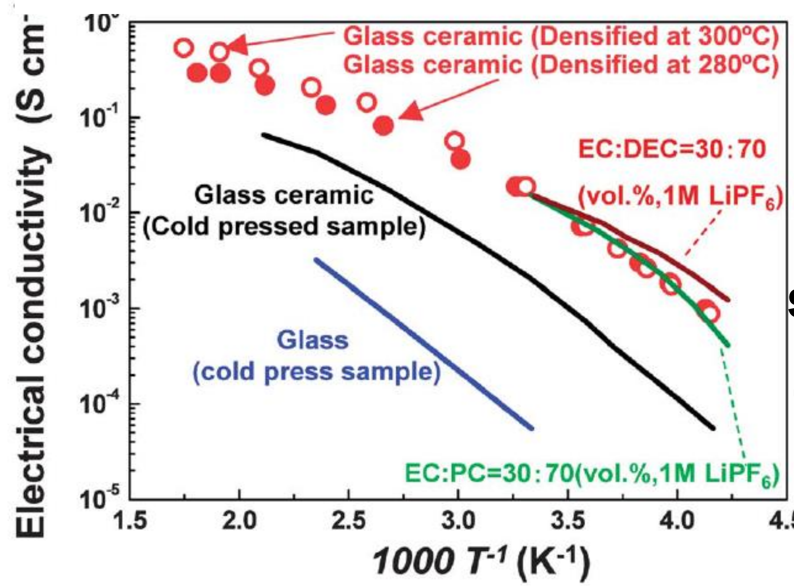
Crystal structure of superionic triclinic $Li_7P_3S_{11}$, consisting of PS_4^{3-} tetrahedra (blue) and $P_2S_7^{4-}$ di-tetrahedra (green) aligned along the *b*-axis.



σ = 7 x 10^{-3} S/cm; E_a = 300 meV, xtalite size 70 nm



ball mill Li_2S & P_2S_5 ➔ hot press



Glass ceramics by a two step process

σ = 1.7 10^{-2}S/cm

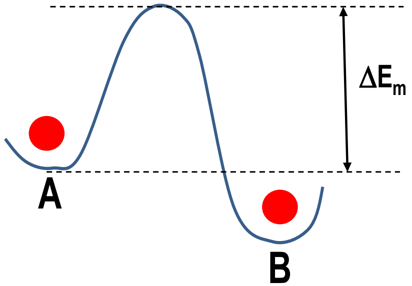
Tatsumisago et al. EES 2014

M. Busche, L.Nazar J. Janek et al. Chem. Mater. 2016

Rationalization of the good ionic conduction in sulfides:

Design principles

→ Ionic diffusion relies in the migration of a cation between stable sites through a higher energy environnment



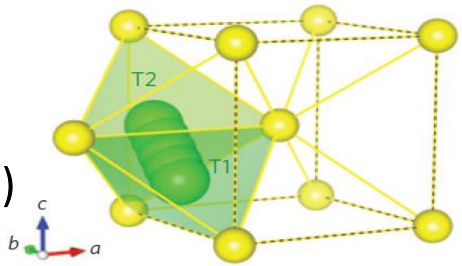
→ Topology of these sites in good ionic conductors.

Design principles of sulfur-based solid state electrolytes

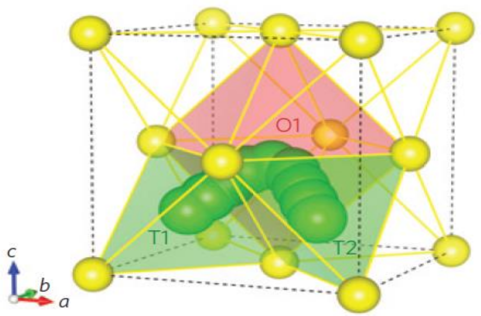
Li-ion migration pathways

Topology of the anion sublattice

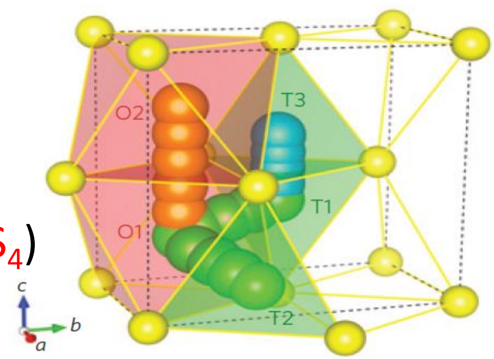
bcc
(LGPS)



fcc
(Li_2S)



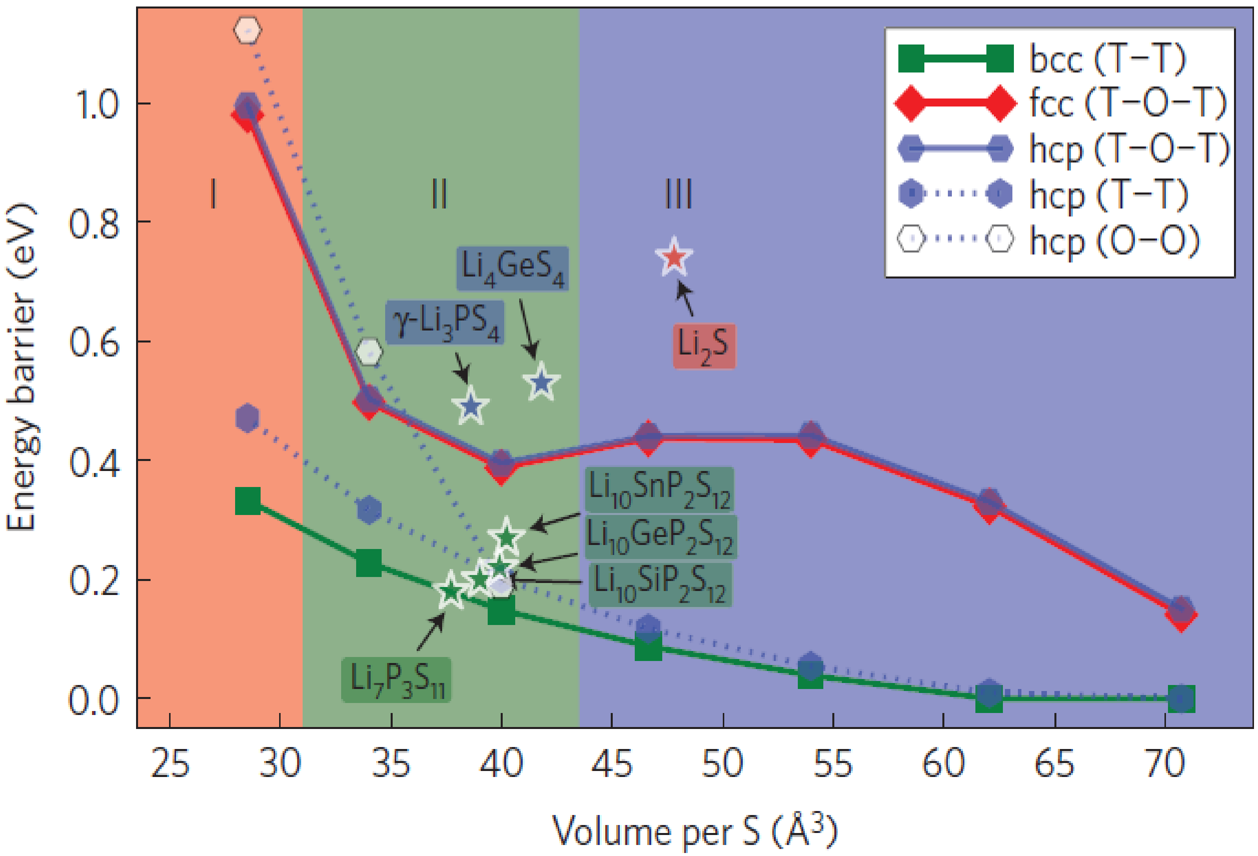
hcp
(γ-Li_3PS_4)



Y. Wang , Nature materials 14 (2015)

Design principles of sulfur-based solid state electrolytes: continuation

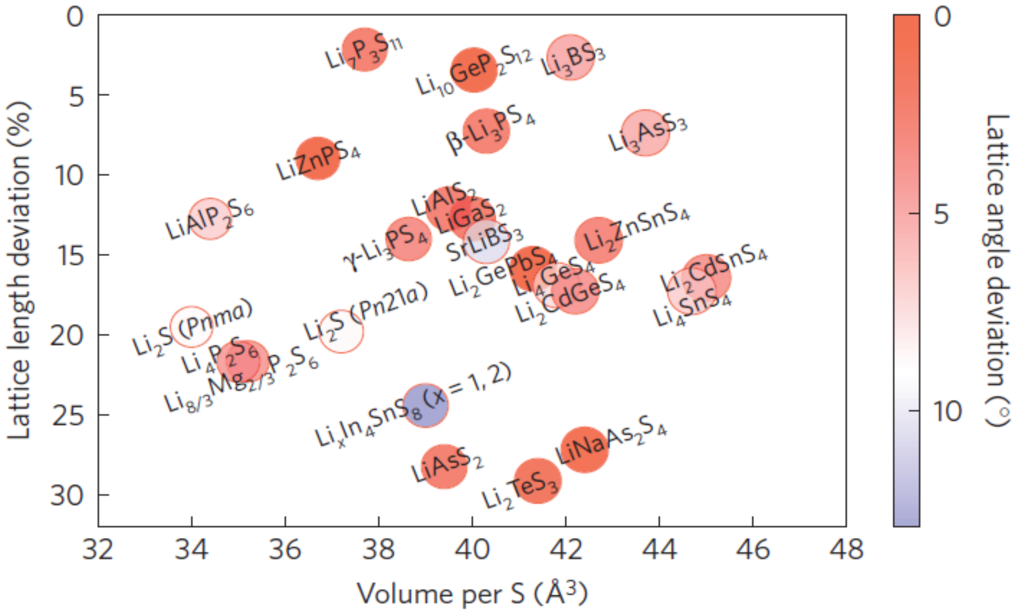
Activation barrier for Li-ion migration versus lattice volume



bcc-like S anion frameworks are superior for Li-ion diffusion with lower activation barrier than other close packed frameworks.

