ELECTROCHEMICAL STORAGE SYSTEMS

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ENAM
Electrochemistry
and Nanotechnologies
for Advanced Materials

Research group of Sapienza University of Rome, at the Department of Chemistry.

FOCUS

Electrode and electrolyte materials for storage and conversion of energy in electrochemical devices
(i.e., lithium-ion batteries and polymer electrolyte membrane fuel cells / electrolyzers)

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CONTENTS of the LECTURE

- Introduction to electrochemical storage systems
- Lithium-based batteries: constituent materials and functional properties
- Different types of electrolytes: liquid, polymer and solid-state conductors
- Focus on ionic liquid additives and gel polymer electrolytes
- Perspectives and alternative chemistries (calcium-based batteries)

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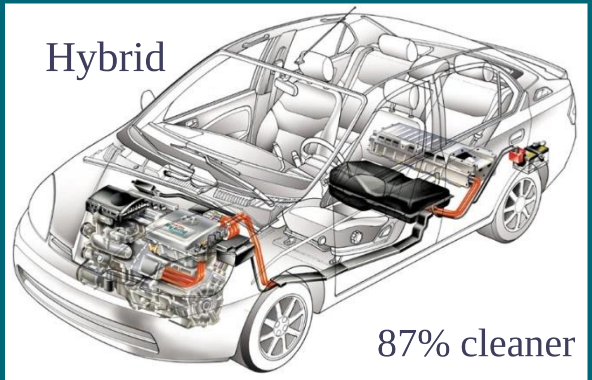
Energy storage systems: a global challenge in the XXI century

Coal, natural gas and oil

Transportation

Electricity

Electric car transition



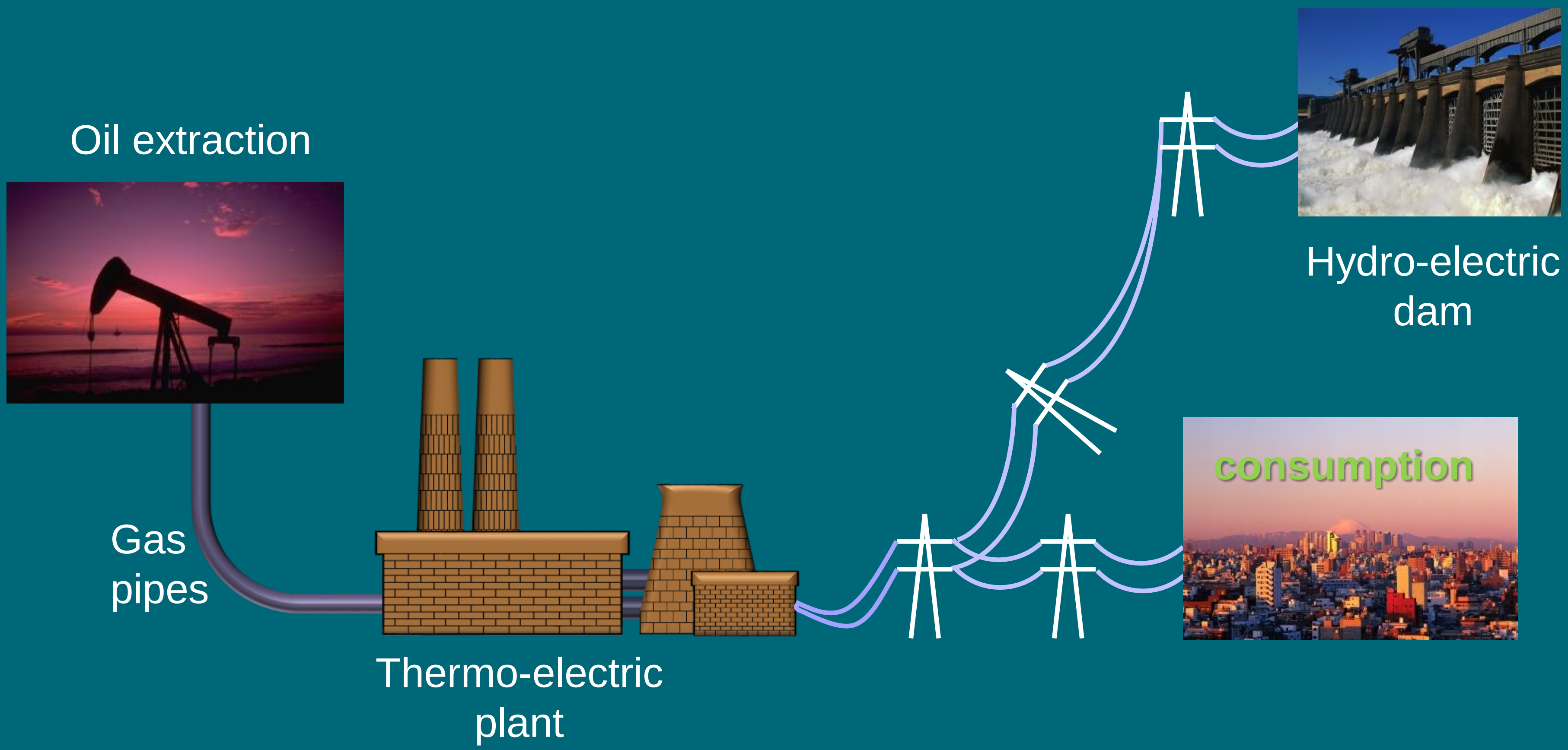
The European Green Deal:

reduce emissions by at least 55% by 2030 compared to 1990 levels!

Production from non-oil energy sources

Stationary storage

A CONVENTIONAL ELECTRIC GRID



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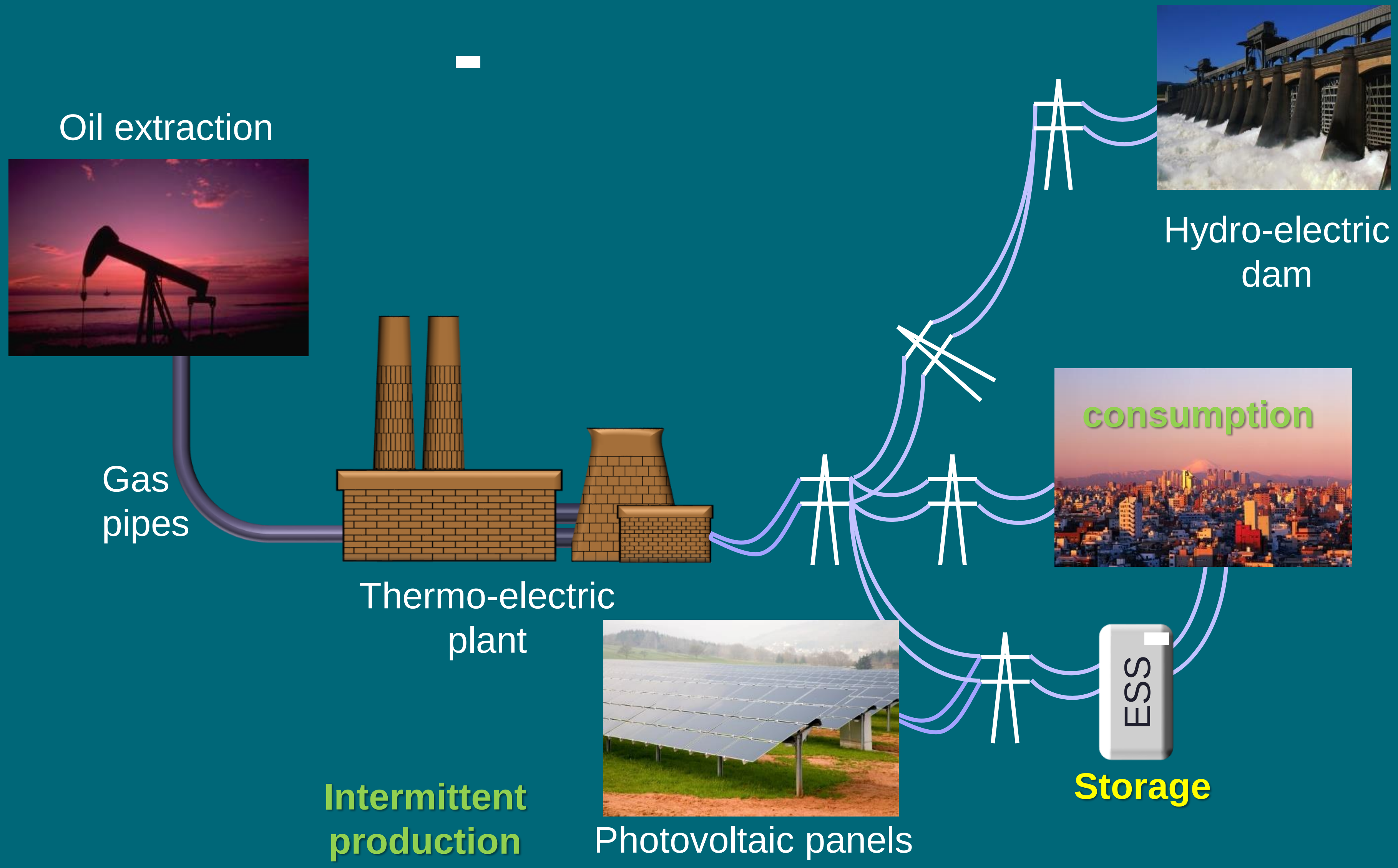
SMART GRID



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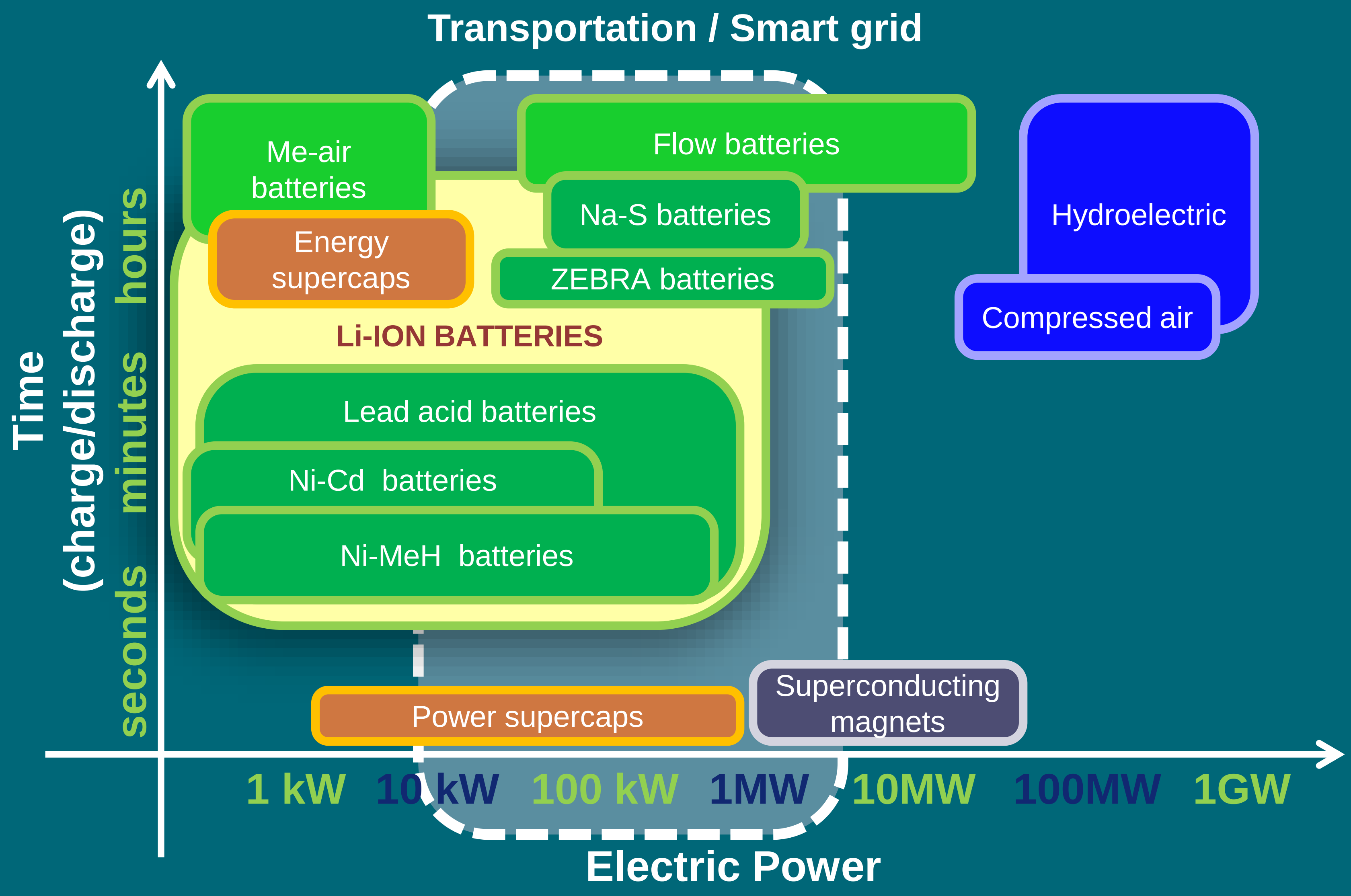
ENERGY STORAGE SYSTEMS



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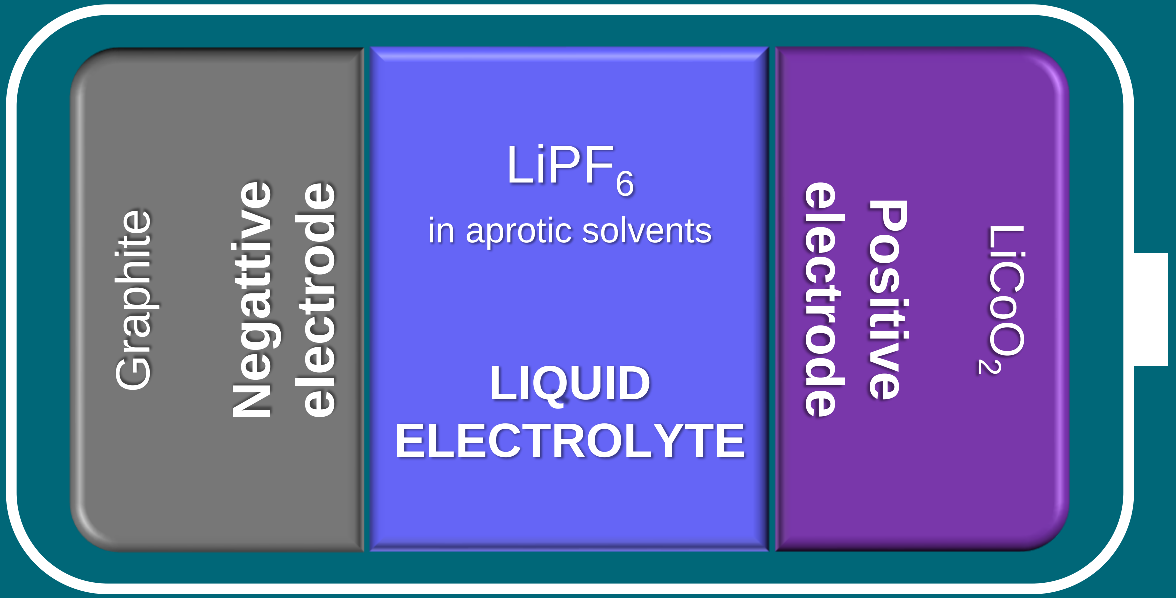
A TYPICAL Li-ION BATTERY



3.6 V
30 mAh/g_{tot}
108 Wh/kg_{tot}

Can store twice the energy of conventional accumulators (Pb-acid batteries)

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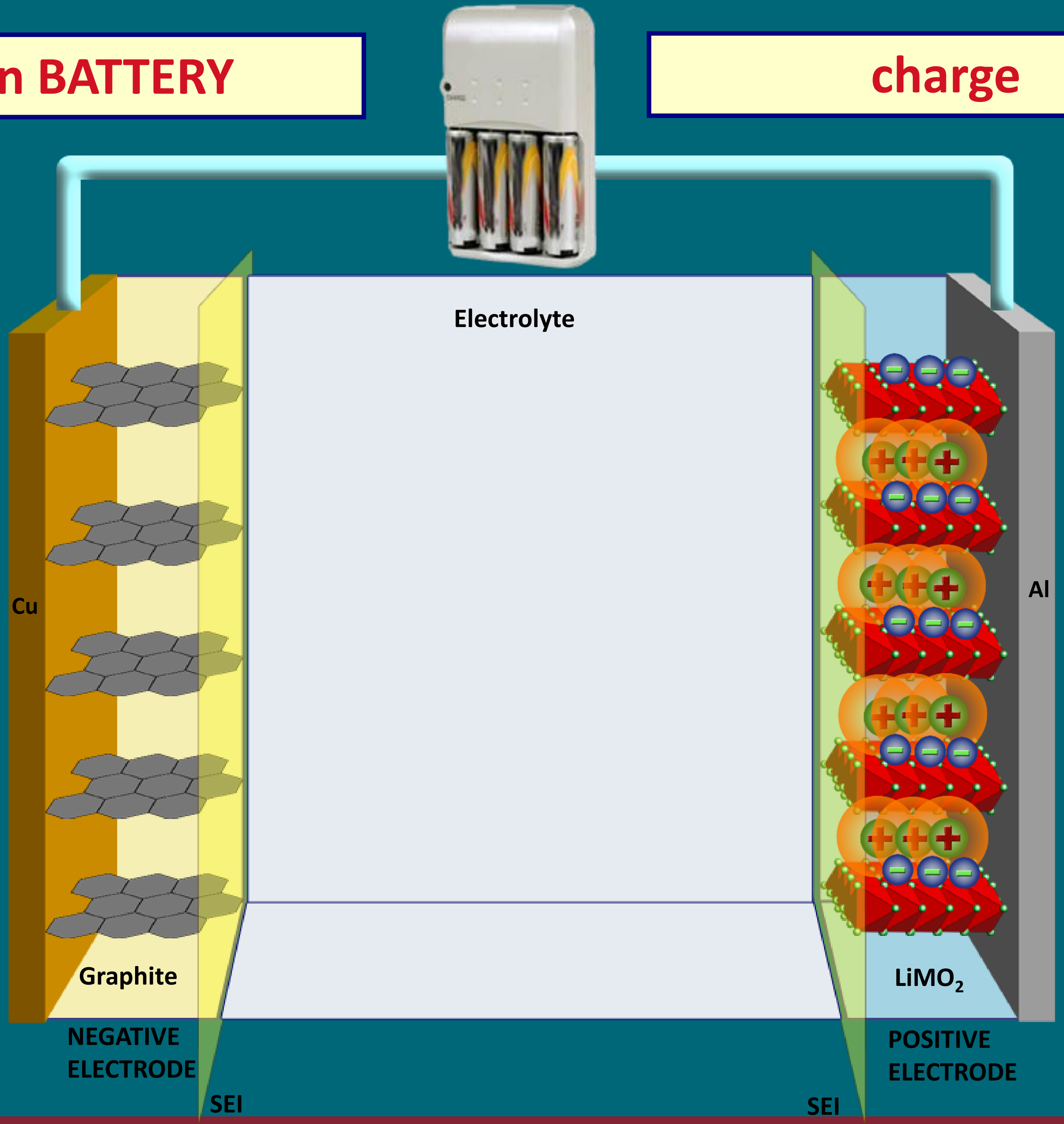
Li-ion BATTERY

charge



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Li-ion BATTERY

discharge

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The history: 1991

https://www.youtube.com/watch?v=VxMM4g2Sk8U

$\Delta E = 4{,}1$ V

Energy density: ~ 80 Wh kg^{-1} (gravimetric) e ~ 200 Wh L^{-1} (volumetric)

Nishi, Y. The Development of Lithium Ion Secondary Batteries. Chem. Rec. 2001, 1, 406–413

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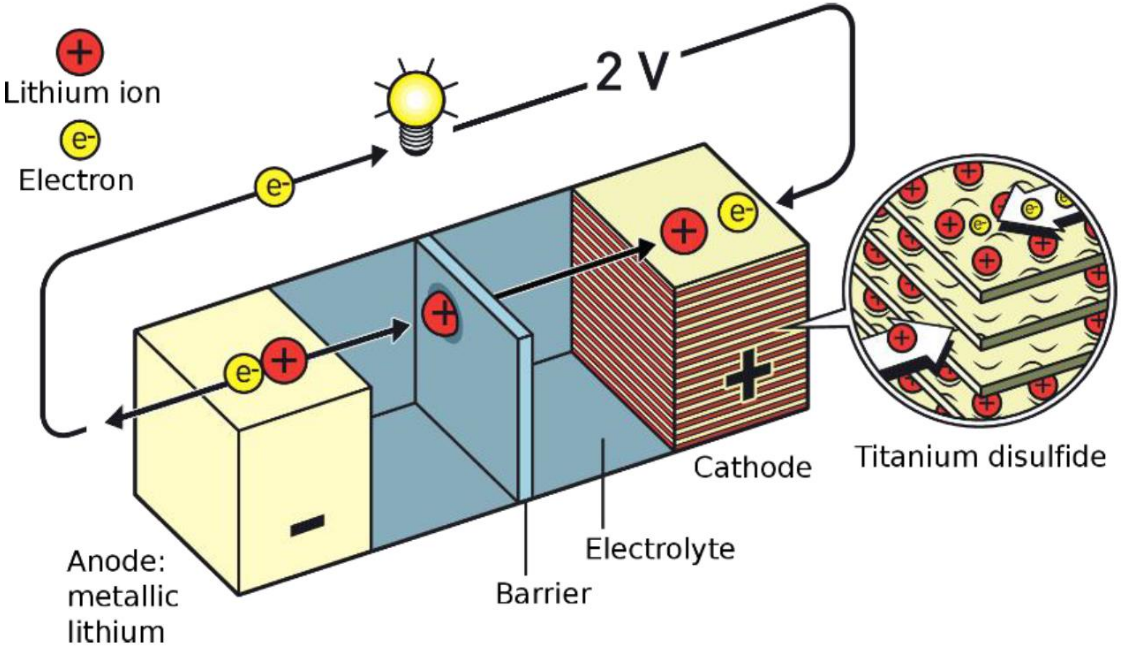
The NOBEL PRIZE 2019 in Chemistry

John B. Goodenough | M. Stanley Whittingham | Akira Yoshino

Fonte: Niklas Elmehed. ©Nobel Media.
https://www.nobelprize.org/prizes/chemistry/2019/summary/

for the development of Li-ion Batteries!

The history: 1976



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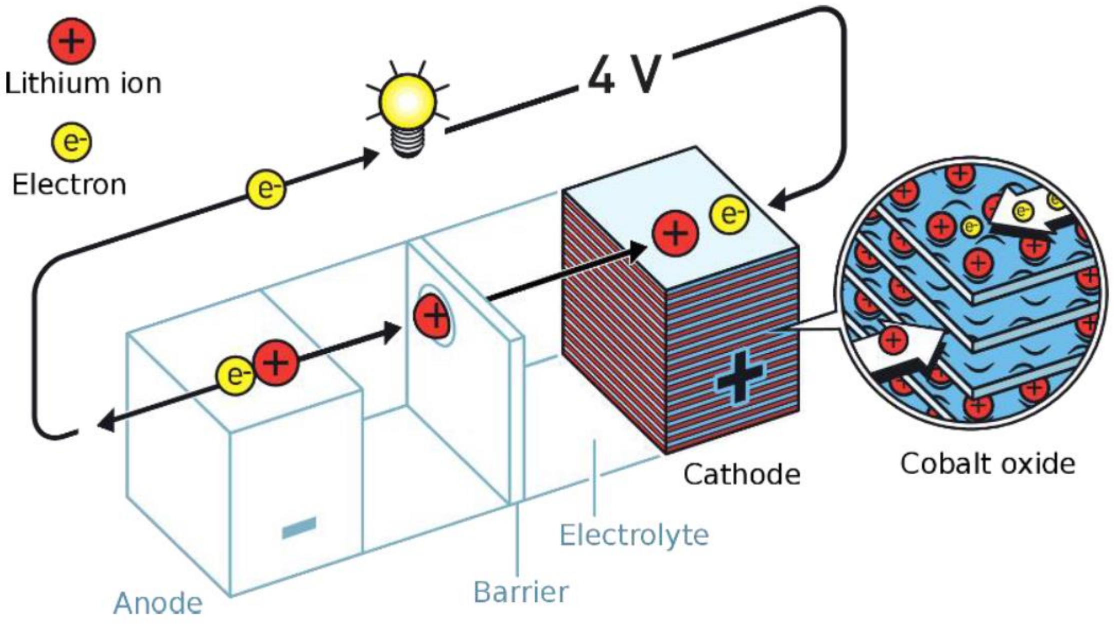
$x\mathrm{Li} + \mathrm{TiS_2} \leftrightarrows \mathrm{Li_xTiS_2}$

- Whittingham, M. S. Batterie à Base de Chalcogénures. Belgian patent no. 819672, **1975**.
- Whittingham, M. S. Electrical Energy Storage and Intercalation Chemistry. *Science* **1976**, 192 (4244), 1126-1127.

The history: 1980



$x\text{Li} + \text{CoO}_2 \leftrightarrows \text{Li}_x\text{CoO}_2$

- Mizushima, K.; Jones, P. C.; Wiseman, P. J.; Goodenough, J. B. LixCoO2 (0<x<1): A New Cathode Material for Batteries of High Energy Density. Mater. Res. Bull. **1980**, 15 (6), 783–789.

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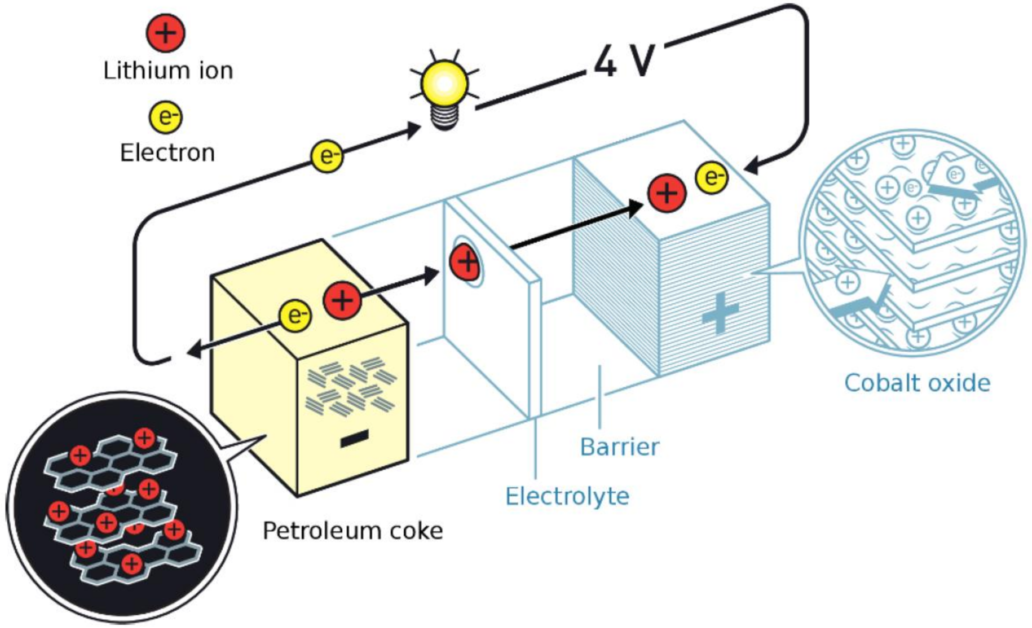
The history: 1985

$yC + LiCoO_2 \leftrightarrows Li_xC_y + Li_{(1-x)}CO_2$



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- Yoshino, A.; Sanechika, K.; Nakajima, T. Japanese patent no. 1989293, **1985**.
- Yoshino, A.; Sanechika, K.; Nakajima, T. Secondary Battery. US patent no. 4,668,595, May 26, **1987**.

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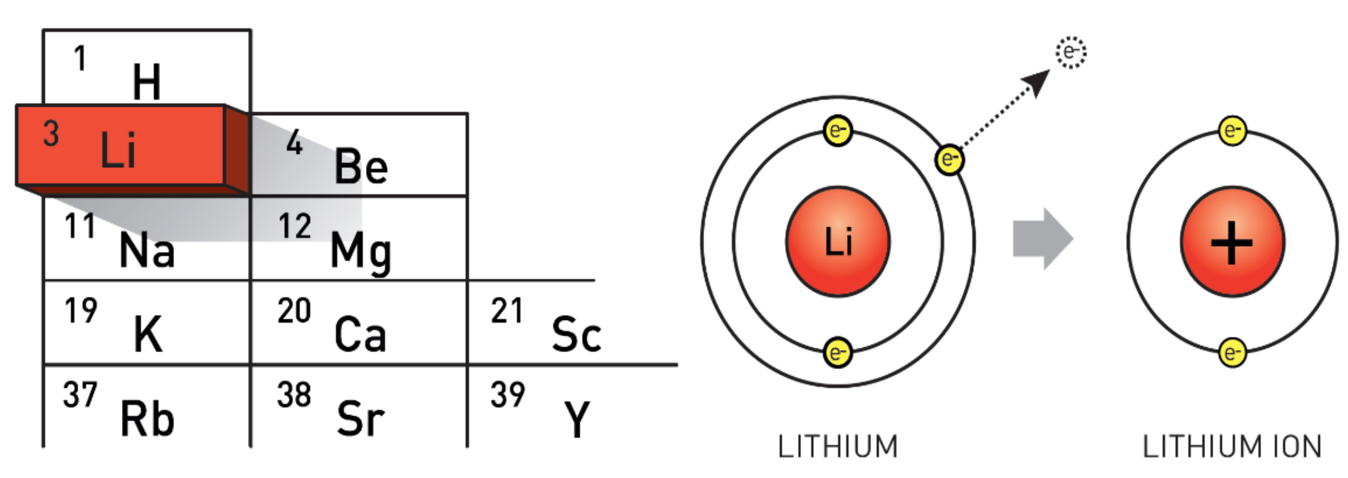
Why Lithium?



It is the lightest metal: 0,53 g cm^{-3}

It has the lowest redox potential: E°= -3,05 V vs SHE

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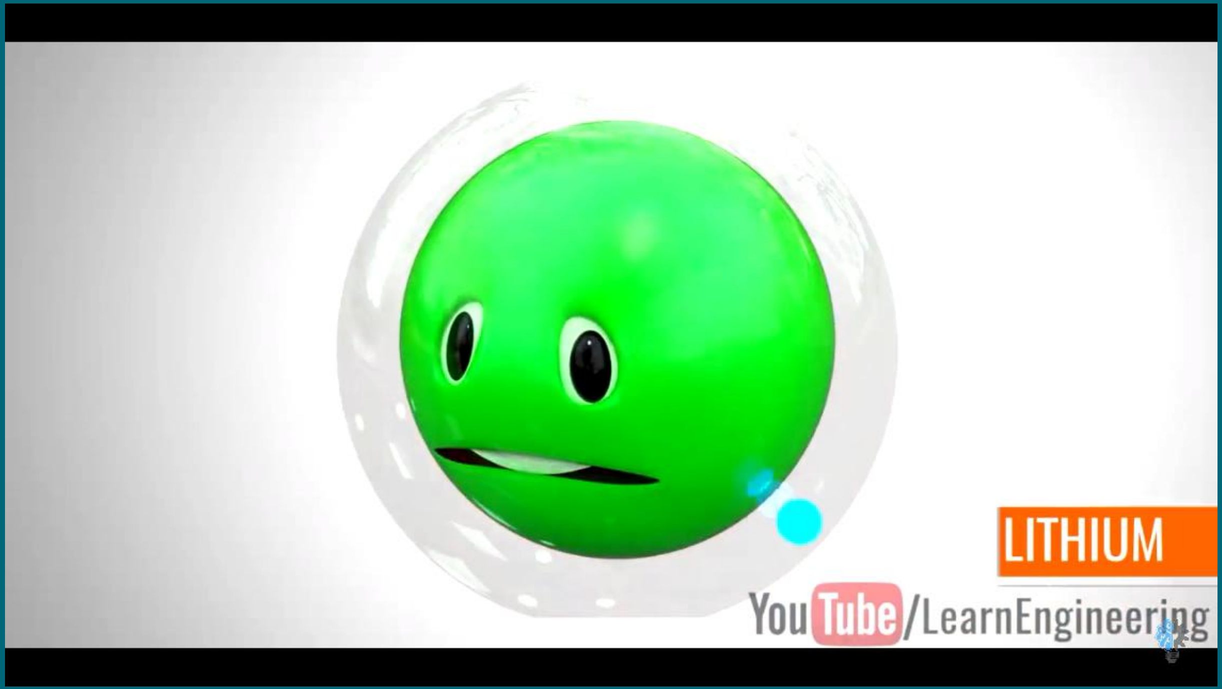
Why (not) Lithium?



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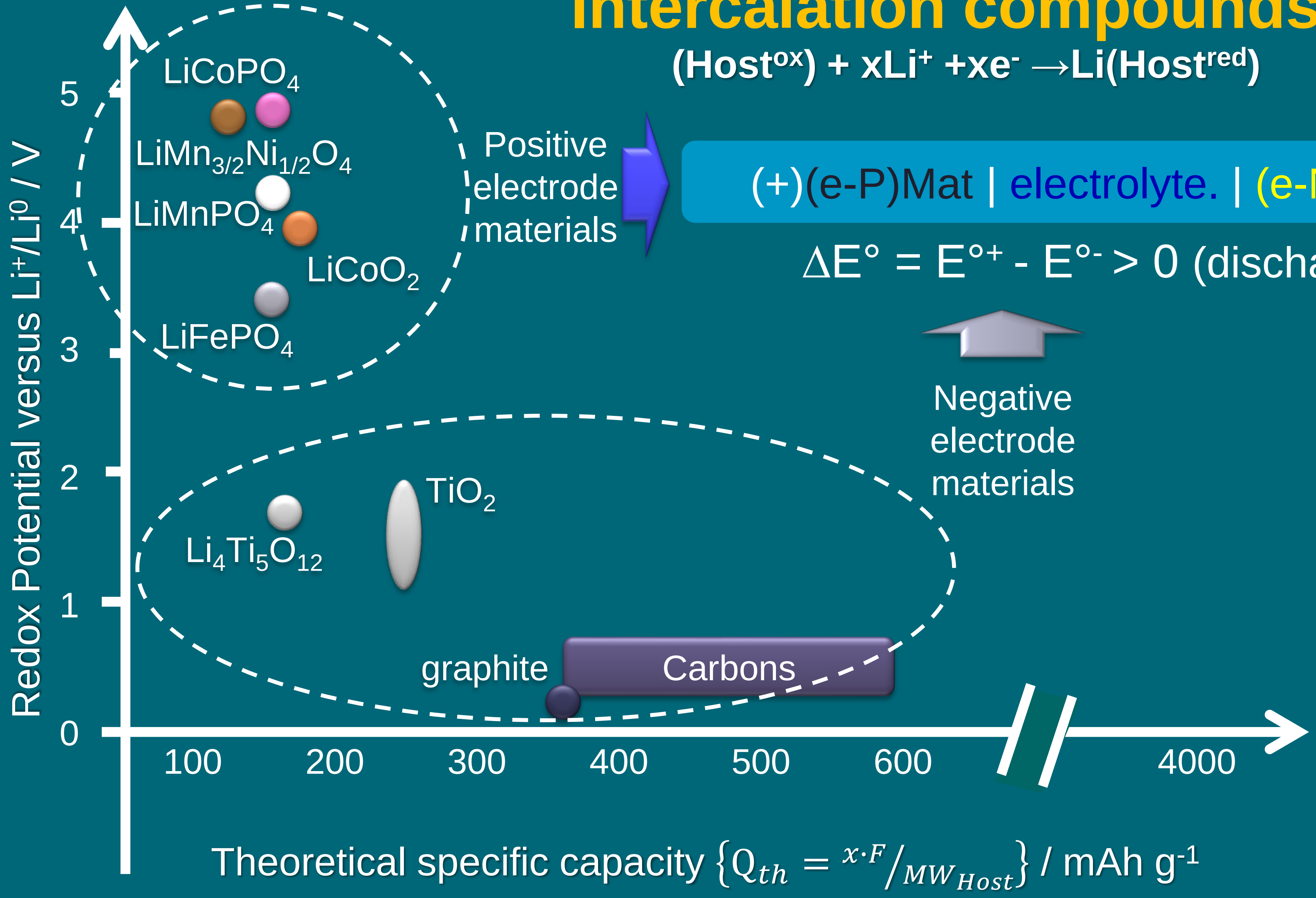
Intercalation compounds