Design principles of sulfur-based solid state electrolytes: continuation

Screening of structures containing Li and S to a bcc anionic framework



bcc-like anion frameworks are much less common than hcp or fcc

Limited amount of candidates

.

Generalization

→ LiOCl and LiOBr have the anti-perovskite structure with bcc packed anions (E_a = 0.17 eV)

→ Ag^+ and Cu^+ ionic conductors (α-AgI) have bcc anion sublattices

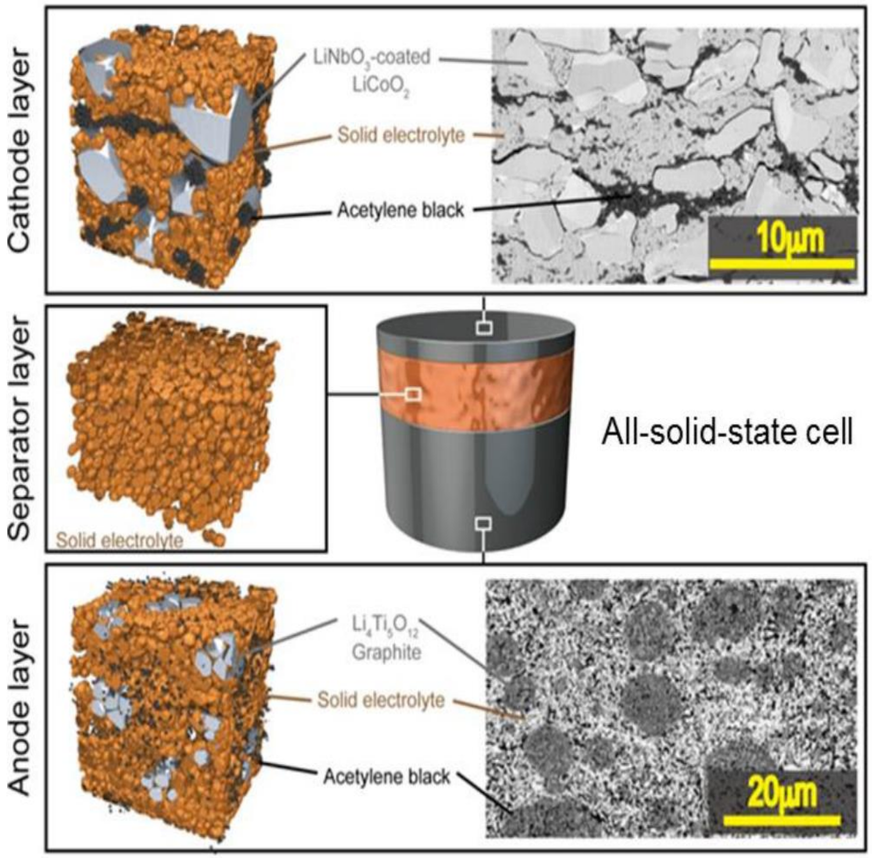
→ Argyrodite-type Li_7PS_6 or Na_3PS_4 (σ = 1 mS cm^{-1}) do not match bcc lattices

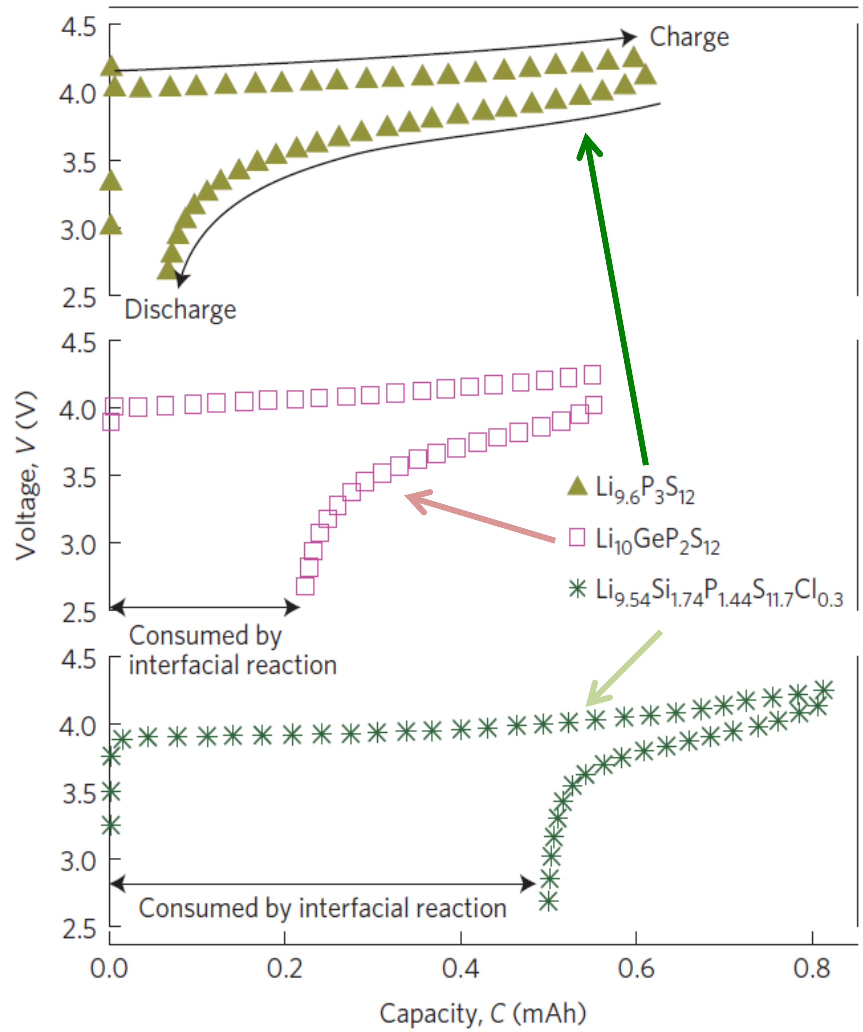
→ Na+, Mg^{2+}, O

The ionic conductors and their chemica/electrochemical stability towards Li

The interfaces

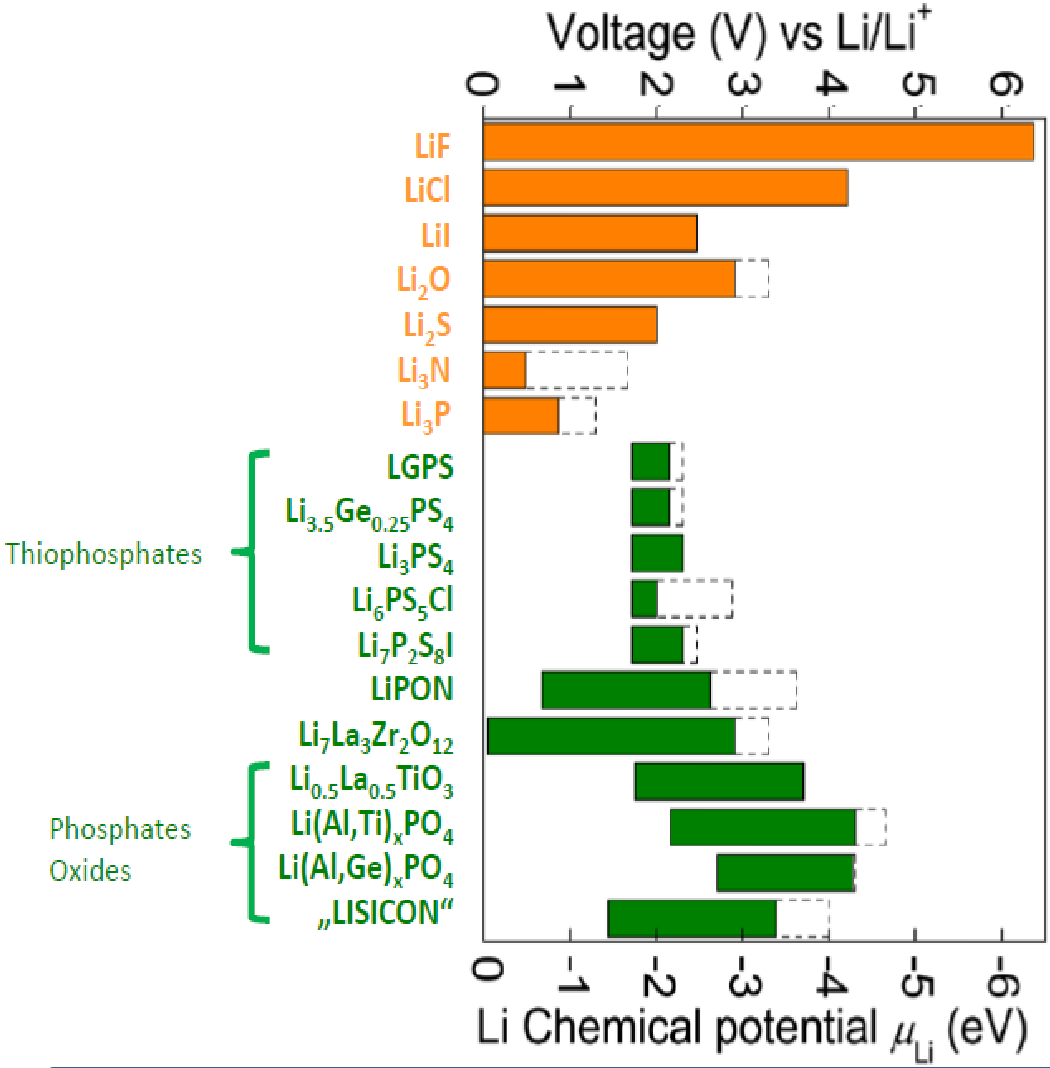
Fabrication and performance of Solid state batteries