$(Host^{ox}) + xLi^+ + xe^- \rightarrow Li(Host^{red})$



(+)(e-P)Mat | electrolyte. | (e-N)Mat (-)

$\Delta E° = E°^{+} - E°^{-} > 0$ (discharge)

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Li-ion battery: negative electrodes families

Intercalation chemistry	Conversion chemistry	Alloying chemistry	Lithium
Graphite $6C+Li^{+}+e^{-}\rightarrow LiC_6$	Oxides $CoO+2Li^{+}+2e^{-}\rightarrow Li_2O+Co$	Tin $5Sn+22Li^{+}+22e^{-}\rightarrow Li_{22}Sn_5$	$Li^{+} + e^{-} \rightarrow Li$
Carbons $nC+Li^{+}+e^{-}\rightarrow LiC_n$	Hydrides $MgH_2+2Li^{+}+2e^{-}\rightarrow 2LiH+Mg$	Silicon $4Si+17Li^{+}+17e^{-}\rightarrow Li_{17}Si_4$	
Lithium titanate $Li_4Ti_5O_{12}+3Li^{+}+3e^{-}\rightarrow Li_7Ti_5O_{12}$	Phosphides $Cu_3P+3Li^{+}+3e^{-}\rightarrow Li_3P+3Cu$	Aluminum $4Al+9Li^{+}+9e^{-}\rightarrow Li_9Al_4$	
Titania $TiO_2+Li^{+}+e^{-}\rightarrow LiTiO_2$			

(Reactions given for the "charge" battery process)

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Li-ion battery: positive electrodes families

Intercalation chemistry	Conversion chemistry	Anionic redox chemistry
Layered phases $Li_{½}CoO_2$+½Li^++½e^- →$LiCoO_2$	Fluorides FeF_3+Li^++e^- →LiF+FeF_2	Oxygen $O_2 + 2\ Li^+ + 2\ e^-$ → Li_2O_2
Spinel phases $Ni_{½}Mn_{3/2}O_4$+Li^++e^- →$LiNi_{½}Mn_{3/2}O_4$		Sulphur $S + 2\ Li^+ + 2\ e^-$ → Li_2S
Olivine phases $FePO_4$+Li^++e^- →$LiFePO_4$		

(Reactions given for the "discharge" battery process)

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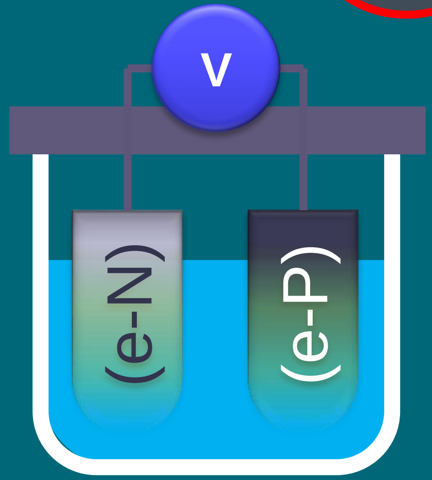
Electrolytes for Li-ion batteries: intro

(+)(e-P)Mat / el. / (e-N)Mat (-)



Electrolyte:
medium for the movement of ions

- e^--**insulating**
- easily **transport** Li^+-ions
- electrochemically **inert** at both electrodes

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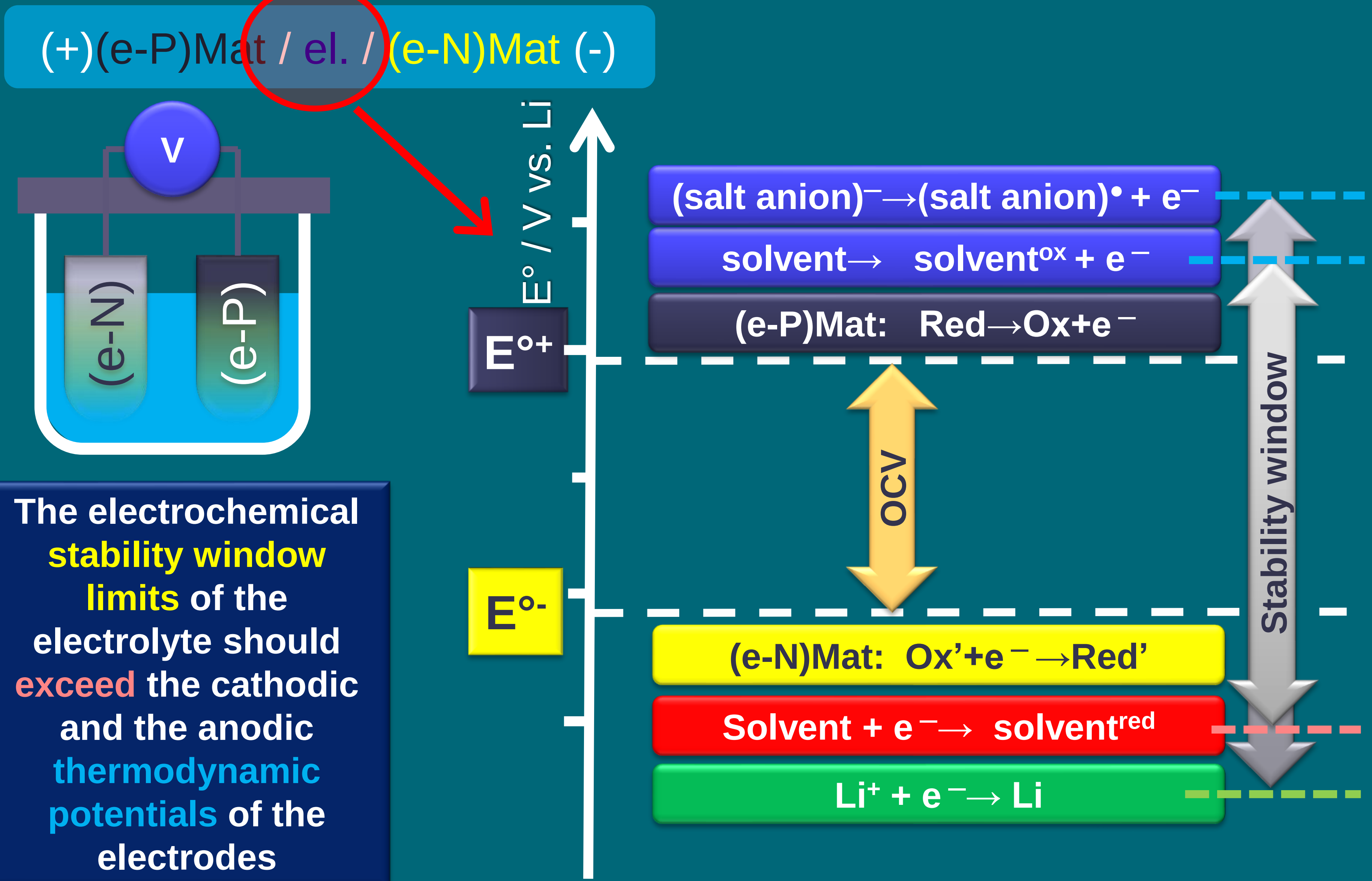
Electrolytes for Li-ion batteries: stability



The electrochemical **stability window limits** of the electrolyte should **exceed** the cathodic and the anodic **thermodynamic potentials** of the electrodes

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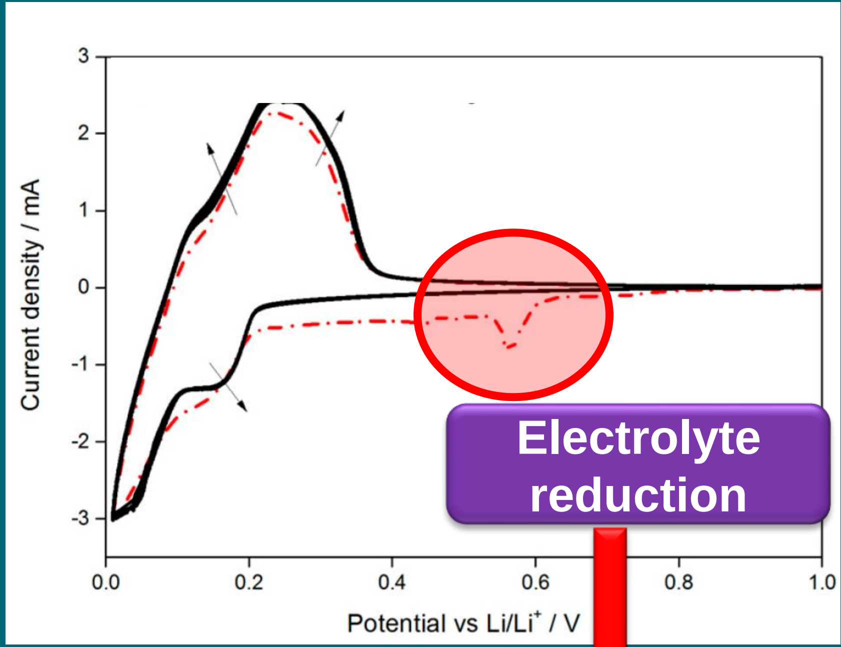
Electrochemical stability window of a good electrolyte

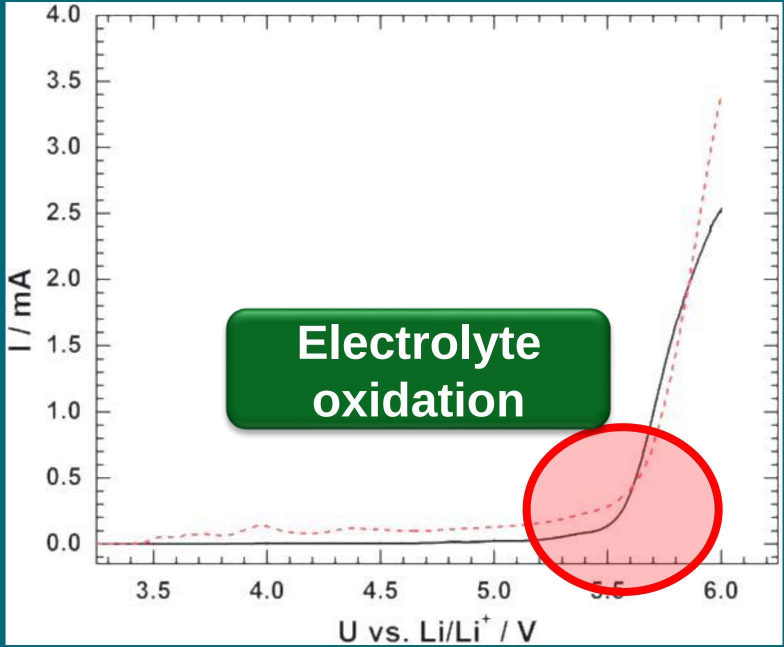
(+) Carbon | electrolyte | Lithium (-)

Cathodic polarization (Cyclic voltammetry)



Electrolyte reduction

Anodic polarization (linear sweep voltammetry)



Electrolyte oxidation

Only in the first cycle,
then the interface becomes inert:
SEI (Solid-Electrolyte Interphase) is formed

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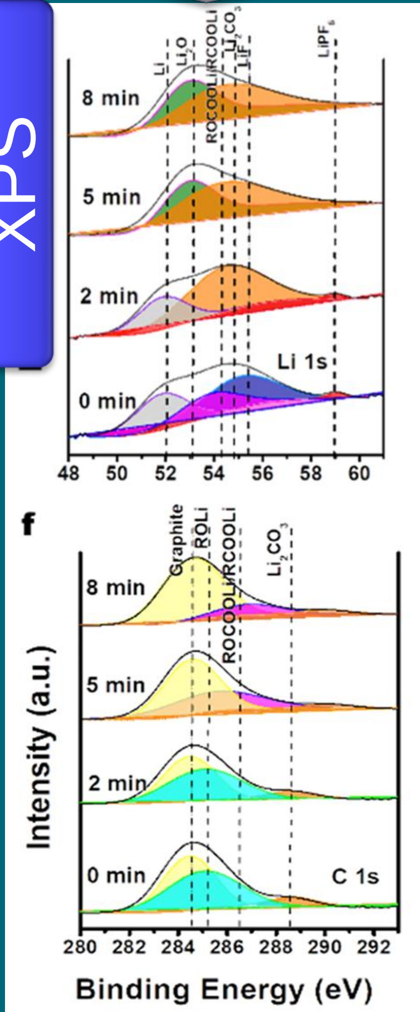
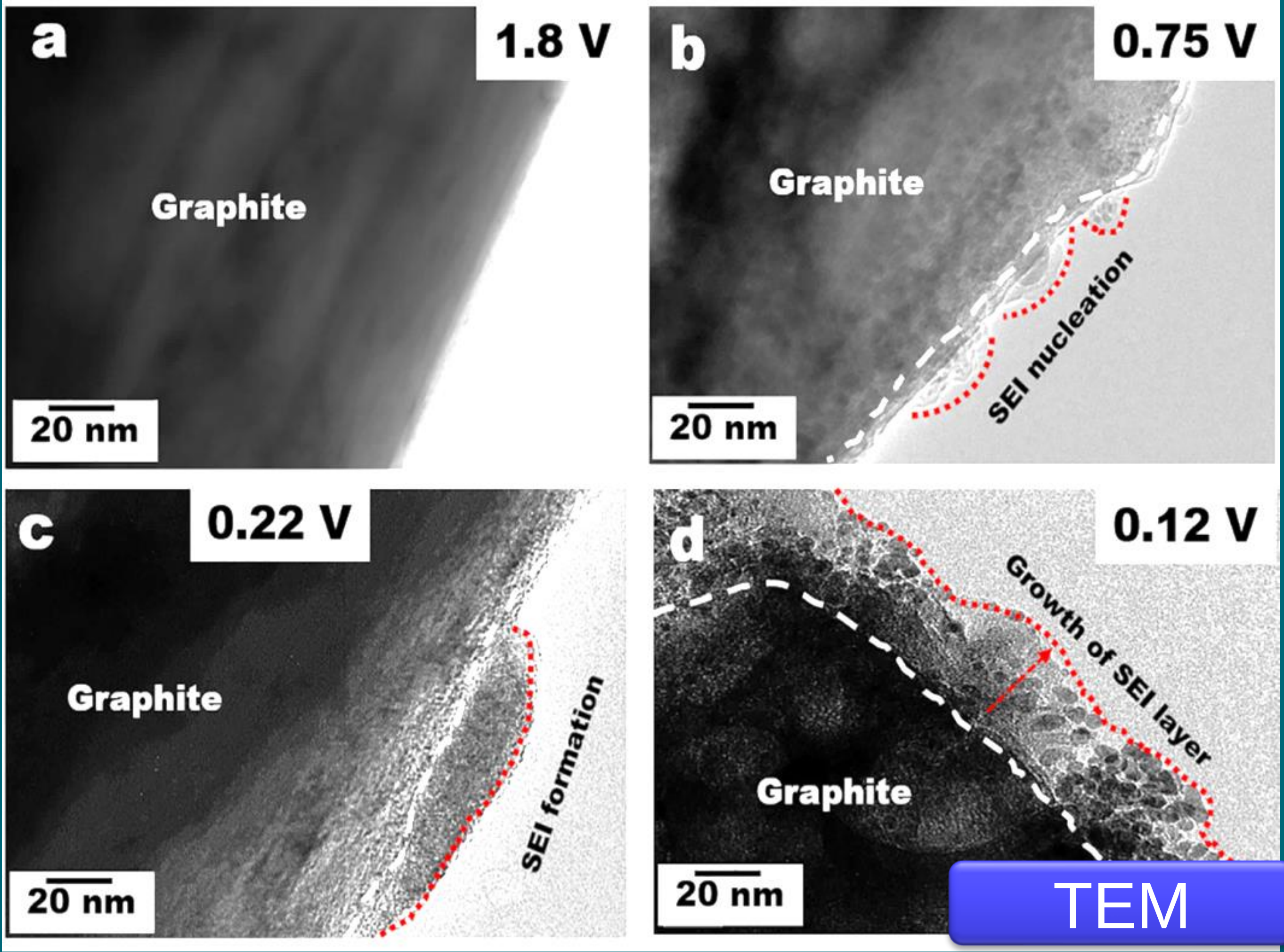
Electrolyte decomposition over graphite

(+) Graphite / electrolyte / Lithium (-)

Ex situ analysis

XPS





TEM

Courtesy of Prof. S. Brutti

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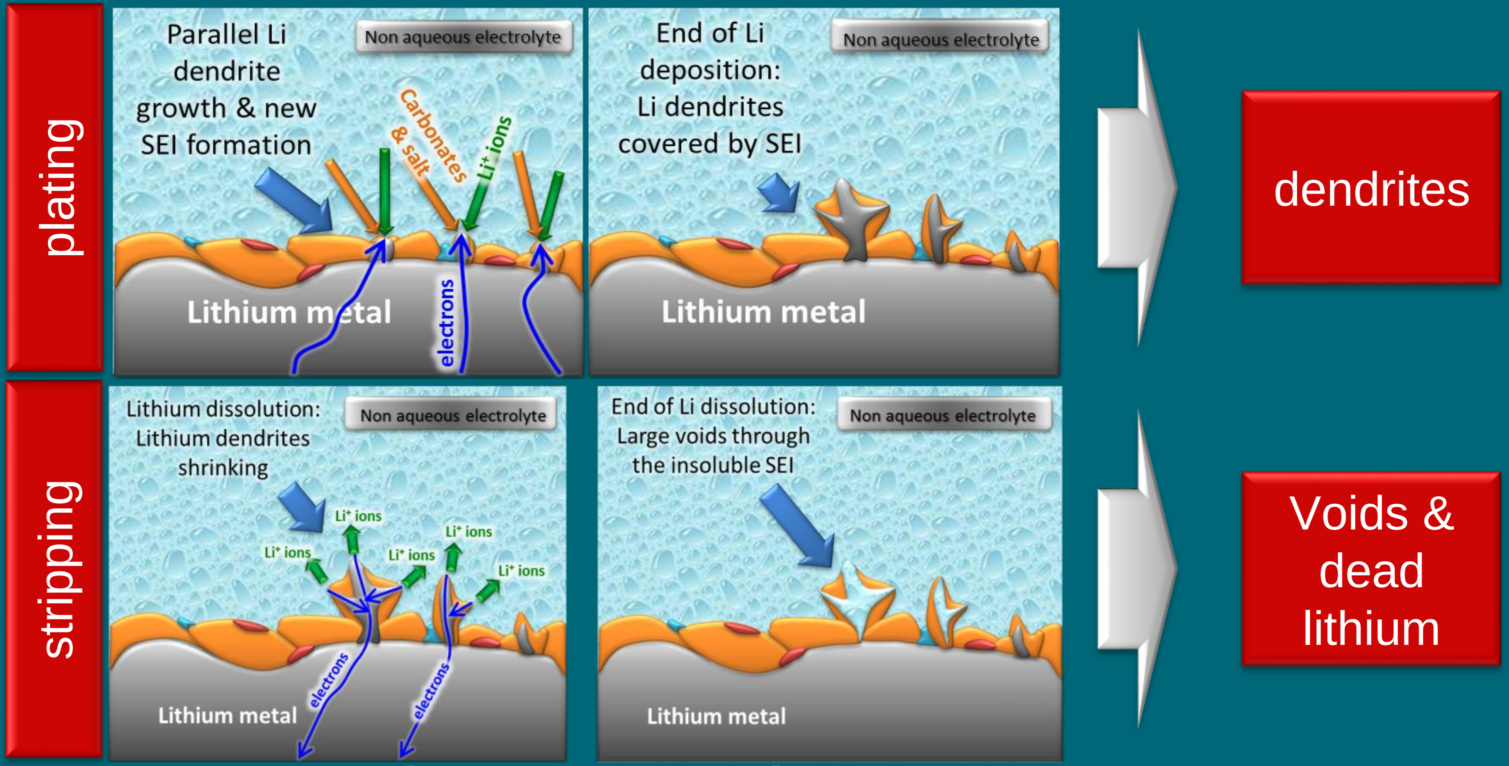
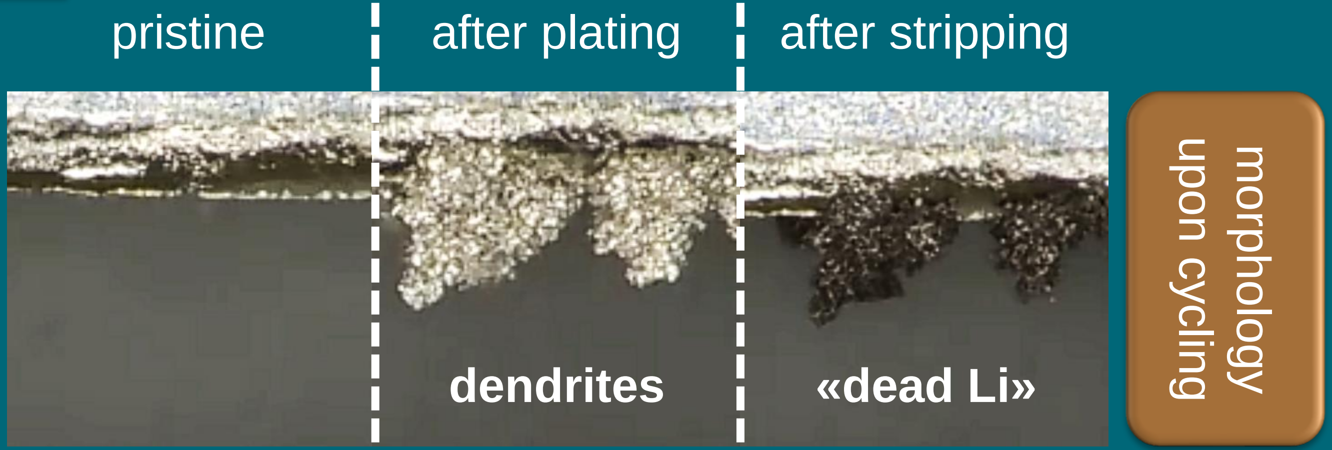
Lithium plating and stripping





Courtesy of Prof. S. Brutti

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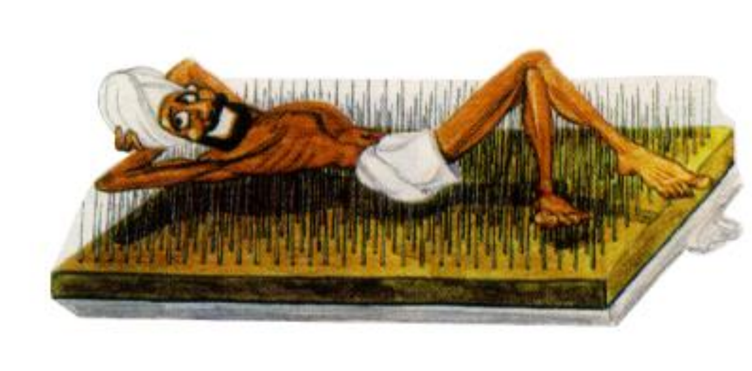
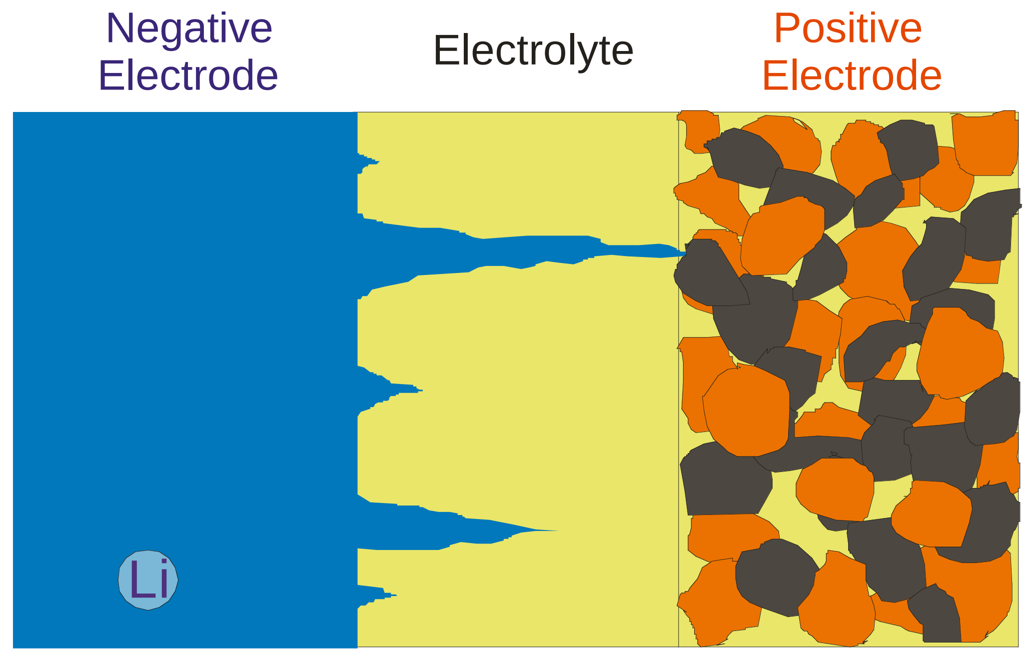


Dendrite problems were solved with 99.5 % efficiency

Not good enough:
One dendrite may be crucial!



Problems with Dendrite Formation:

Short-Circuit

⇩

Thermal Runaway

⇩

Explosion

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Electrolytes: general requirements and types

Suitable ionic conductivity >1 mS/cm @ RT

High chemical & electrochemical stability on electrodes

Stable & functionally active in a wide T range (-20°C and 60°C)

Low cost (simple and cost-effective synthetic routes)

High safety and low hazard (low toxicity, high flesh points)

Liquid electrolyte (Li^+ salt in solvents)

Gel electrolyte (Li^+ salt, solvents and polymer)

Polymer electrolyte (Li^+ salt in polymer)

Composite solid electrolyte (polymer, Li^+ salt and inorganic filler)

Solid electrolyte (inorganic, ceramic Li^+ ion conductor)

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Liquid electrolytes

Solvent	Li-salt	Possible Additives
Organic liquid substances inert and supporting conductivity	Ionic lithium substance easily dissociated and inert	Substances to tune the electrolyte functional properties
~~water~~	~~Small anions~~	High ionic conductivity up tp 10^{-2} S/cm @ RT

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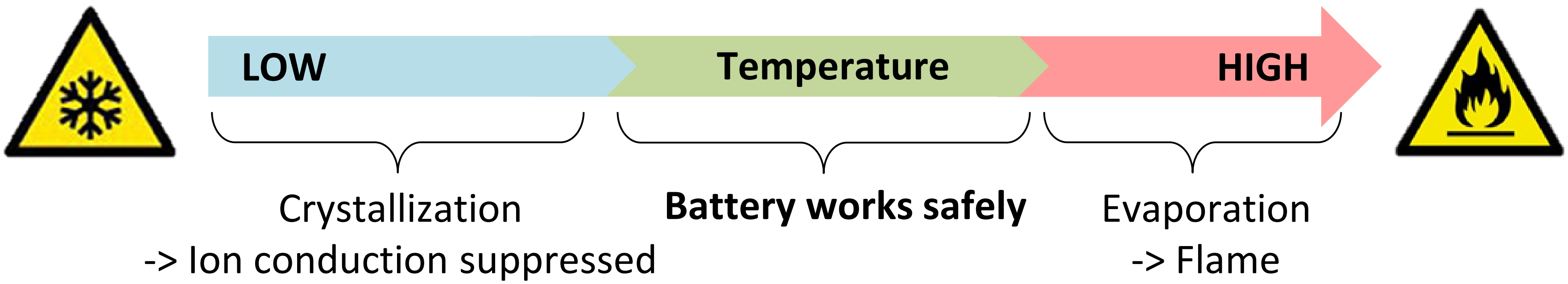
SAFETY and RELIABILITY ISSUES of LIQUID ELECTROLYTES

Conventional liquid electrolytes, based on $LiPF_6$ salt and alkyl carbonate solvents, suffer from:

- incompatibility with the environment and human health (manipulation hazards)
- high vapor pressure and flammability
- narrow thermal stability domain

A Dell computer went on fire in a conference in Osaka in June 2006. Sony and Dell announced recall of Sony's lithium ion batteries packs (more than 4.5 million).



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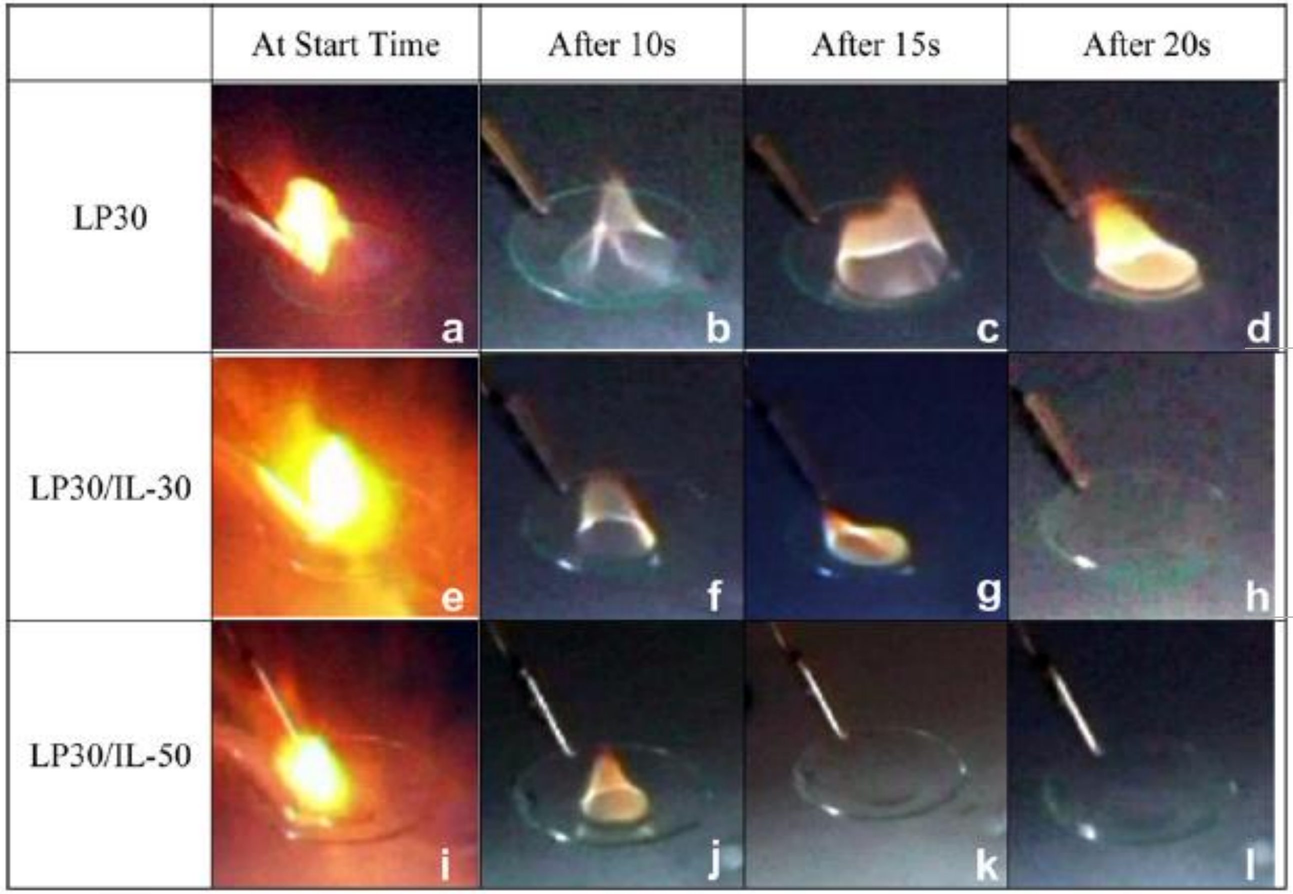
Ionic Liquid additives in liquid electrolytes



IL 0%

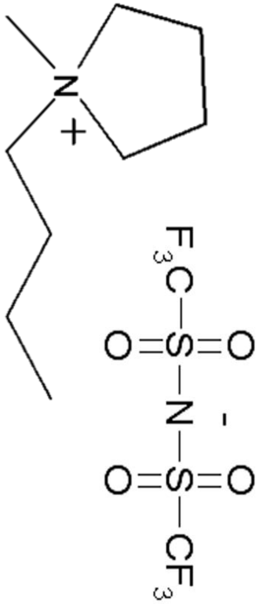
IL 30%

IL 50%

Pictures of the flammability performances of LP30 at starting time (a), after 10 s (b), after 15 s (c) and after 20 s (d); of LP30/Py_{14}TFSI 70/30 wt/wt at starting time (e), after 10 s (f), after 15 s (g) and after 20 s (h); and of LP30/Py_{14}TFSI 50/50 wt/wt at starting time (i), after 10 s (j), after 15 s (k) and after 20 s (l).

LP30: EC-DMC (ethylene carbonate-dimethyl carbonate), 1M $LiPF_6$

The Ionic Liquid (IL)



Py_{14}TFSI

L. Lombardo, S. Brutti, M.A. Navarra, S. Panero, P. Reale, *J. Power Sources,* 227 (2013) 8

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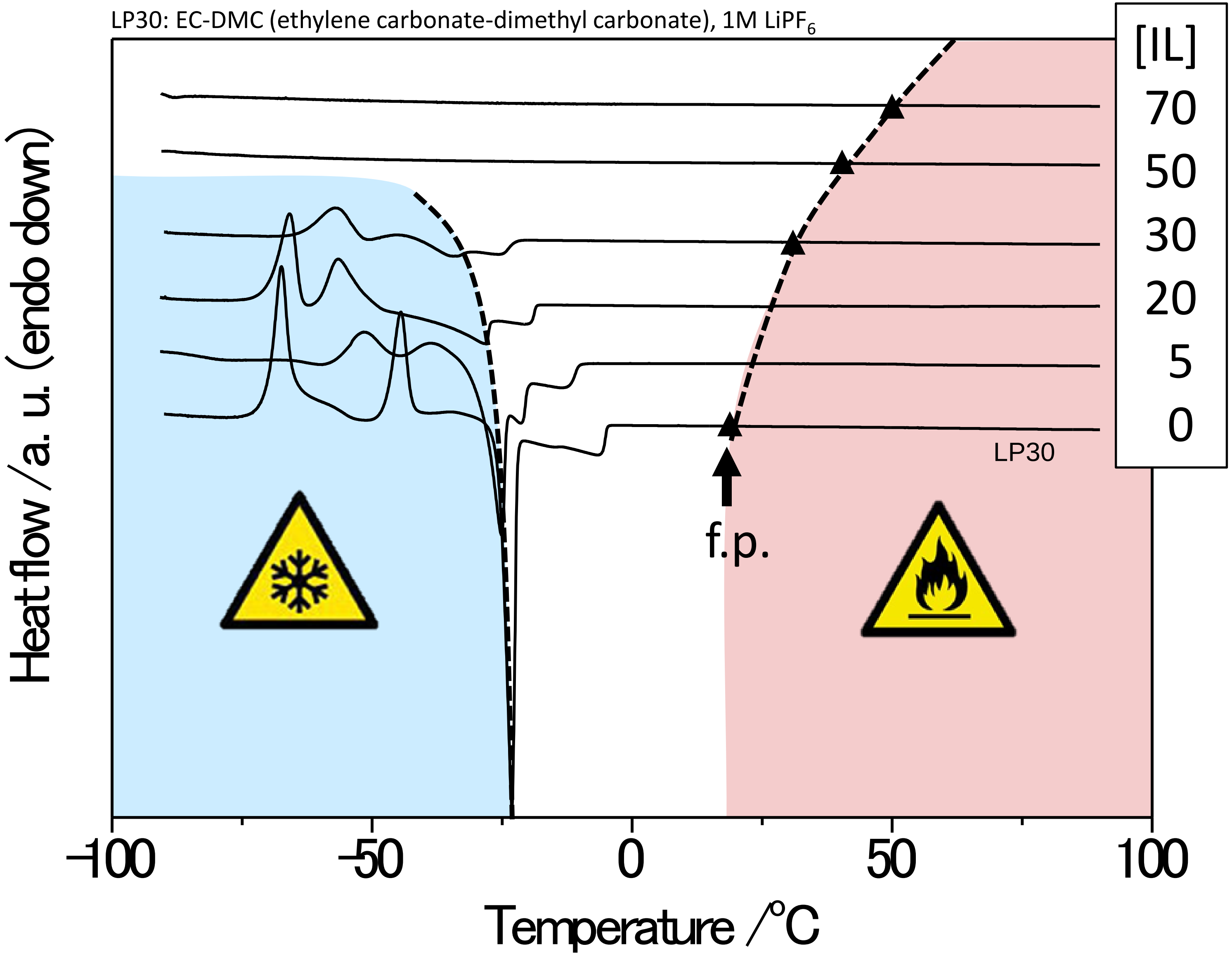
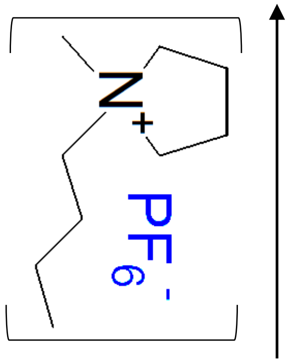
Ionic Liquid additives in liquid electrolytes