$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ is the best ionic conductor but not stable to low potential

The interface problem with metallic lithium



→ Most solid electrolyte materials are not thermodynamically stable vs. Li

→ Their stability if any results from sluggish kinetics of decomposition reactions at Interfaces

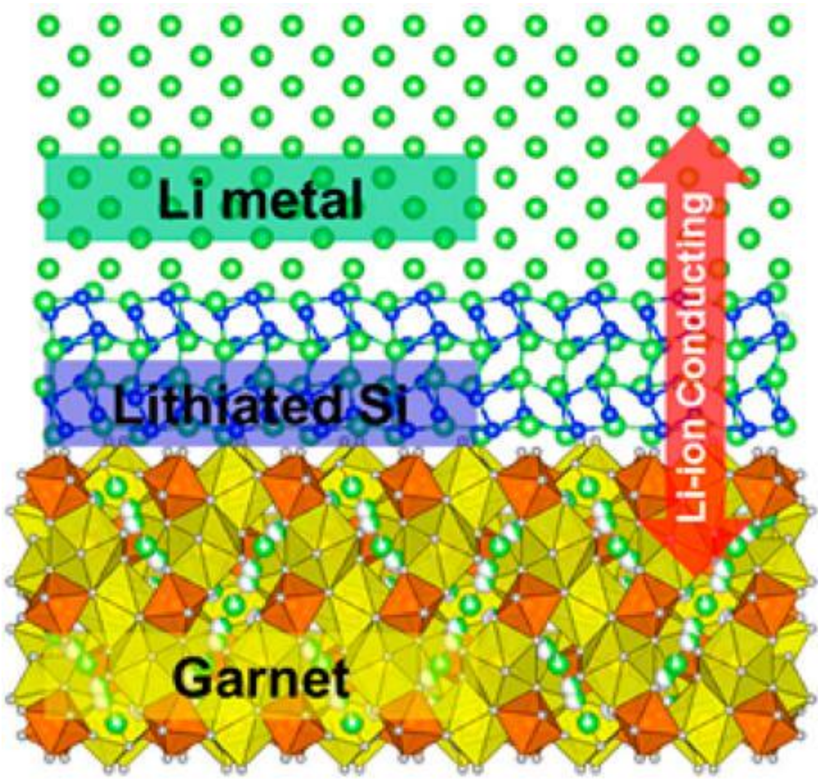
→ The passivation of the interface is at the origin of the electrolyte stability

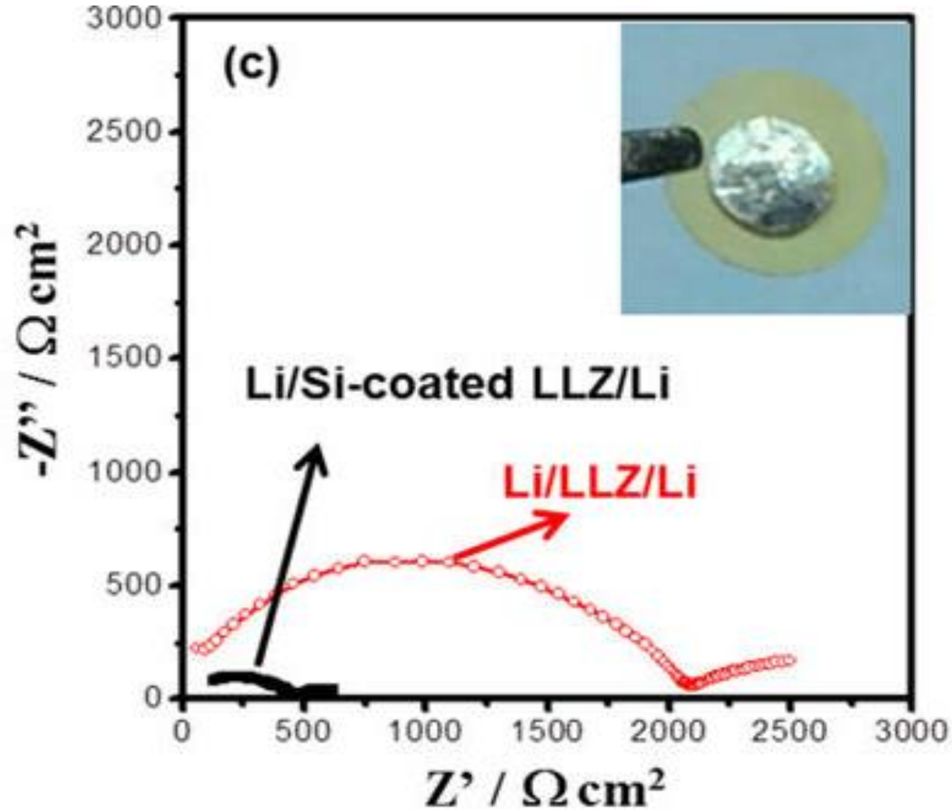
$LiCoO_2$/**$LiNbO_3$**/$Li_{10}GeP_2S_{12}$

Interface engineering is ESSENTIAL for enhancing electrolyte stability

Y. Zhu et al. ACS Appl. Mater. Interf (2015)

Fighting the Li / solid state electrolyte interface

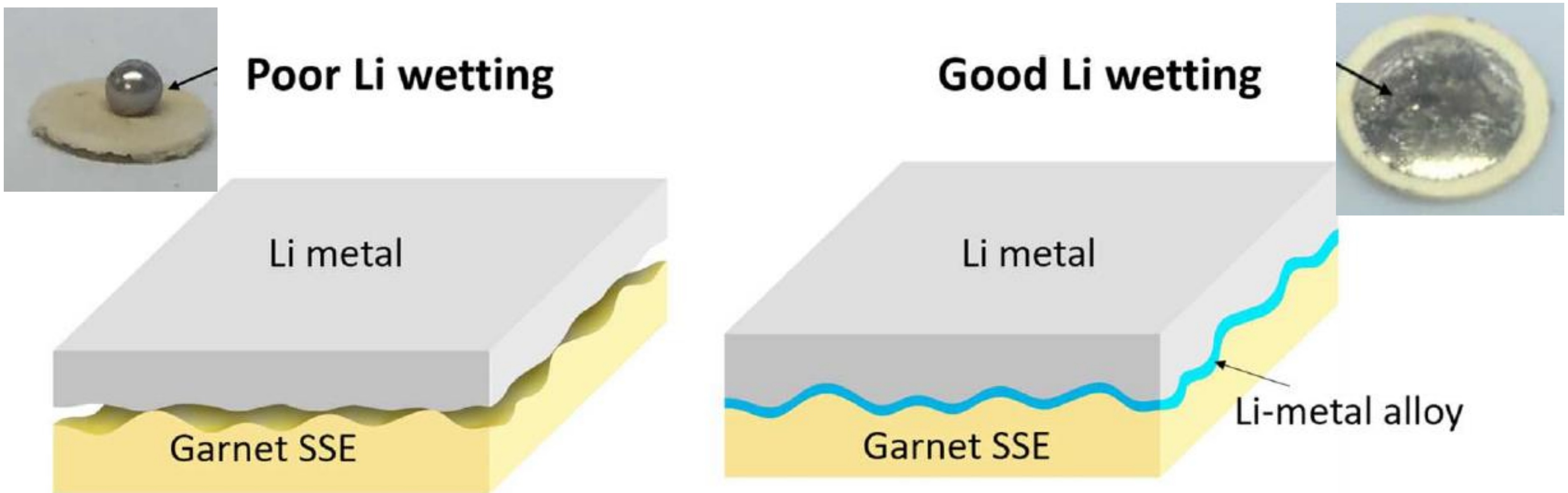




Transition from Super-lithiophobicity to Super-lithiophilicity leads to a much smaller interfacial resistance

F. Lauo , J. Am. Chem. Soc. 2016, 138, 12258−12262

Fighting the Li / solid state electrolyte interface



$Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN)

$Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN)

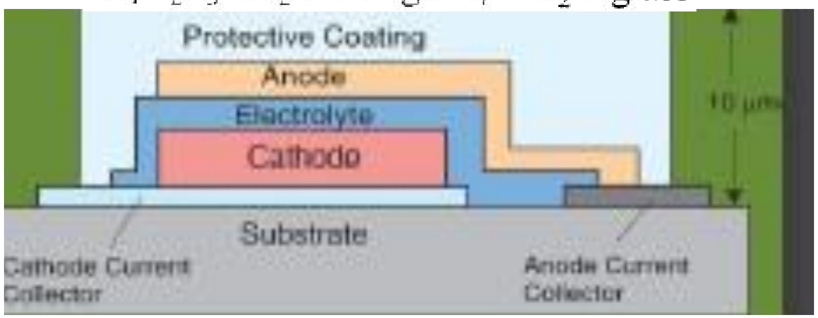
Assembling all solid state batteries

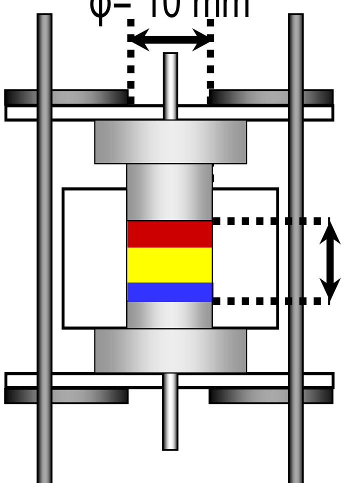
Thin film and bulk all Solid State batteries:

"All-solid state batteries"

Micro-batteries

$Li/P_2S_5{-}Li_2S{-}LiI\ glass/TiS_2 + glass$

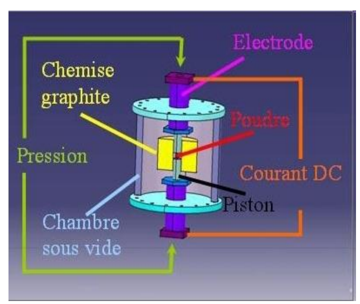




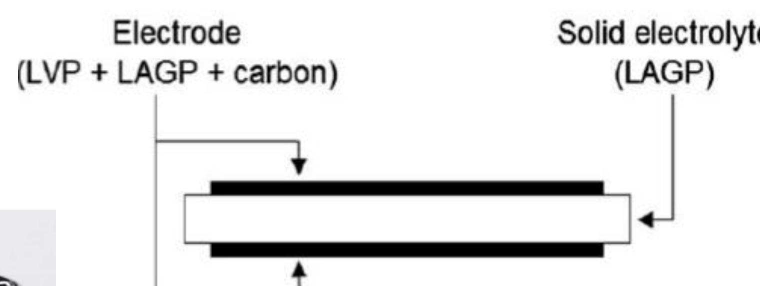
Bulk-type batteries

High densification
(ceramics)

Spark Plasma Sintering (SPS)



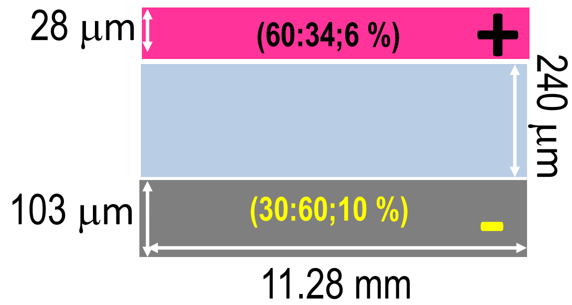
Others
(Deposition, hot pressing)



State of the art All Solid State Batteries: performances

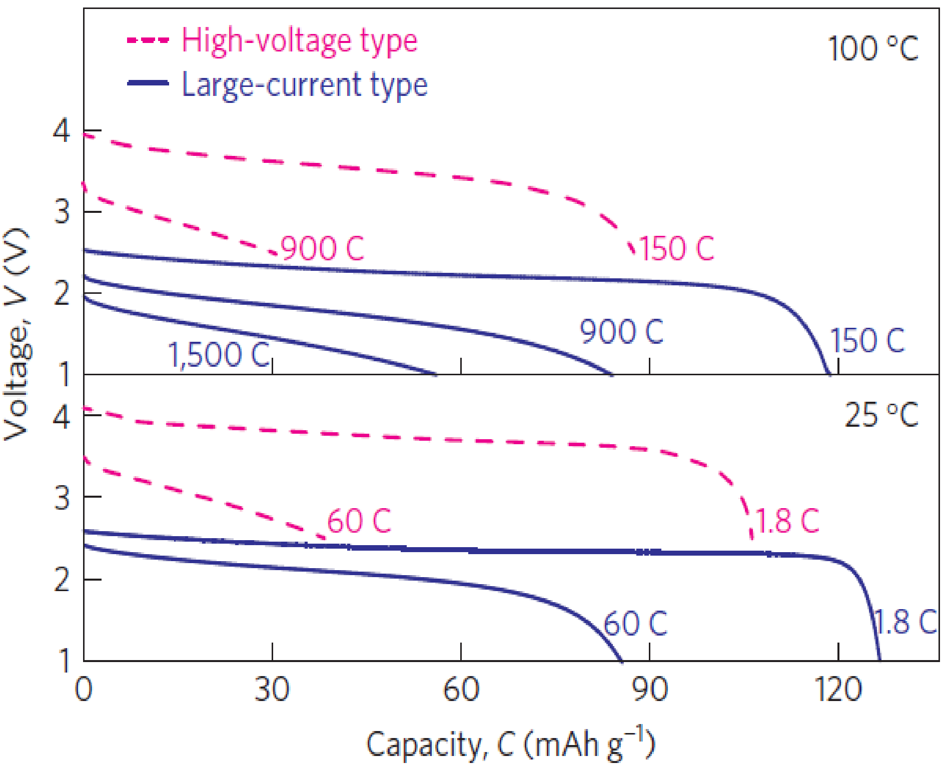
High voltage type:

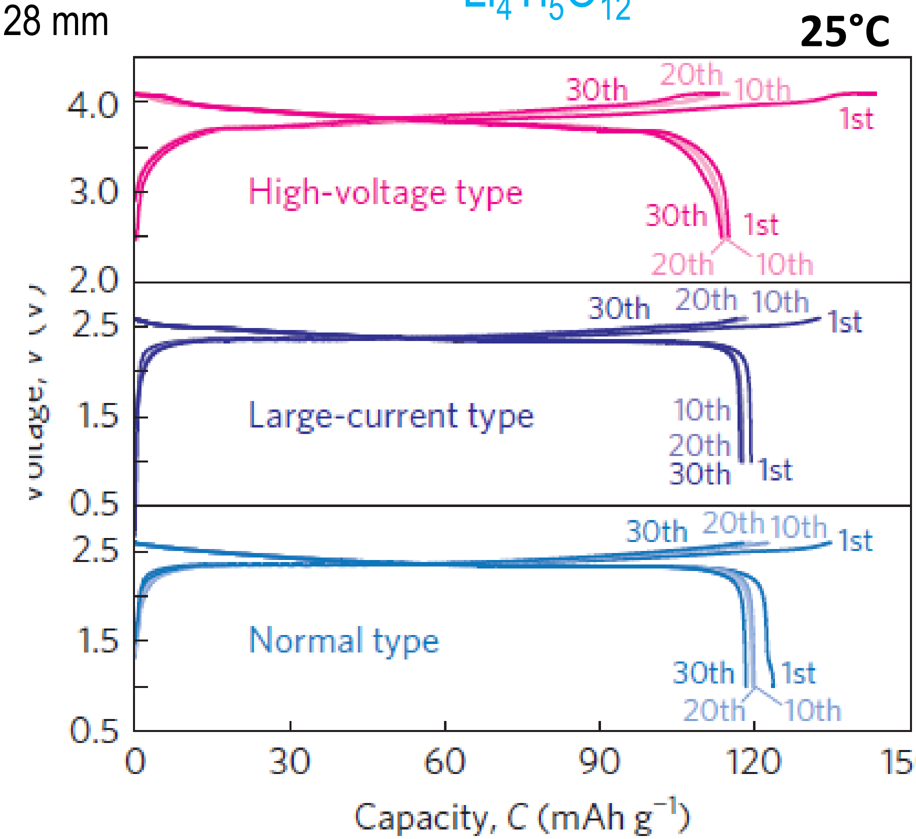
$LiNbO_3$ coated $LiCoO_2$/
$Li_{9.6}P_3S_{12}$/
graphite



Large-current type:

$LiNbO_3$ coated $LiCoO_2$/
$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$/
$Li_4Ti_5O_{12}$





State of the art All Solid State Batteries: performances

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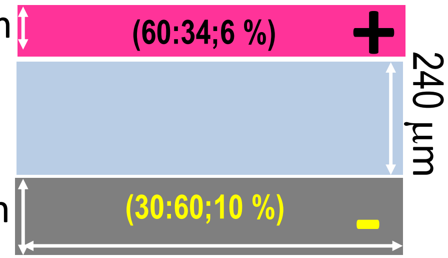