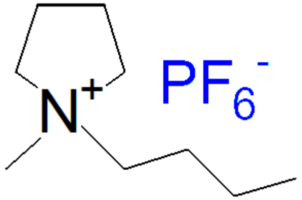
LP30: EC-DMC (ethylene carbonate-dimethyl carbonate), 1M $LiPF_6$



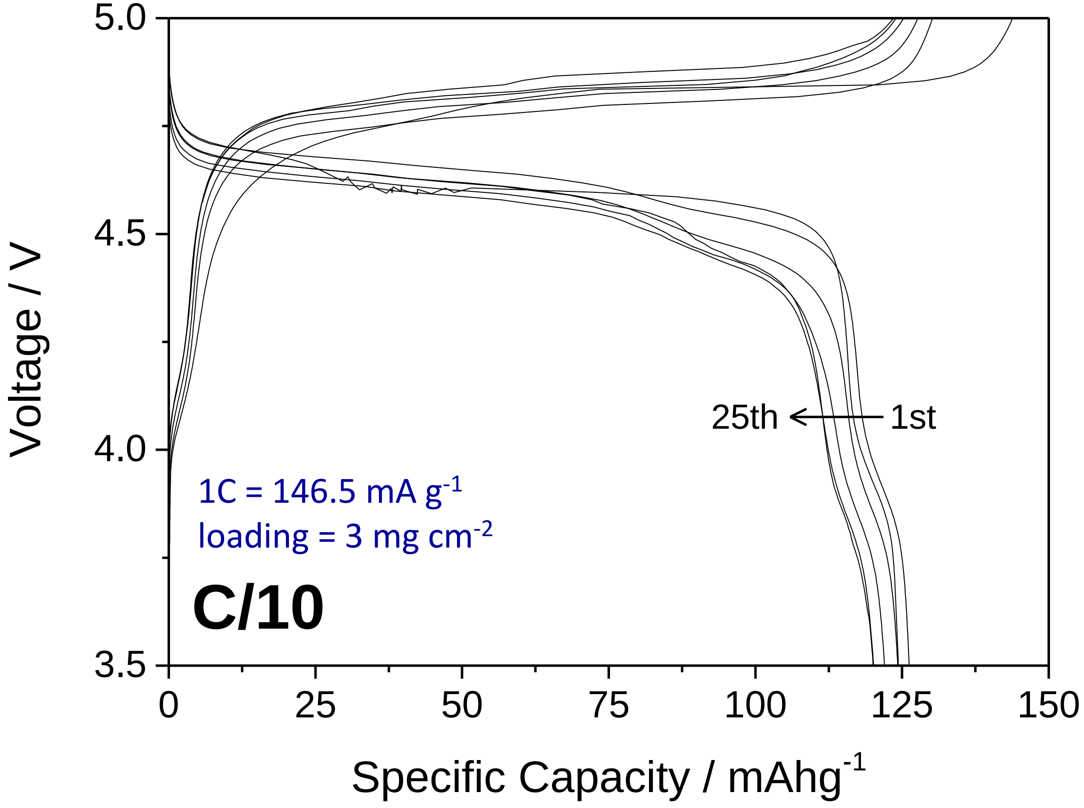


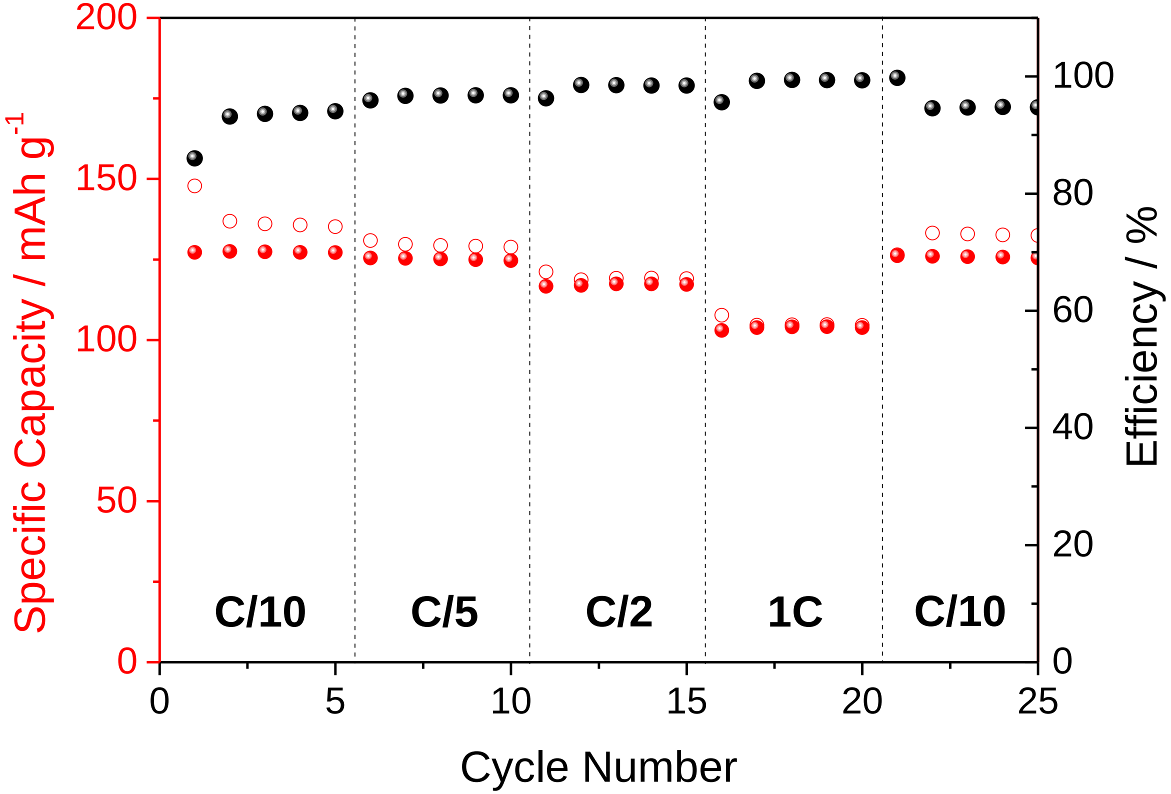
A. Tsurumaki, M. A. Navarra, S. Panero, B. Scrosati, H. Ohno, *J. Power Sources*, 233 (2013) 104

Ionic Liquid additives in liquid electrolytes



Li | IL50 | $LiNi_{0.5}Mn_{1.5}O_4$





A. Tsurumaki et al., *Electrochimica Acta,* 2019, 316, 1-7

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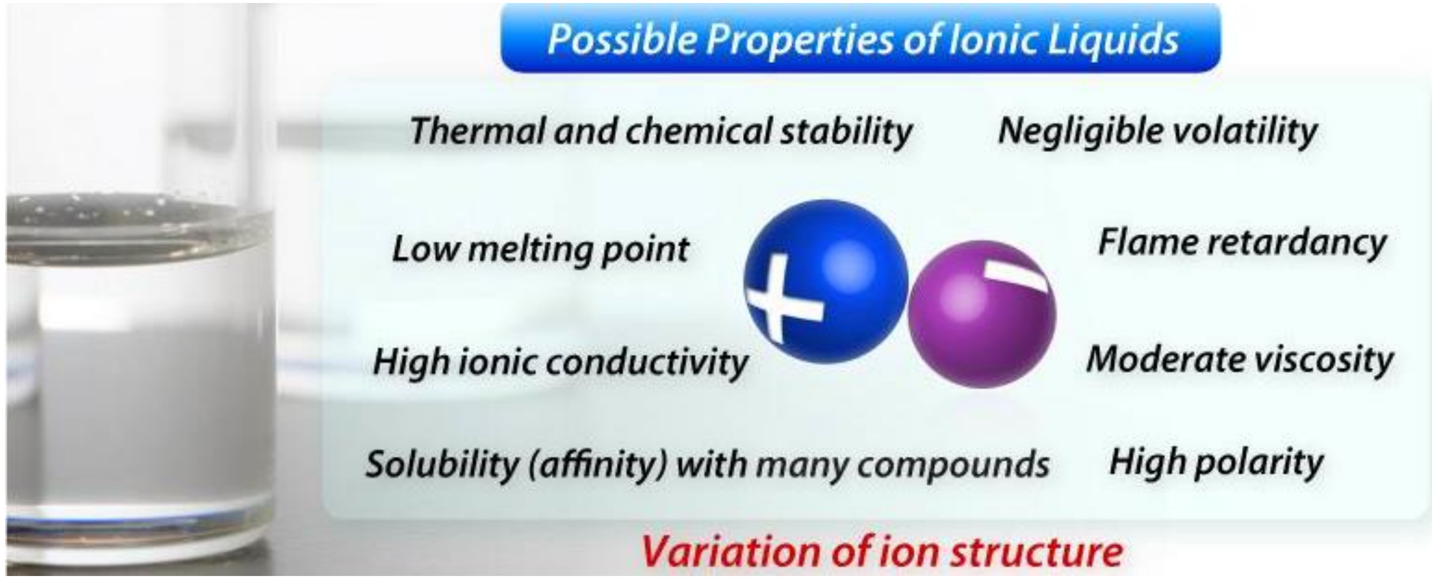
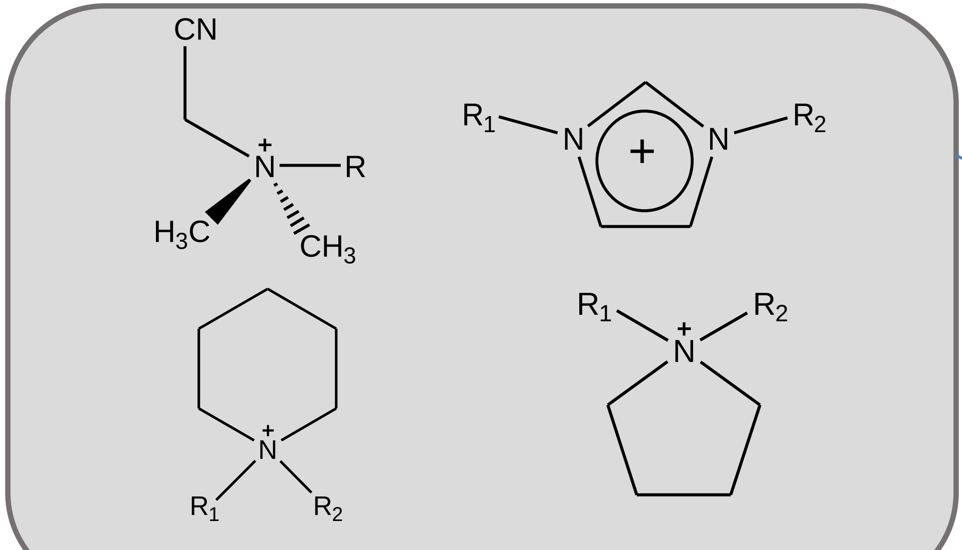
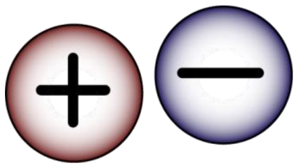
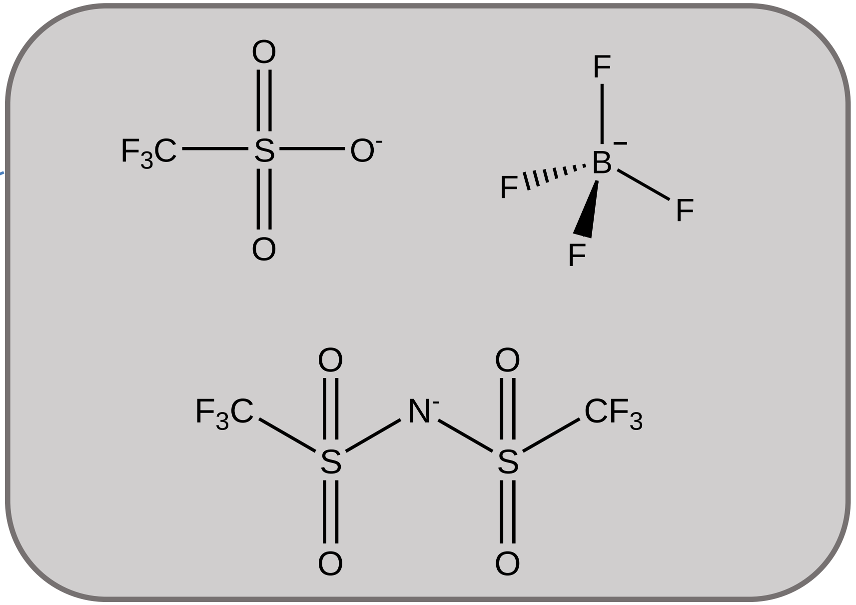
Why Ionic Liquids?





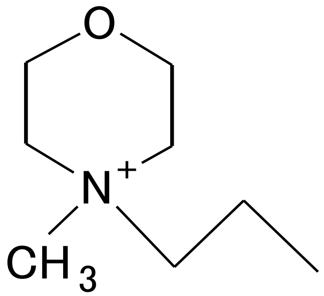
R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$, $(CH_2)nCH_3$, etc





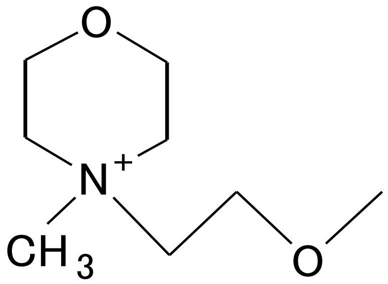
SYNTHESIS OF ILs

New cations:

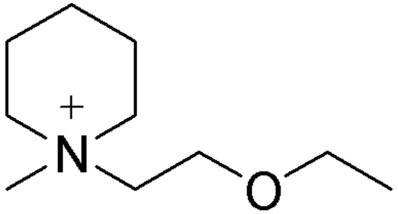


$M_{1,3}$: *N*-methyl-*N*-propylmorpholinium

and

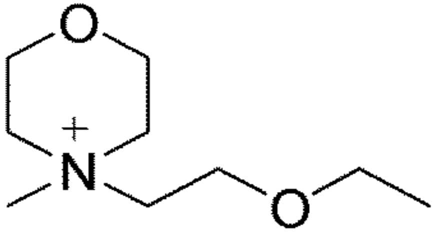


$M_{1,2O1}$: *N*-methoxyethyl-*N*-methylmorpholinium



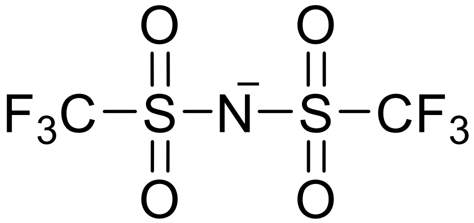
$P_{1,2O2}$: *N*-ethoxyethyl-*N*-methylpiperidinium

and

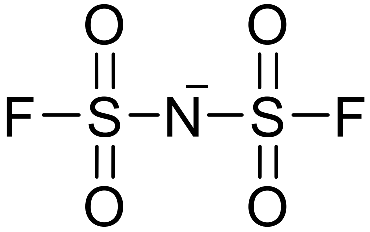


$M_{1,2O2}$: *N*-ethoxyethyl-*N*-methylmorpholinium

Anions:

1) 

TFSI: bis(trifluoromethanesulfonyl)imide

2) 

FSI: bis(fluorosulfonyl)imide

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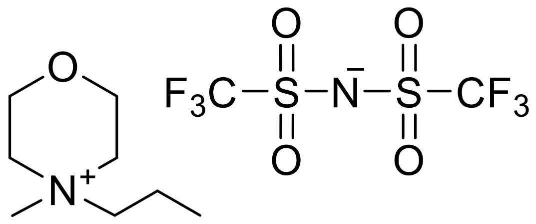
ILs thermal properties – from DSC

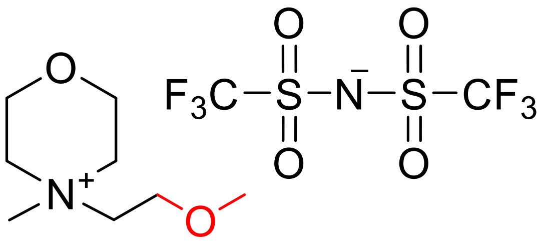
$M_{1,3}$TFSI



T_m = 40.8 °C

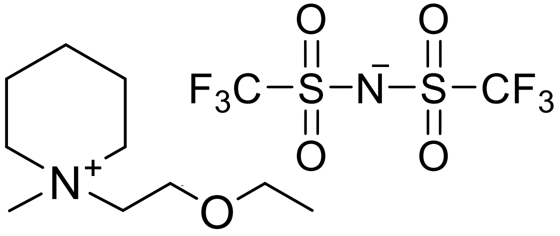
Ether modification on **cation** side-chain →

$M_{1,2O1}$TFSI



T_m was not observed

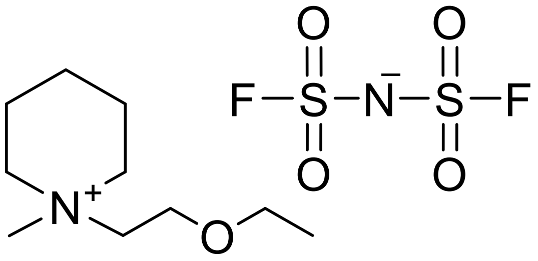
$P_{1,2O2}$TFSI



T_m was not observed

Anion substitution →

$P_{1,2O2}$FSI



T_m = -12.0 °C

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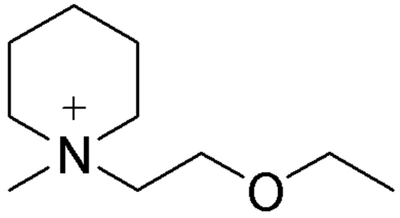
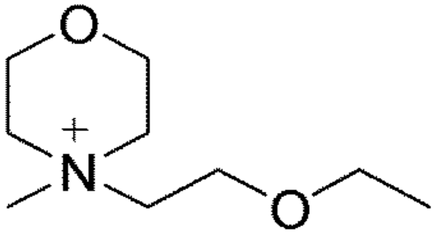
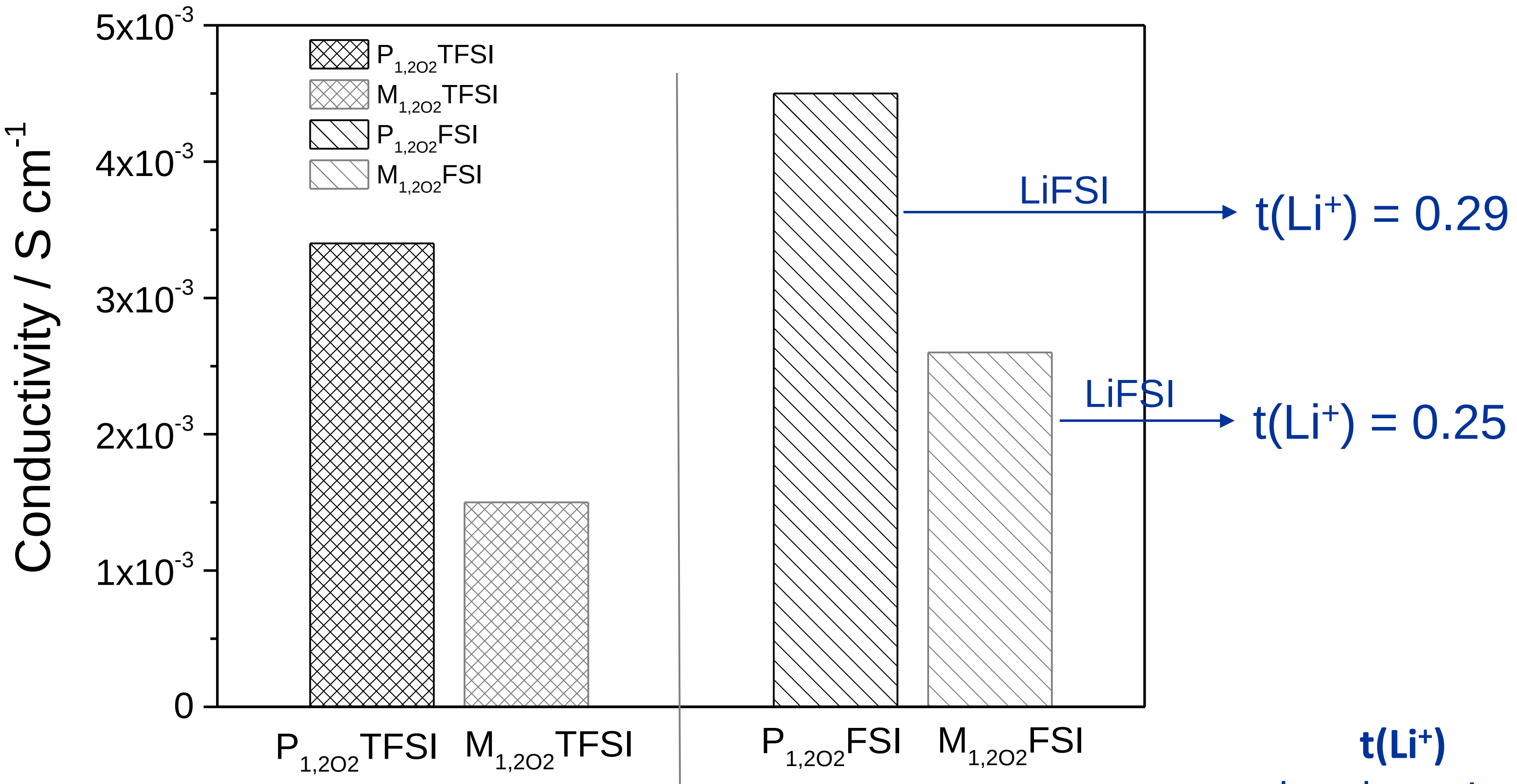
ILs ionic conductivity at 40 °C

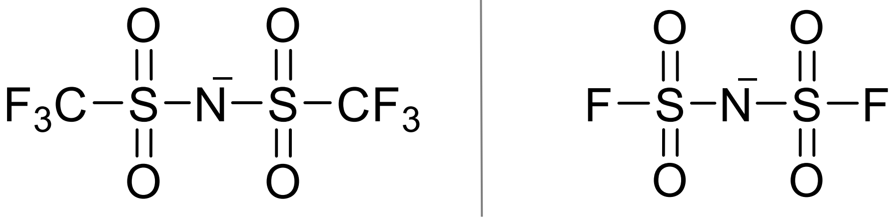


$P_{1,2O2}$: *N*-ethoxyethyl-*N*-methylpiperidinium



$M_{1,2O2}$: *N*-ethoxyethyl-*N*-methylmorpholinium

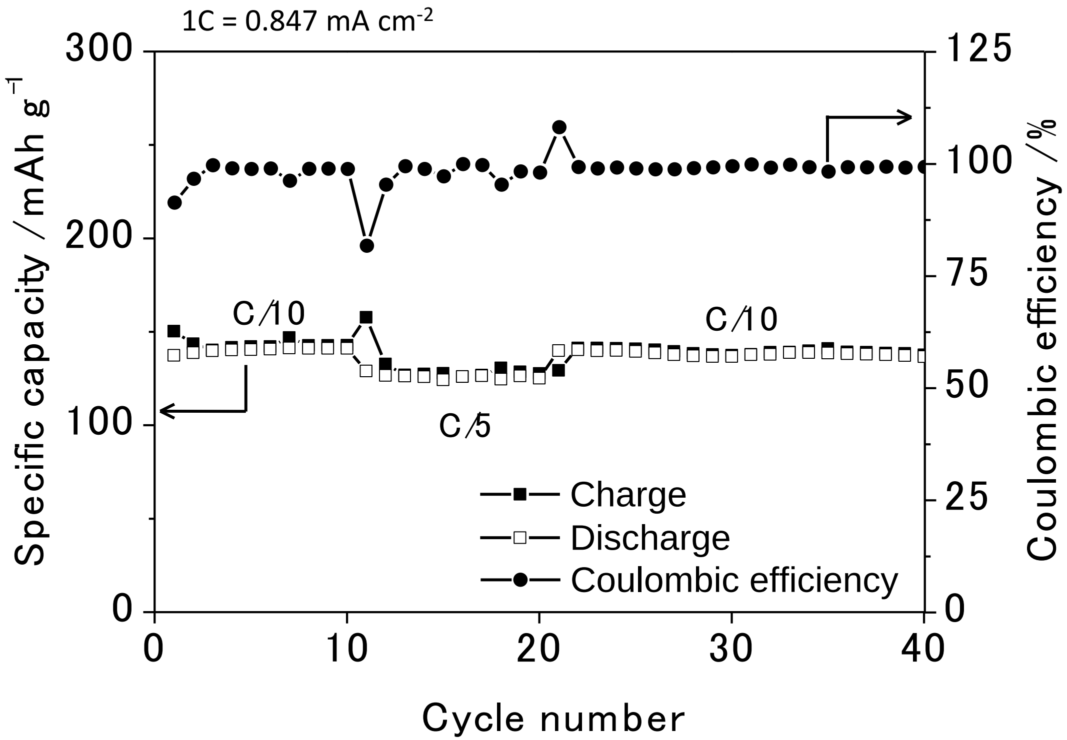


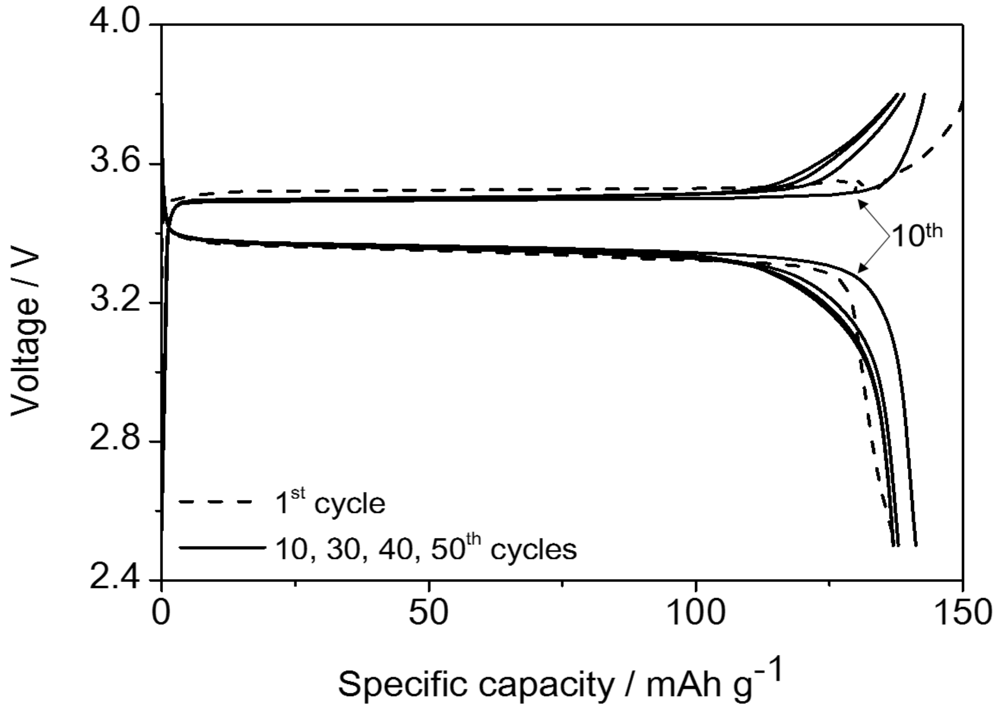


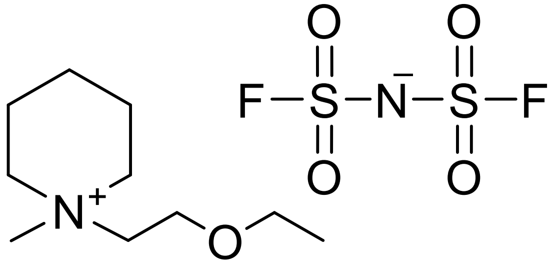
$t(Li^+)$
equal to the ratio of the mobility of lithium ions to the sum of mobilities of all ions

M.A. Navarra, K. Fujimura, M. Sgambetterra, S. Panero, A. Tsurumaki, N. Nakamura, H. Ohno, B. Scrosati, *ChemSusChem*, 10 (2017) 2496

Cycling performance: Li | $P_{1,2O2}$FSI - LiFSI | $LiFePO_4$ (LFP)





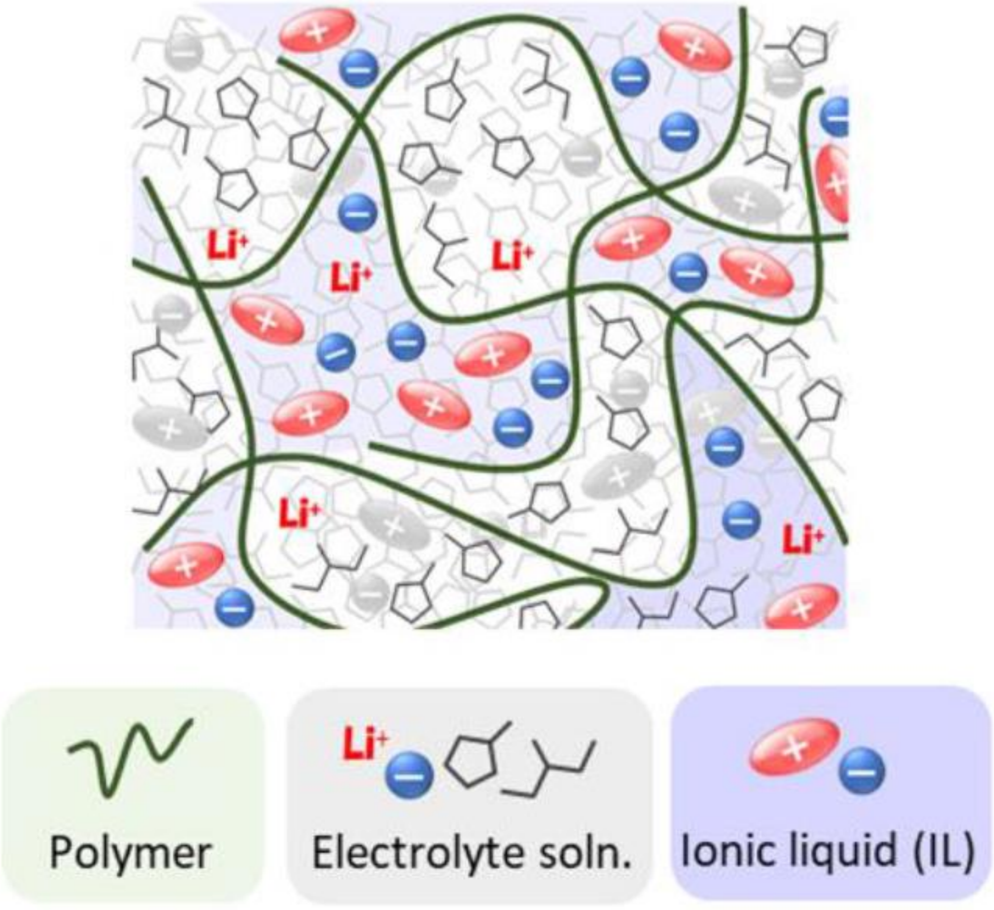


Akiko Tsurumaki, Hiroyuki Ohno, Stefania Panero, and Maria Assunta Navarra, *Electrochimica Acta*, 2018, 293, 160-165:
"Novel bis(fluorosulfonyl)imide-based and ether-functionalized ionic liquids for lithium batteries with improved cycling properties"

Further Improvements in SAFETY and RELIABILITY of BATTERIES

Gel Polymer Electrolytes (GPEs)

- ✓ Negligible leakage of liquid
- ✓ No flammability
- ✓ Stability and versatility in geometry
- ✓ Electronic insulation



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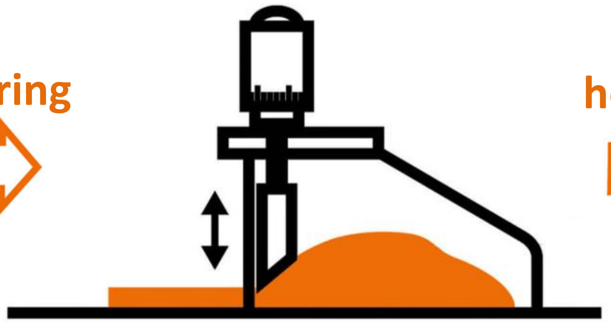
Gel Polymer Electrolytes (GPEs): preparation

Doctor Blade casting

Polymer + solvents
(e.g., PVdF-HFP in EC:DMC)

stirring ⇨



glass substrate

heating ⇨

vacuum drying ⇩

AMBIENT CONDITIONS

up to 1 mm thick

⇦ cut

⇦ activation by liquid electrolyte

GPE

Ar-filled DRY BOX

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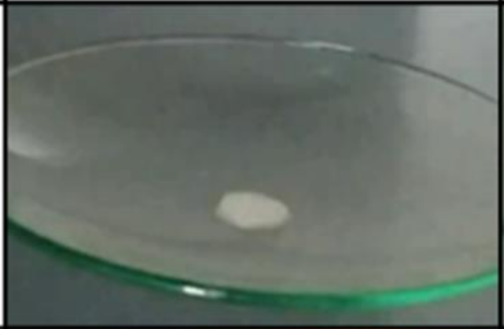
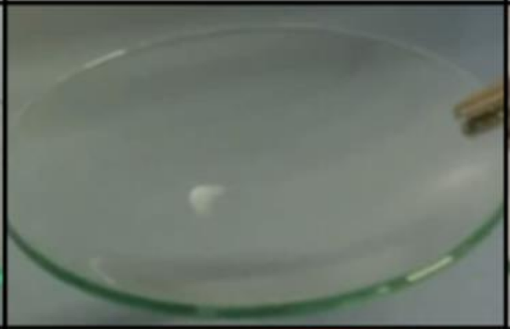
Gel Polymer Electrolytes (GPEs): flammability test

	LP30 soaked in a Whatman® separator	G-LP	G-IL50
Pristine GPE			
During ignition (2 sec)			
After ignition			

GPE samples:
- **G-LP** (polymer matrix activated by LP30)
- **G-IL50** (polymer matrix activated by LP30:IL 50:50 mixture)

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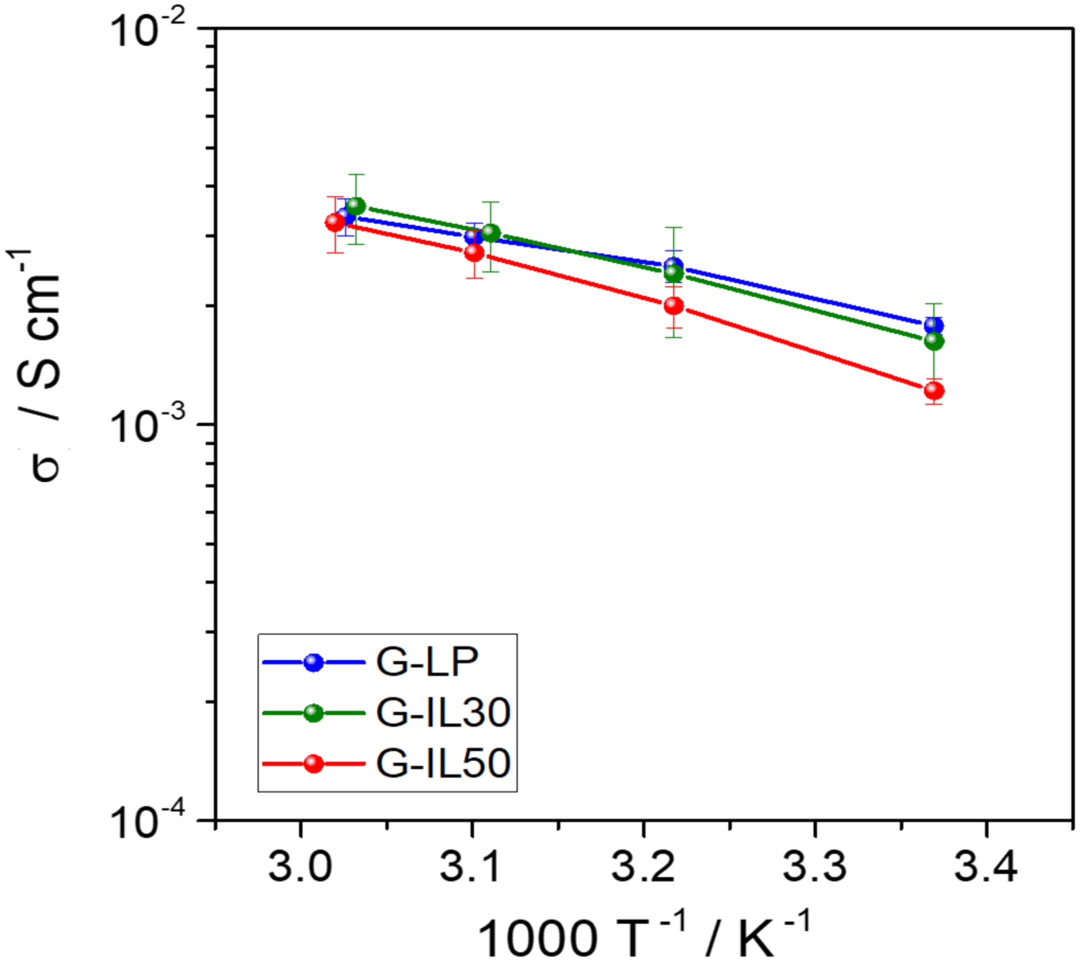
Gel Polymer Electrolytes (GPEs): ionic conductivity



- All GPEs exhibit a room temperature ionic conductivity higher than **10^{-3} S cm^{-1}**.
- The conductivities of G-LP and G-IL30 are similar and higher than that of G-IL50.