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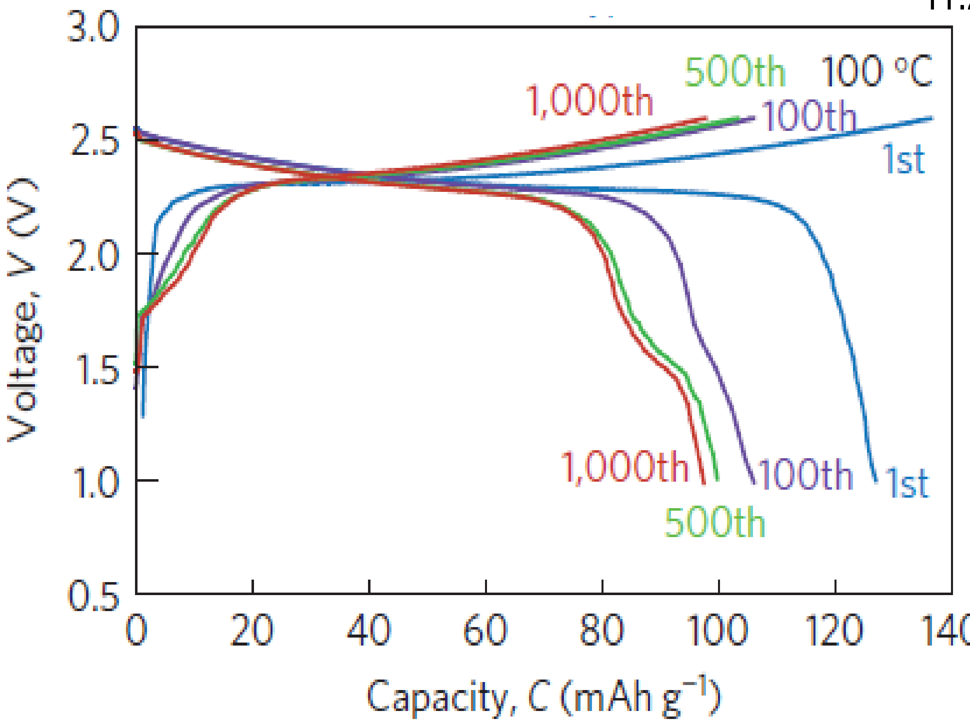
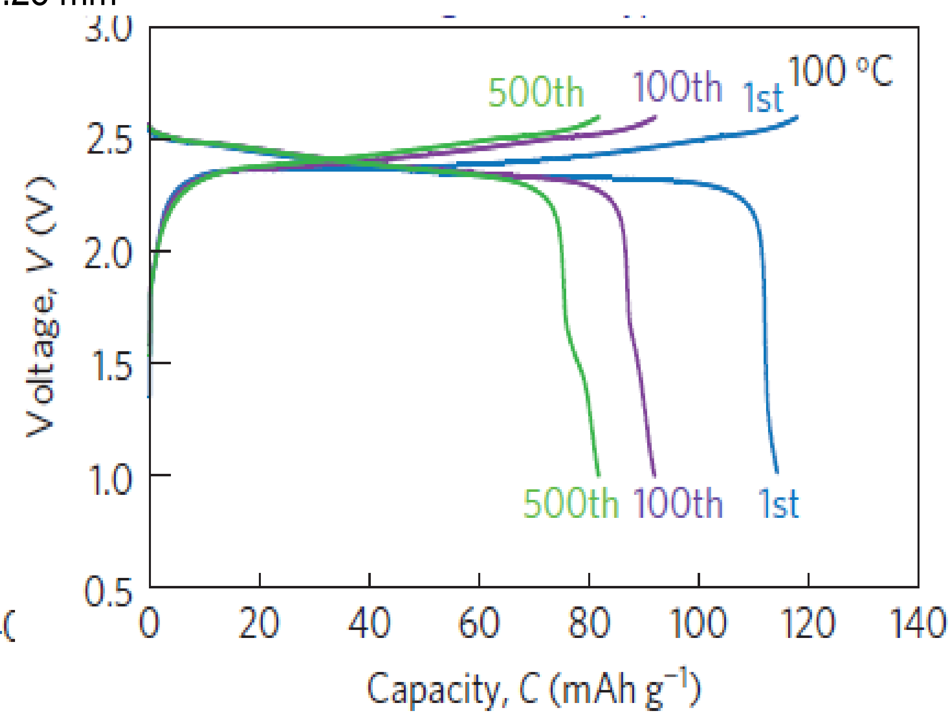


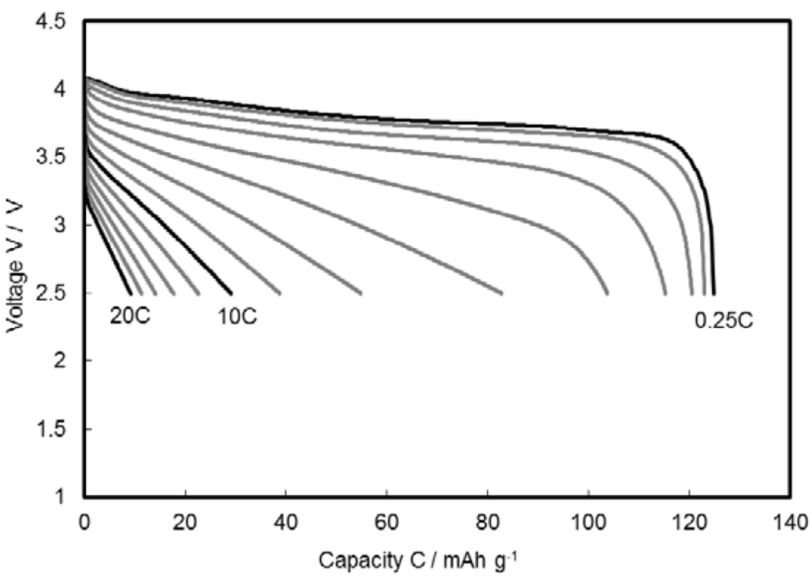


Encouraging results: Although technological issues still need to be addressed ASBBs stand as promising candidates for energy storage devices

Effect of electrodes thicknesses in ASSBs: More metrics

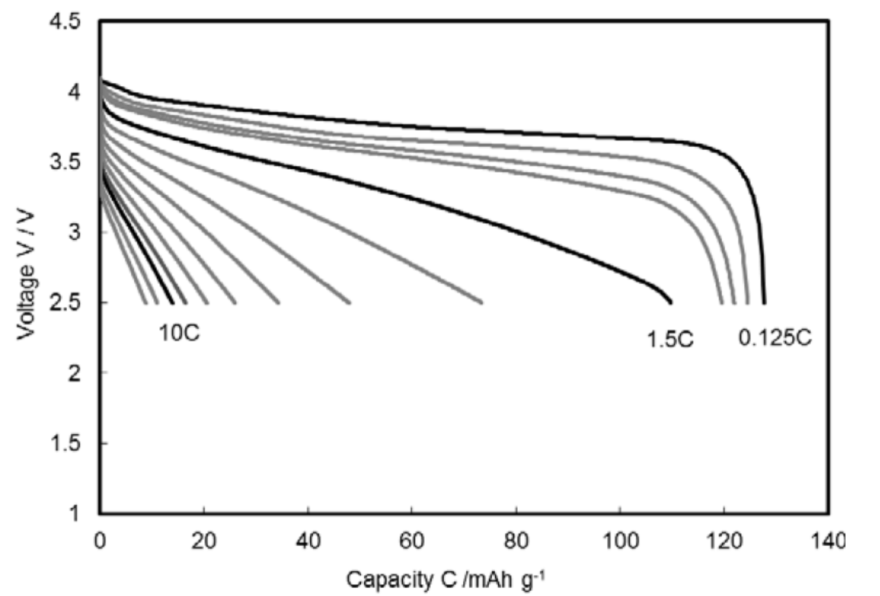
70/27/3)%	28 μm	$LiCoO_2$(LGPS)C	308 μm	(61/36/3)%
	240μm	LGPS-LPS	240μm	
(60/40)%	28 μm	C(LPS	320 μm	(60/40)%

High active material content electrode



Specific energy: 45.6 Wh kg^{-1} (cell based)

Ultra-thick electrode



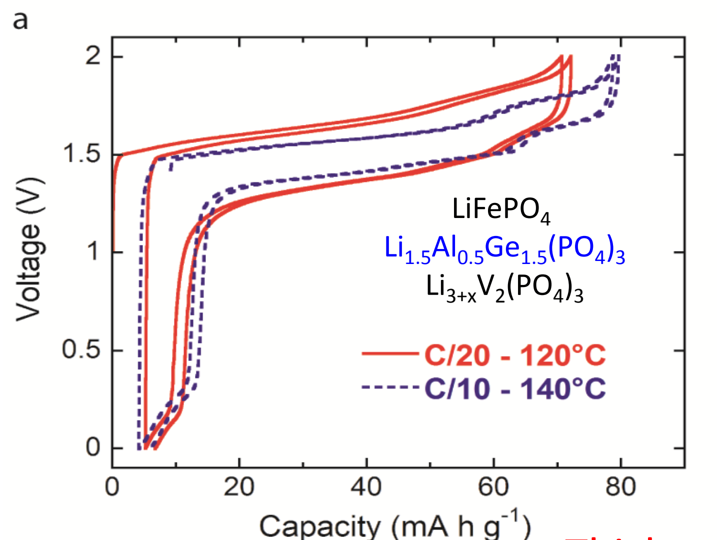
Specific energy: 133 Wh kg^{-1} (cell based)

Importance of the thin film separator thickness in governing the specific energy

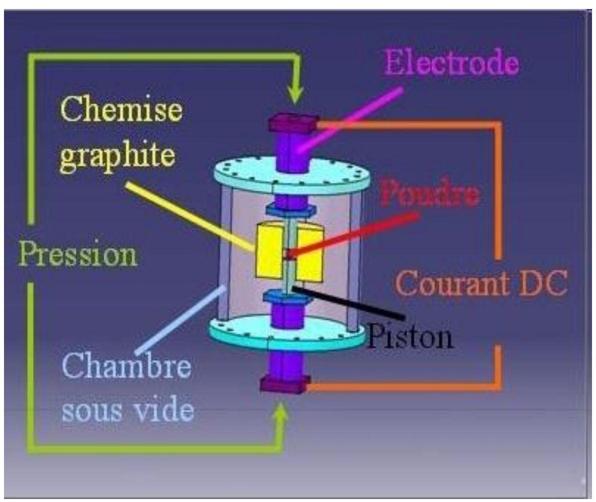
Kanno et al., Nature Energy 1 (2016): 16030

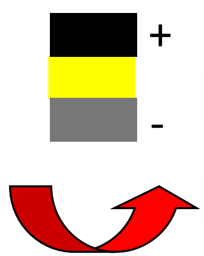
New approach for assembly of all solid-state batteries

Spark Plasma (SPS) synthesis

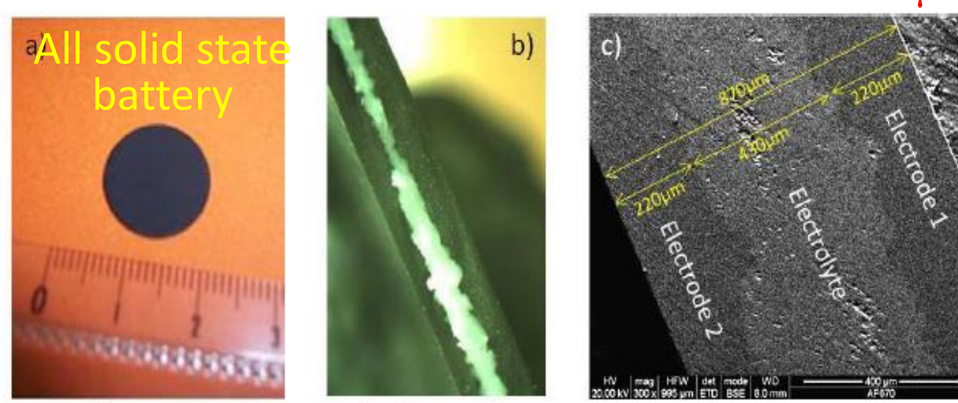


> 100 cycles





Thickness 900 μ

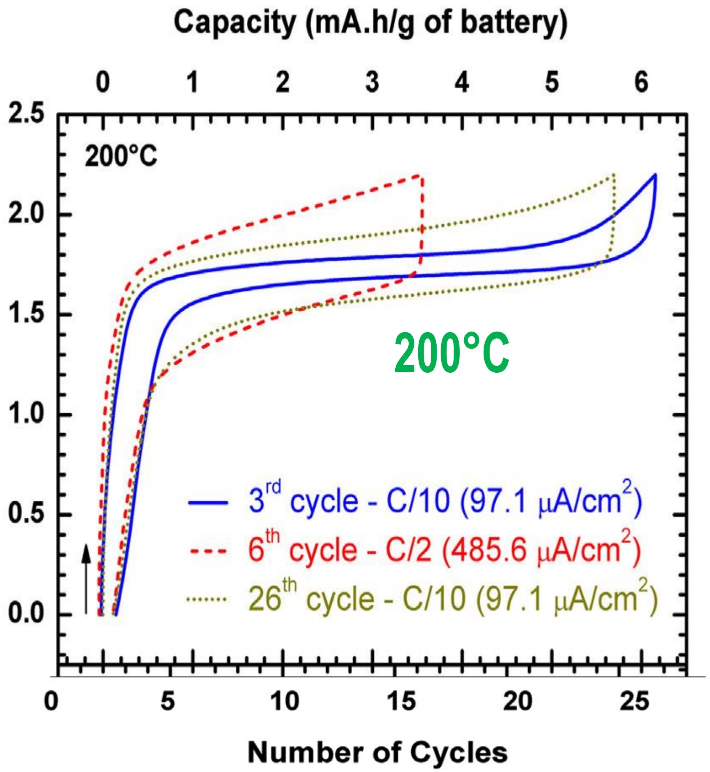


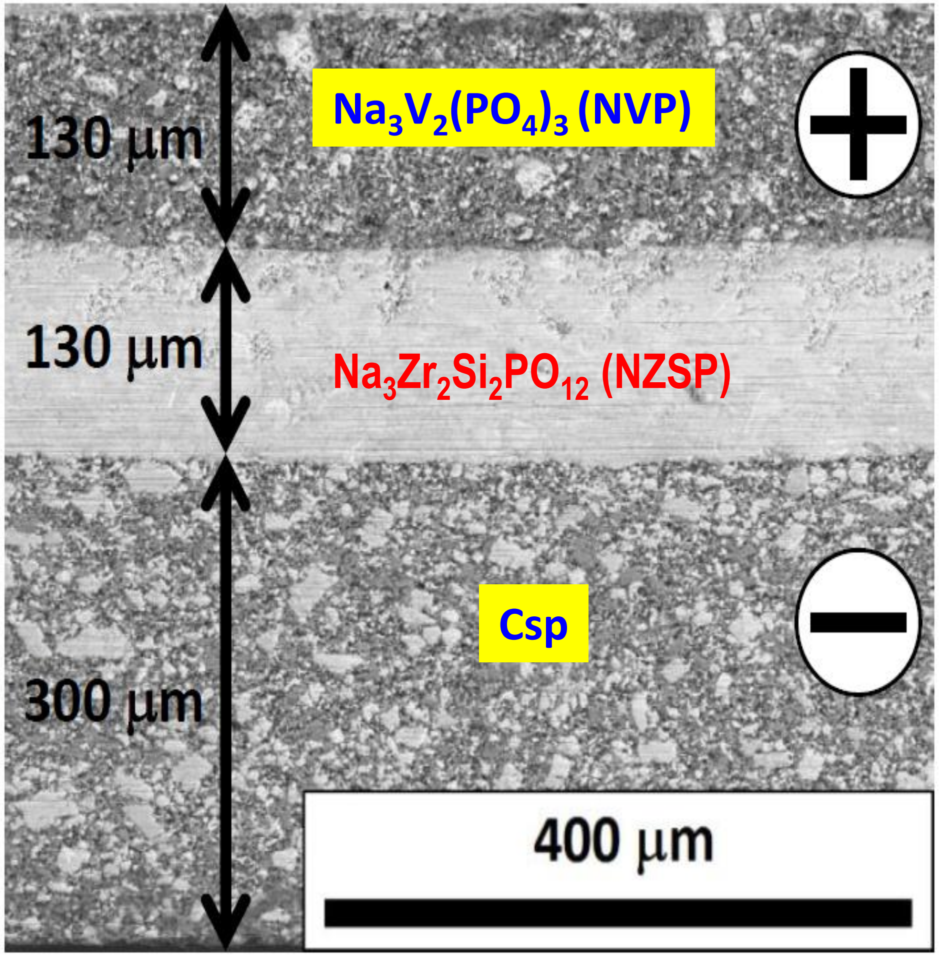
TEM cross-section

Aboulaich A, Bouchet R, Tarascon J-M, Viallet V, Dollé M. " Advanced Energy Materials, 1, 179-183, 2011

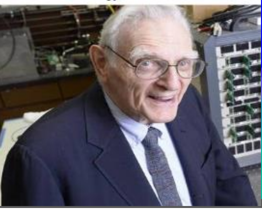
Fabrication of an ASSB: From Li to Na

Assembly by Spark Plasma Sintering (SPS)