GPE samples:
- **G-LP** (polymer matrix activated by LP30)
- **G-IL30** (polymer matrix activated by LP30:IL 70:30 mixture)
- **G-IL50** (polymer matrix activated by LP30:IL 50:50 mixture)

Ruggero Poiana, Ernestino Lufrano, Akiko Tsurumaki, Cataldo Simari, Isabella Nicotera and Maria Assunta Navarra, *Electrochimica Acta*, 401 (2022) 139470: "Safe Gel Polymer Electrolytes for High Voltage Li-Batteries".

A polymer-electrolyte lithium-ion «pouch-cell»

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Battery Generation	Electrodes active materials	Cell Chemistry / Type	Forecast market deployment
Gen 1	• Cathode: LFP, NCA • Anode: 100% carbon	Li-ion Cell	current
Gen 2a	• Cathode: NMC111 • Anode: 100% carbon	Li-ion Cell	current
Gen 2b	• Cathode: NMC523 to NMC 622 • Anode: 100% carbon	Li-ion Cell	current
Gen 3a	• Cathode: NMC622 to NMC 811 • Anode: carbon (graphite) + silicon content (5-10%)	Optimised Li-ion	2020
Gen 3b	• Cathode: HE-NMC, HVS (high-voltage spinel) • Anode: silicon/carbon	Optimised Li-ion	2025
Gen 4a	• Cathode NMC • Anode Si/C • Solid electrolyte	Solid state Li-ion	2025
Gen 4b	• Cathode NMC • Anode: lithium metal • Solid electrolyte	Solid state Li metal	>2025
Gen 4c	• Cathode: HE-NMC, HVS (high-voltage spinel) • Anode: lithium metal • Solid electrolyte	Advanced solid state	2030
Gen 5	• Li|O_2 – lithium air / metal air • Conversion materials (primarily Li|S) • new ion-based systems (Na, Mg or Al)	New cell gen: metal-air/ conversion chemistries / new ion-based insertion chemistries	>2030

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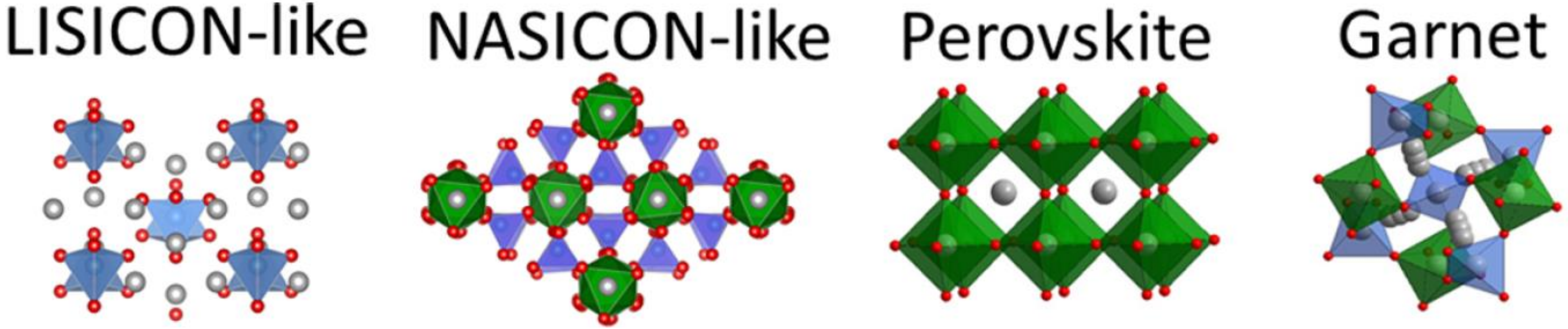
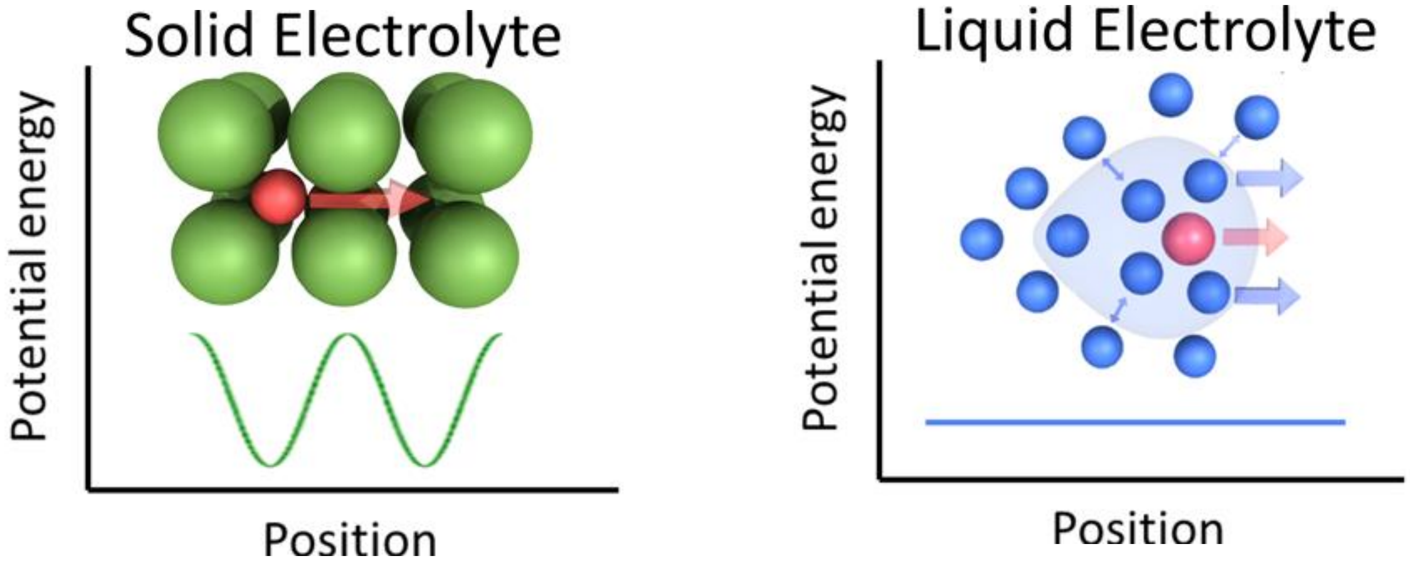


Solid ion-conductors *vs.* Liquid electrolytes: migration of charged species



SOLID ELECTROLYTES (SE):

- high Li+ transference number (~1) compared to liquid electrolytes;
- great electrochemical stability voltage window → increased battery lifetime;
- enhanced thermal stability;
- reduced flammability → increased battery safety.

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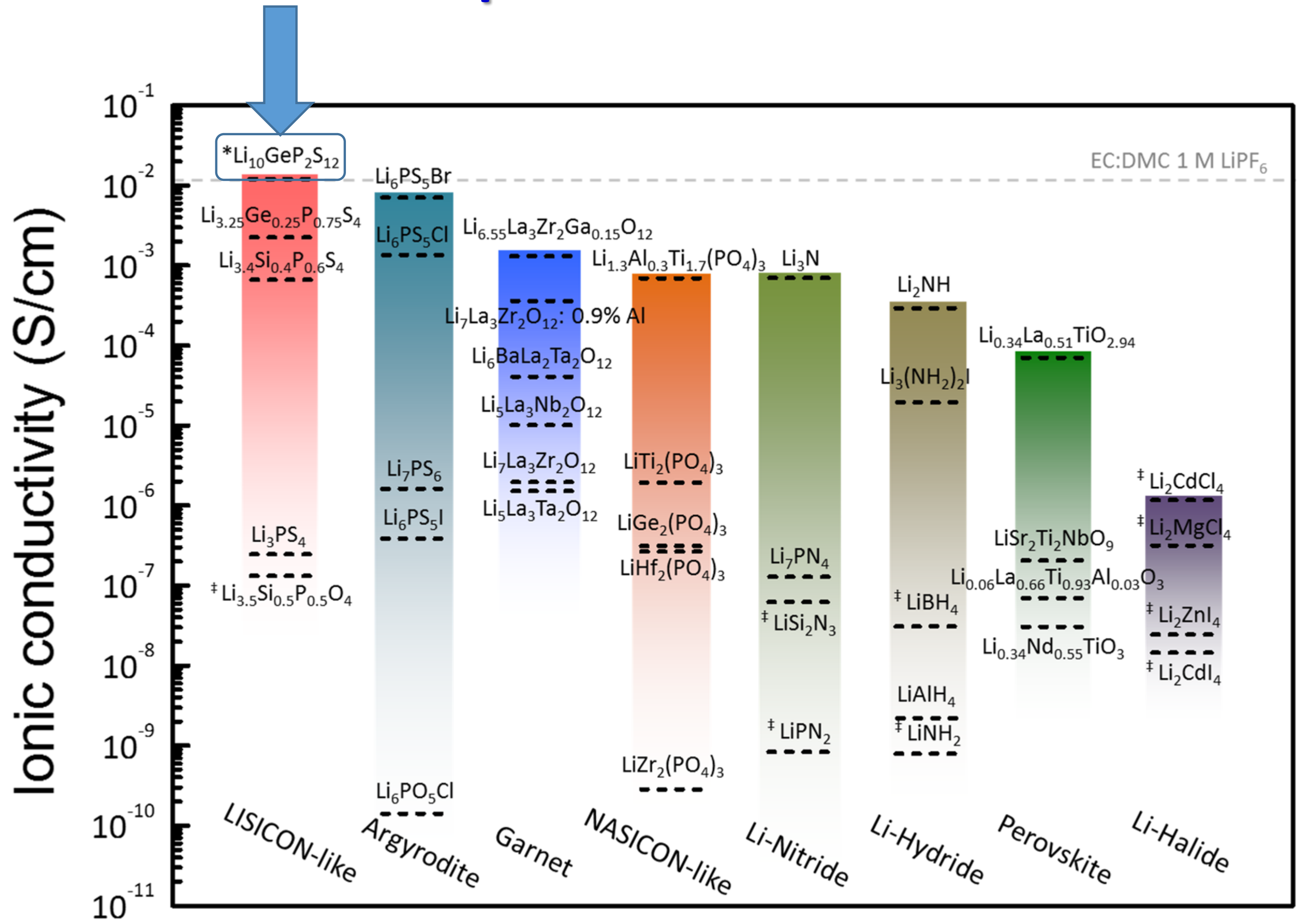
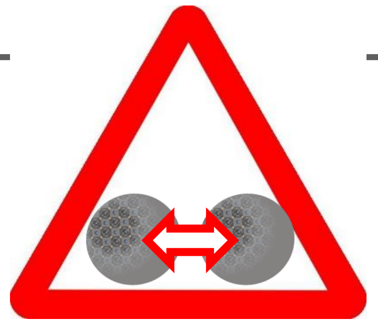
Room-temperature total Li-ion conductivity in crystal structures.

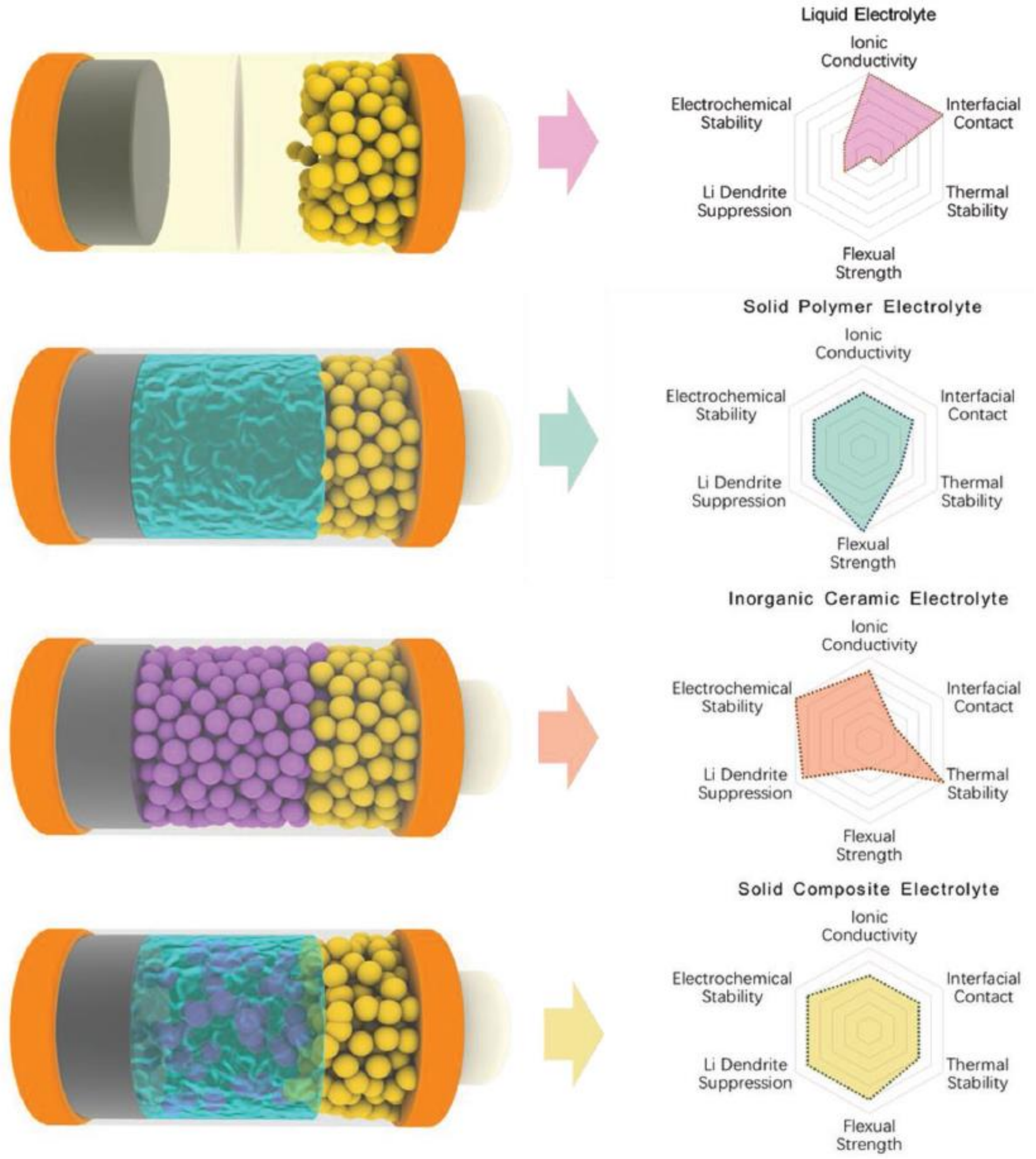


Chem. Rev. 2016, 116, 140–162

Main practical issue in SE:
- High **grain boundary** and **electrode interfacial resistances**



* $Li_{10}GeP_2S_{12}$ (**LGPS**): *Nature Materials*, Vol 10, September **2011**



The performance comparisons of liquid, polymer, inorganic and composite electrolytes in Lithium batteries

Song Li, Shi-Qi Zhang, Lu Shen, Qi Liu, Jia-Bin Ma, Wei Lv, Yan-Bing He,*
and Quan-Hong Yang,
Adv. Sci. 2020, 7, 1903088

Ca-BATTERIES: an emerging storage technology

Why not multivalent elements (Mg, Ca, Al and Zn)
where the ability to drive multiple electron exchange for every charge transfer event counterbalances the larger atomic weight?