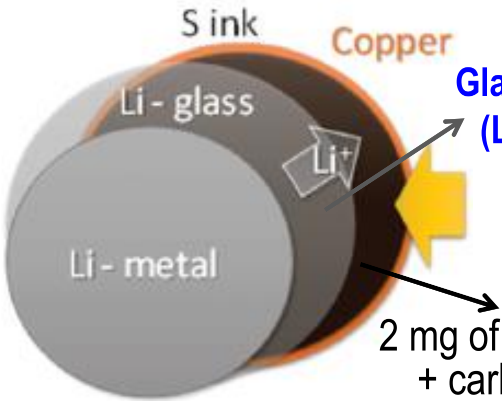




F. Lalére et al. J. Power sources, 247 (2014) 975- 980

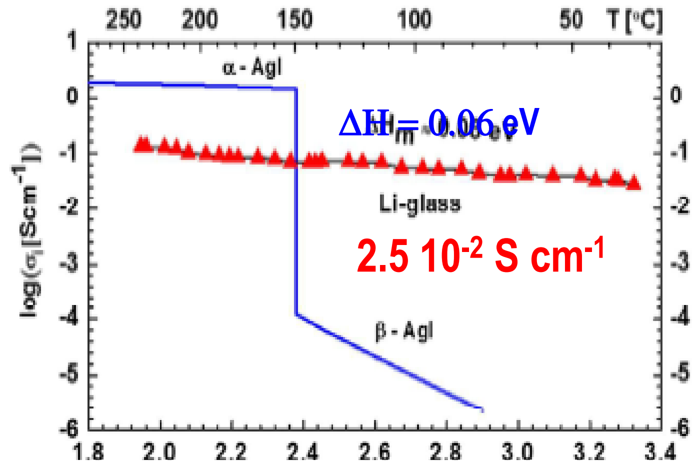


A new strategy for all solid state batteries

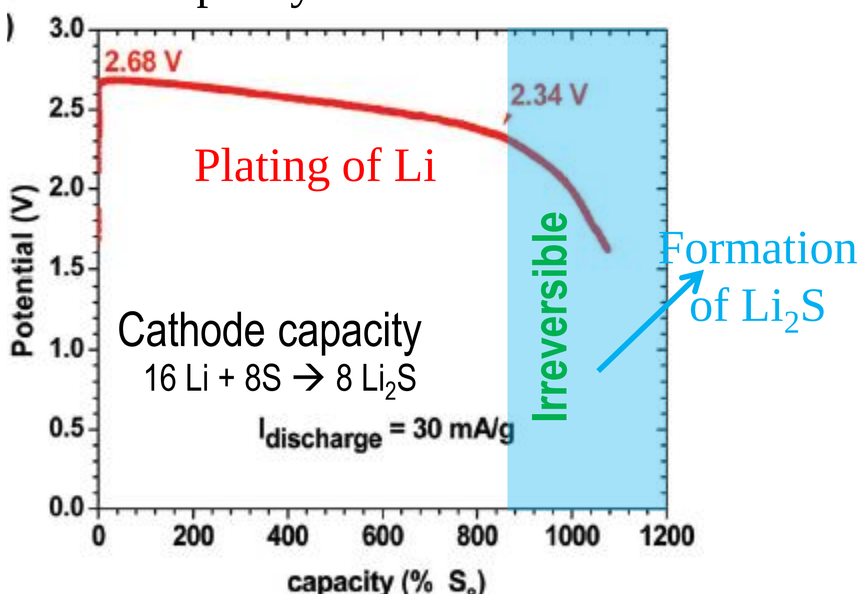


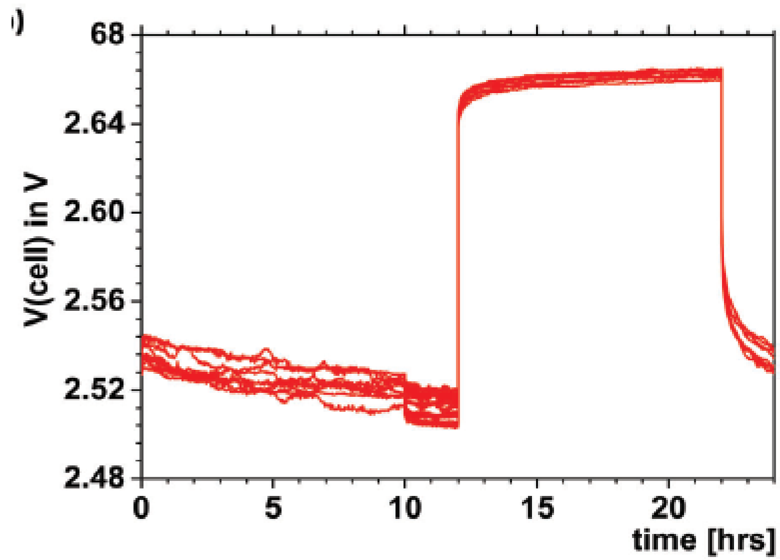
Glass electrolyte : Water glass
$(Li/Na)_{2,99}Ba_{0,005}OCl_{1-x}(OH)_x$

2 mg of sulfur+ glass electrolyte + carbon (47: 43: 10 Wt %)



Capacity based on S

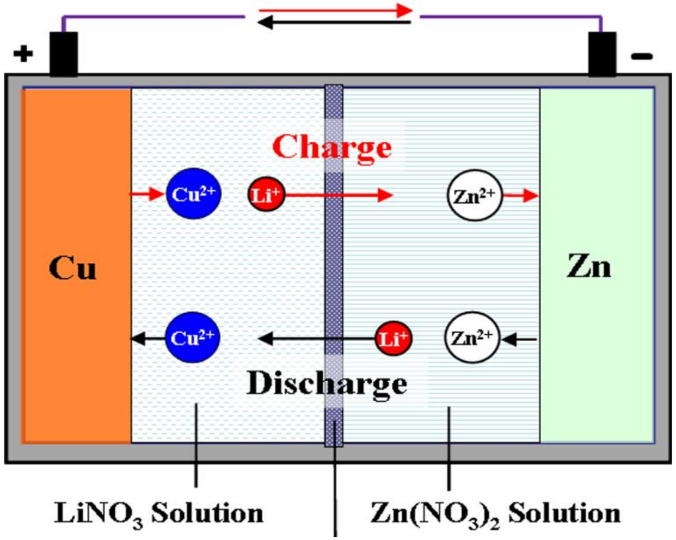


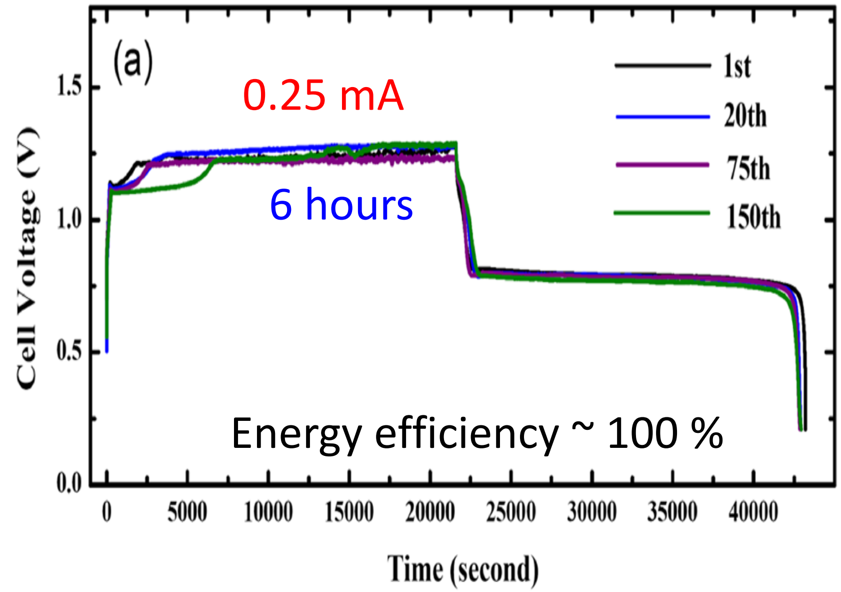


Cu reacts with Cl to form CuCl $CuCl + Li^+ + e^- \longleftrightarrow LiCl + Cu$

M.H. Braga, Energy &environment science , 2016, DOI: 10.1039/c6ee02888h

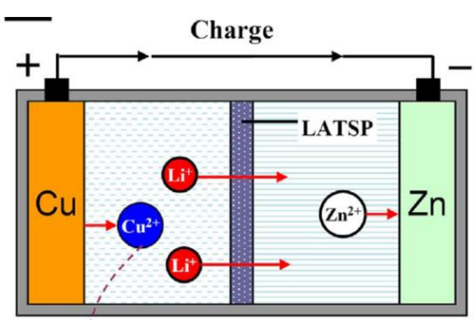
Use of Li-ionic conducting membranes as messenger to fabricate aqueous rechargeable Zn-Cu battery

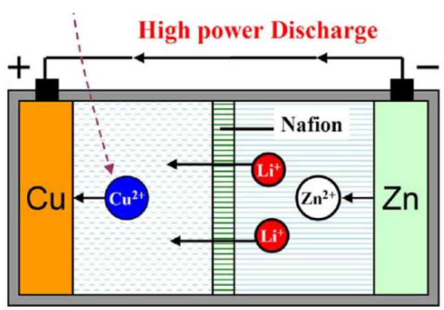


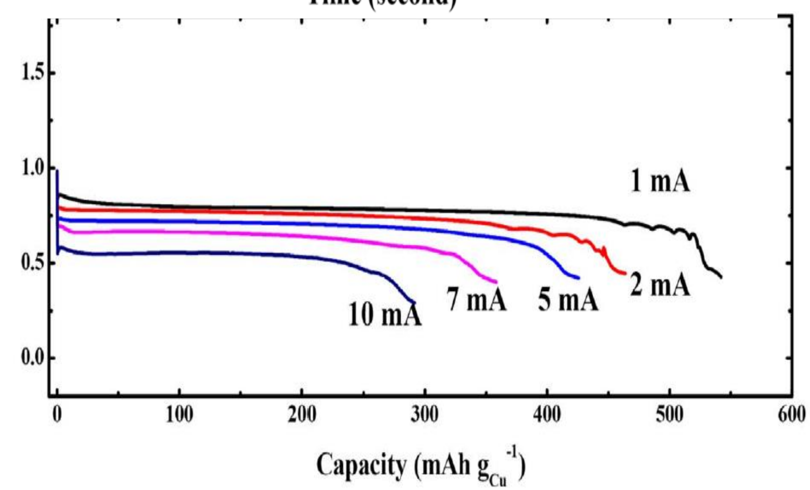


$(Li_{1+x+y}Al_xTi_{2-x}Si_yP_{3-y}O_{12}$, LATSP)

$$[Cu + 2LiNO_3] + Zn(NO_3)_2 \leftarrow \rightarrow Cu(NO_3)_2 + [2LiNO_3 + Zn]$$



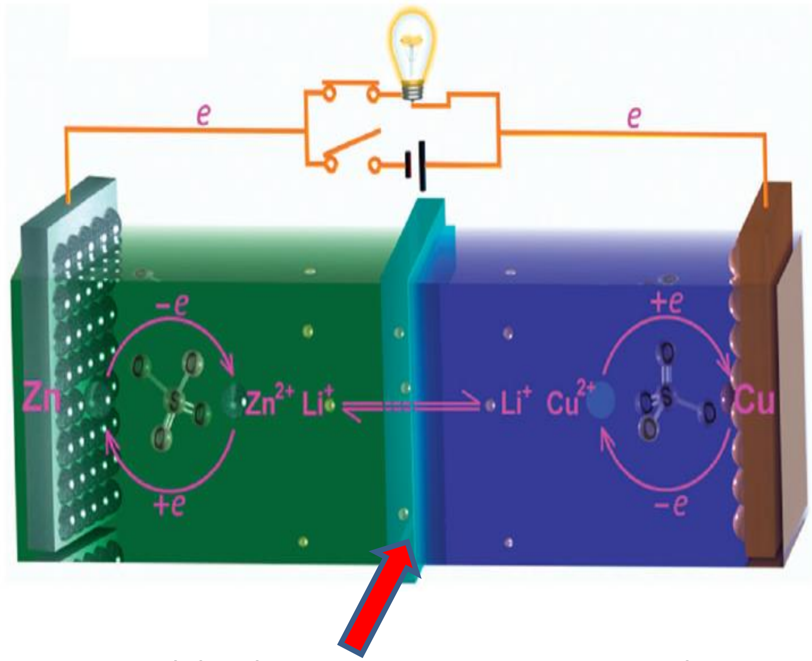




Theoretically 68.3 Wh/kg could be expected: Practically 34 Wh/kg could be feasible

X. Dong, Scientific Reports DOI: 10.1038/srep06916

Use of Li-ionic conducting membranes as messenger to fabricate a queous rechargeable Zn-Cu battery

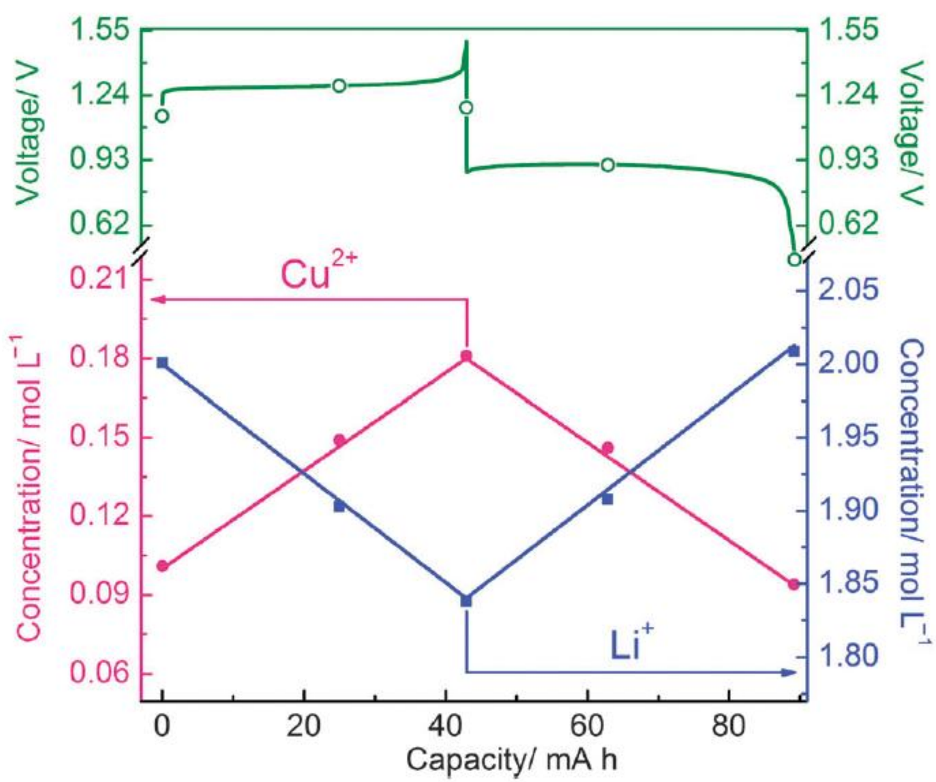


An ion-block type separator membrane made of PVDF/PMMA-LiClO4/PVDF

Anode: $Zn \rightarrow Zn^{2+}(aq) + 2e^{-}$ (−0.7618 V)

Cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu$ (+0.340 V)

$Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$ (+1.1018 V)



Concentration changes of Cu^{2+} and Li^{+} in cathode during a typical charge-discharge at 6mA/cm²

Crossover of Cu^{2+} upon cycling °

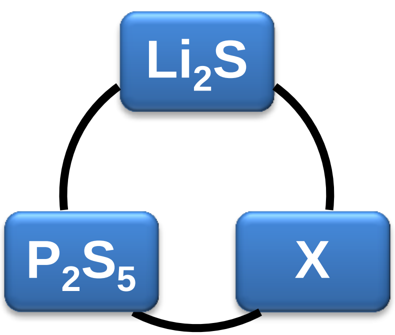
The solid electrolytes for Li-ion: Conclusions

The ceramics

- Garnets : $Li_5La_3Nb_2O_{12}$
- NaSICon : $Na_{1+x}Zr_2P_{3-x}Si_xO_{12}$
  $LiA'_{2-x}{}^{IV}A''_x{}^{IV}(PO_4)_3$
- LiSICon : Li_4XO_4 - Li_3YO_4

The Thio-LiSICON

- Li_3PS_4, Li_4MS_4 (Si, Ge, Sn)
- $Li_{4-x}M_{1-x}P_xS_4$ (Si, Ge)
- $Li_{10}MP_2S_{12}$ (Si, Ge, Sn)



- MS_2 (Si, Ge, Sn)
- LiX (Cl, Br, I)
- B_2S_3
- Li_3PO_4
- Li_2SO_4
- …

S-based vitro-ceramics

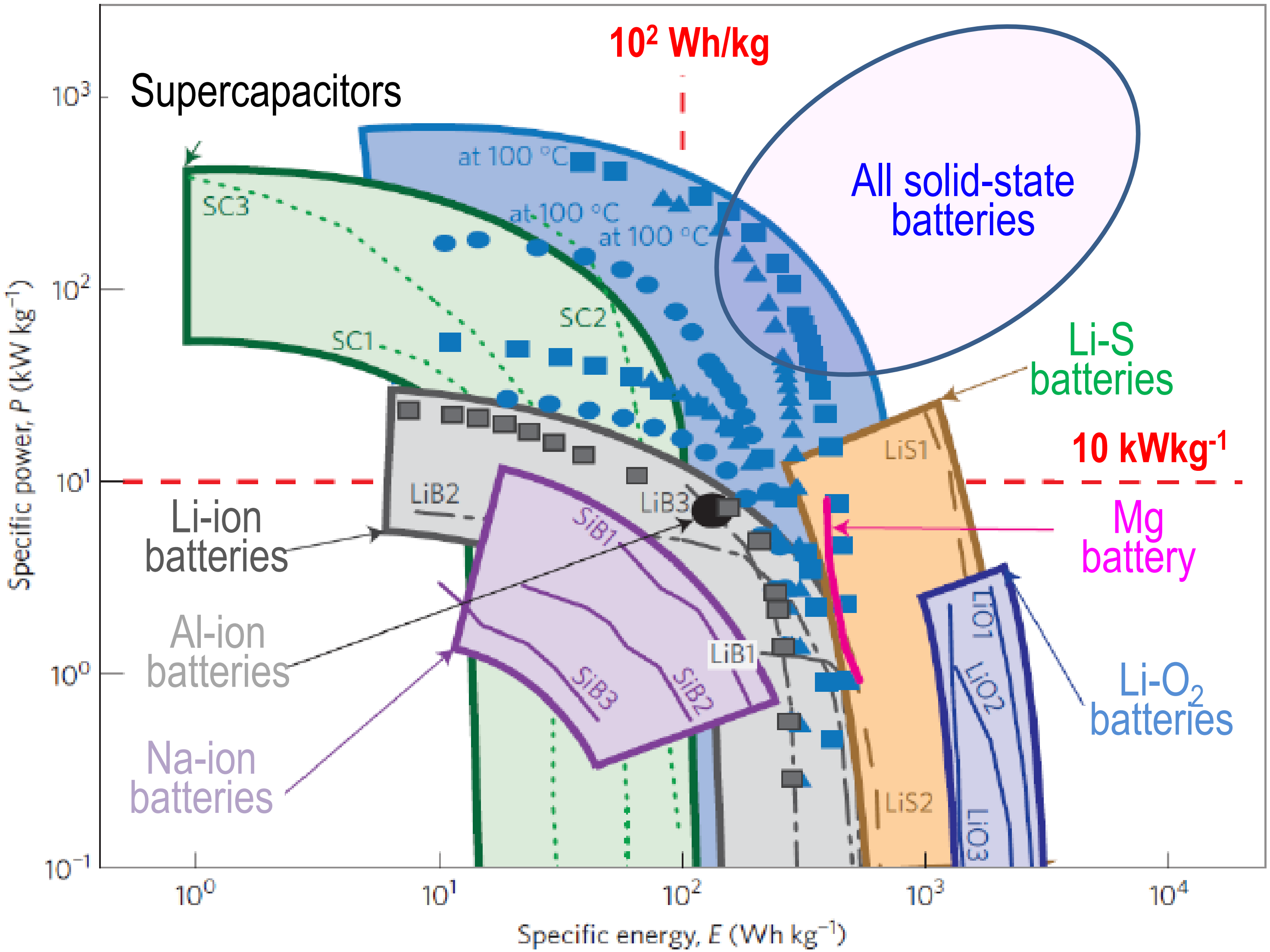
$$A^{m+}_{12-n-x}\,B^{n+}\,Ch^{2-}_{6-x}\,X^{-}_{x}$$

A^{m+} = Cu, Ag, Li
B^{n+} = Ge, Al, P
Ch^{2-} = O, S, Se
X^{-} = Cl, Br, I

Li_6PS_5X (Cl, Br, I)

The Argyrodites

State of the art of « All Solid State Batteries »: The Ragone plot



R. Kanno et al.; Toypta Motors, Nature Energy,: 16030 (2016).

Acknowledgments

Thank you for your attention

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