Lorenzo Stievano
University of Montpellier
France

Iratxe de Meatza
CIDETEC
Spain

Jan Bitenc
National Institute of Chemistry
Slovenia

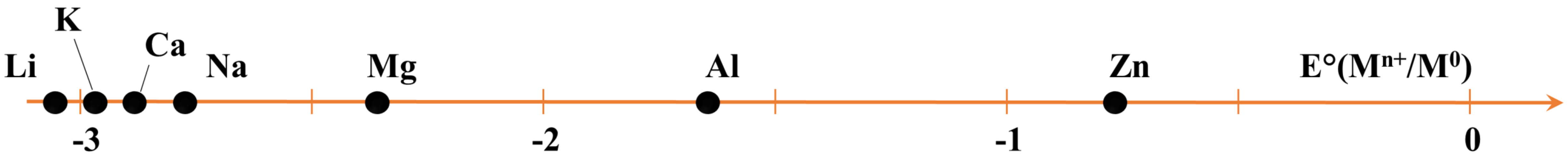
Carmen Cavallo
Oslo University
Norway

Sergio Brutti
Sapienza University of Rome
Italy

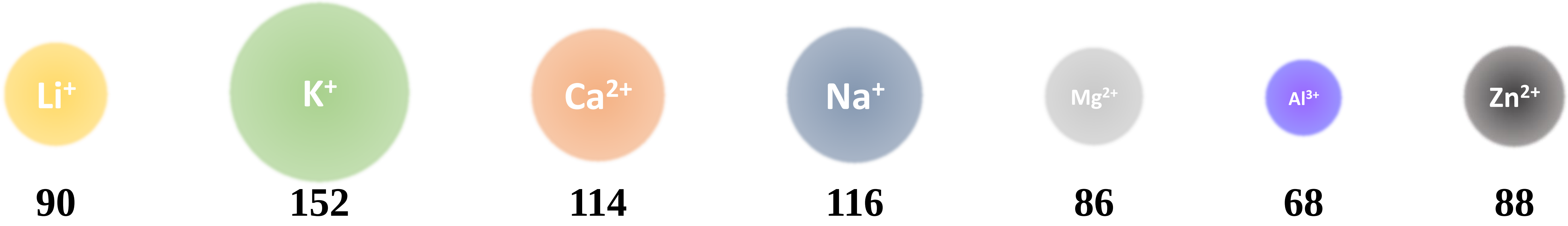
Lorenzo Stievano, Iratxe de Meatza, Jan Bitenc, Carmen Cavallo, Sergio Brutti, Maria Assunta Navarra, **Emerging Calcium Batteries,** *Journal of Power Sources*, 2021, 482, 228875

Ca-metal: properties

Metal/ion redox potential vs SHE



Ionic radius (pm)



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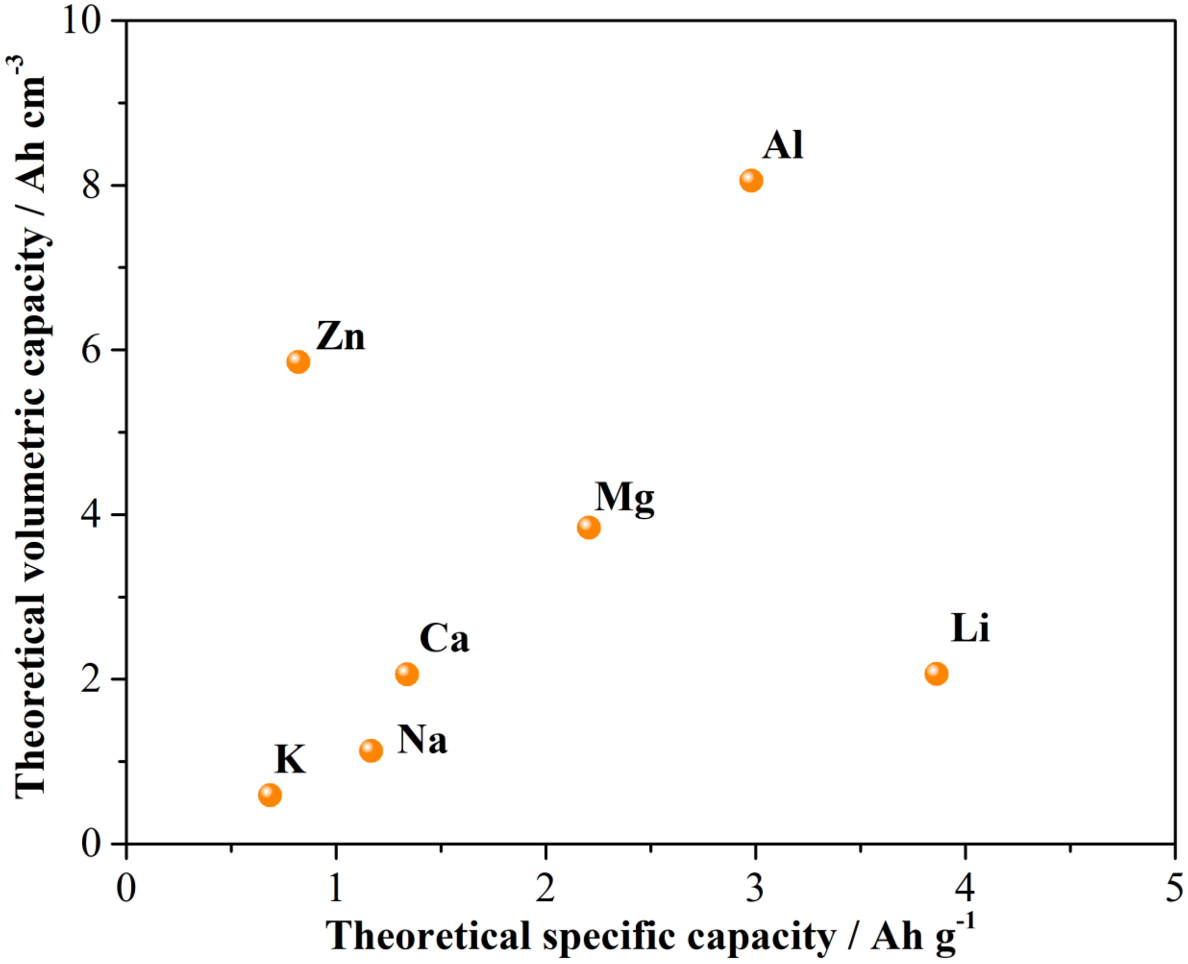
Ca-metal: properties

Theoretical capacities of metal electrodes



Abundance on earth-crust and mean commodity costs

Element	Abundance on earth crust mg kg^{-1}	Commodity quotes US$ $mton^{-1}$
Li	20	7000-8000
Na	23600	150-200
K	20900	200-300
Mg	23300	300-1000
Ca	41500	200-500
Zn	70	1500-2500
Al	82300	1000-2000

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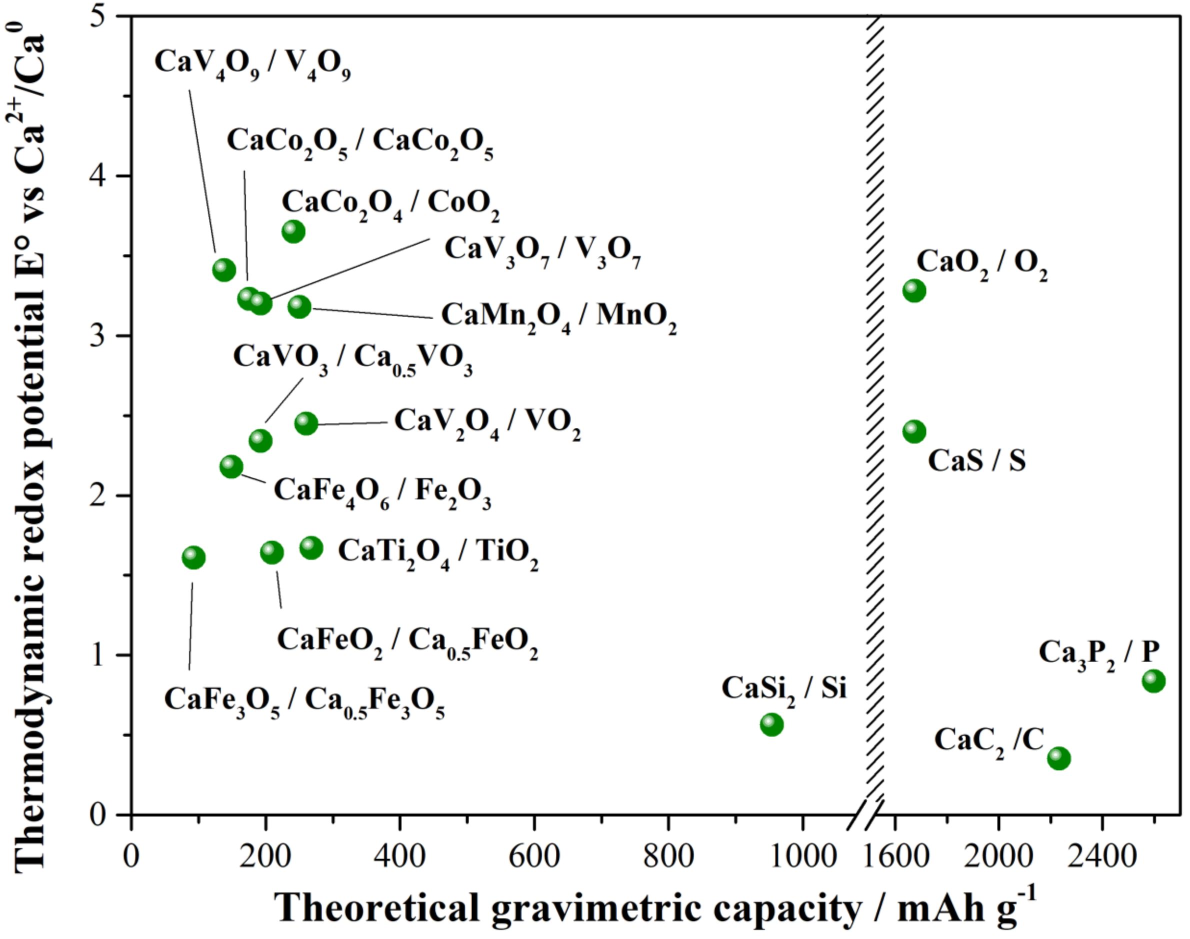
Ca-based electrode materials: theoretical properties

Thermodynamic redox potential and specific capacities for calcium redox couples



Even though calcium has an atomic weight 7 times larger than lithium, the specific capacities of the **oxides** vary in the 100-250 $mAhg^{-1}$ range. Their capacity and thermodynamic potentials match the figures of lithium intercalation positive electrodes!

Silicon, **phosphorus** and **carbon** negative electrodes can reach large theoretical capacities at relatively low redox potentials.
To date: calcium carbide is expected to suffer great kinetic limitation/overpotentials being the crystal structures of all CaC_2 polymorphs remarkably different from graphite.

In conversion electrodes, outstanding theoretical performance is achievable for **Ca-O_2** and for **Ca-S**!

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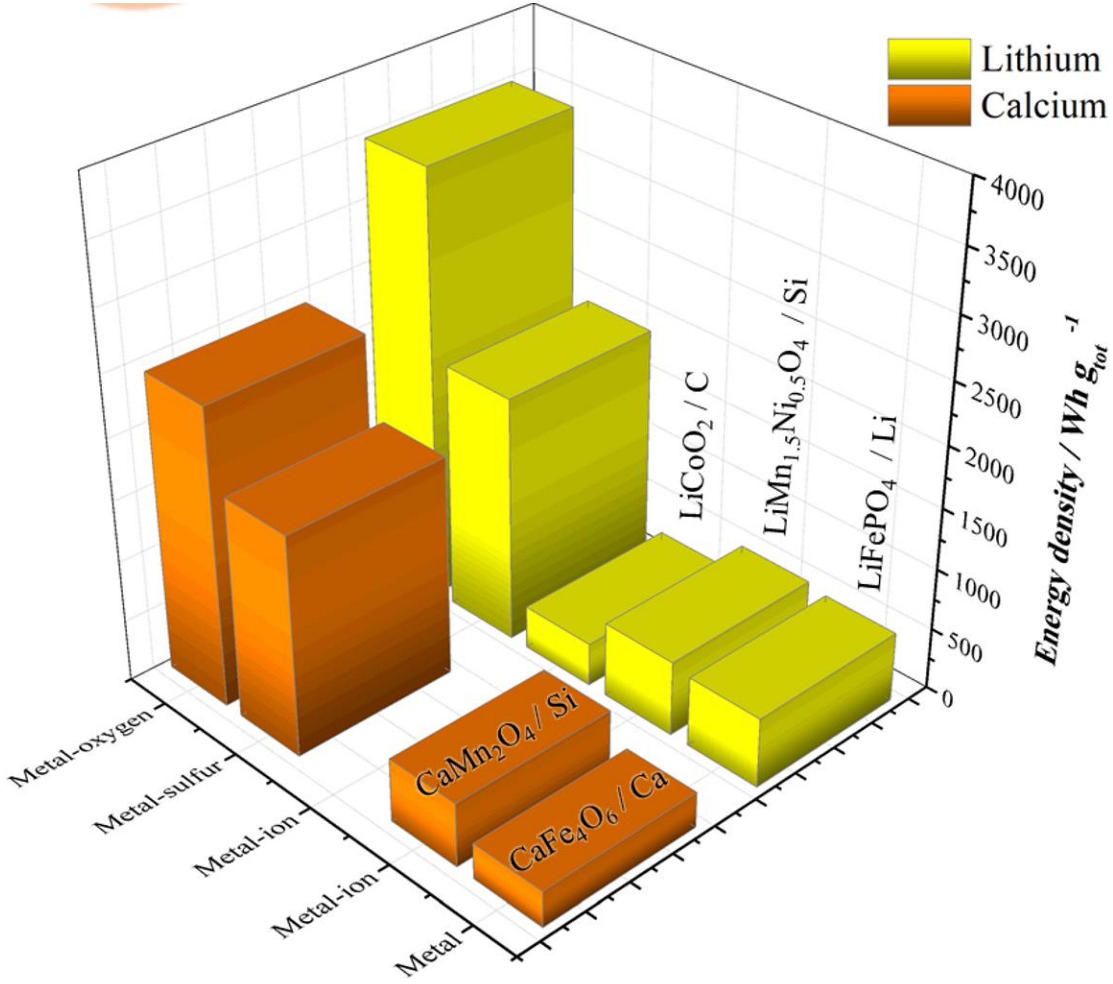
Ca-based single cells: theoretical properties

Estimates of the theoretical energy densities for calcium-based batteries compared to lithium-based analogues



$CaMn_2O_4$|Si Ca-ion battery (CIB) can disclose a theoretical energy density of about 520 mWh g^{-1}, overcoming the benchmark $LiCoO_2$|C LIB (360 Wh kg^{-1}) and approaching the theoretical figures of the $LiMn_{1.5}Ni_{0.5}O_4$|Si and $LiFePO_4$|Li formulations.

Both Sulphur battery chemistries, i.e. **Ca|S** and Li|S, have a comparable theoretical performance (approximately 1800-2000 Wh kg^{-1}) that is, in both cases, exceeded by the Ca|O_2 and Li|O_2 ones (~2400 and ~3500 Wh kg^{-1}, respectively).

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Ca-metal electrodes: a practical challenge

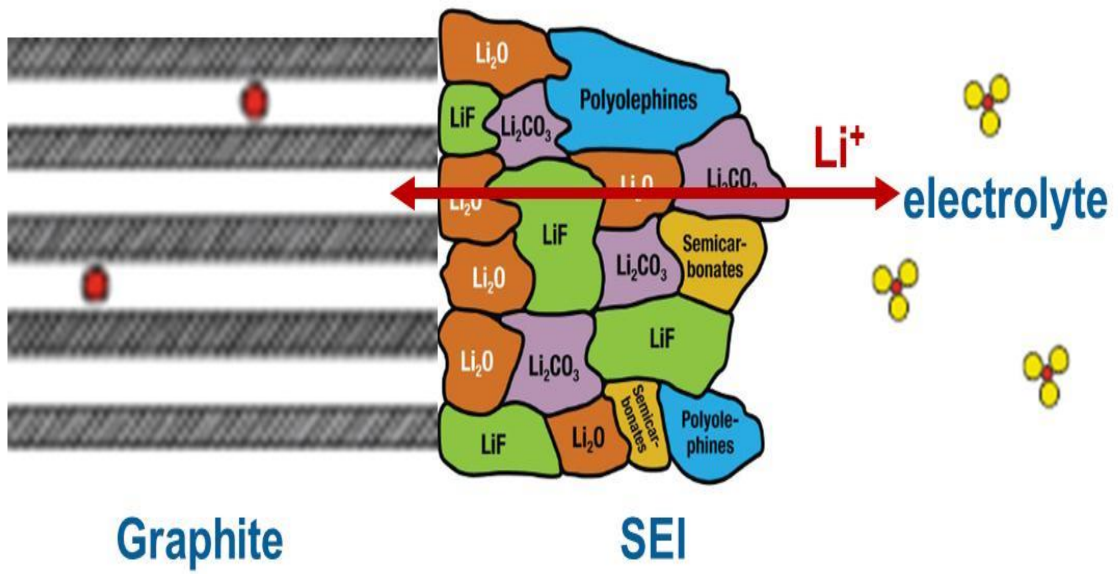
Low redox potential

⇩

reduction of the electrolyte components

⇩

passive films of variable nature



In the case of **Li**, the Solid-Electrolyte Interface (SEI) layer has beneficial effects and a relatively facile diffusion of the Li^+ ions through the passive film is found.

Ca^{2+} ions have twice the charge and are significantly larger than Li^+

⇩

poor Ca^{2+} mobility through the surface films

D. Aurbach, R. Skaletsky, Y. Gofer,
The Electrochemical Behavior of Calcium Electrodes in a Few Organic Electrolytes,
J. Electrochem. Soc. 138 (1991) 3536–3545

Ca-metal electrodes: a practical challenge

The revesible Ca plating/stripping was demonstrated only very recently!

In 2016
from solutions of **$Ca(BF_4)_2$** in a mixture of ethylene carbonate (**EC**) and propylene carbonate (**PC**) at 75 and 100 °C.

Coulombic efficiency around 80% and oxidative stability up to 4 V

A. Ponrouch, C. Frontera, F. Bardé, M.R. Palacín, Towards a calcium-based rechargeable battery, Nature Mater. 15 (2016) 169–172.

In 2018
from 1.5 M **$Ca(BH_4)_2$** in tetrahydrofuran (**THF**) at room T on precious metal surfaces (Au or Pt).

Coulombic efficiency between 94-96 % and oxidative stability up to 3 V

D. Wang, X. Gao, Y. Chen, L. Jin, C. Kuss, P.G. Bruce, Plating and stripping calcium in an organic electrolyte, Nature Mater. 17 (2018) 16–20.

Ca metal and the electrolytes

Different **electrolytes** used for Ca stripping/plating

Electrolyte	Coulombic efficiency	Working electrode	Year
$Ca(AlCl_4)_2$ $SOCl_2$	Only stripping	Ni	1980
$Ca(AlCl_4)_2$ $SOCl_2$	<10%, indirect evidence	Stainless steel	1982
$Ca(BF_4)_2$ EC:PC	85%, above 75 °C	Stainless steel	2016
$Ca(BH_4)_2$ THF	95%	Au	2018
$Ca(B(hfip)_4)_2$ DME	80%	Pt	2019
$Ca(B(hfip)_4)_2$ Bu_4NCl DME	90%	Au	2019
$Ca(BH_4)_2$ $LiBH_4$ THF	99%	Au	2020

Only a very small number of Ca salts are available commercially!

Ca salt solubility is a major issue, stating the need for development of new highly dissociative salts.

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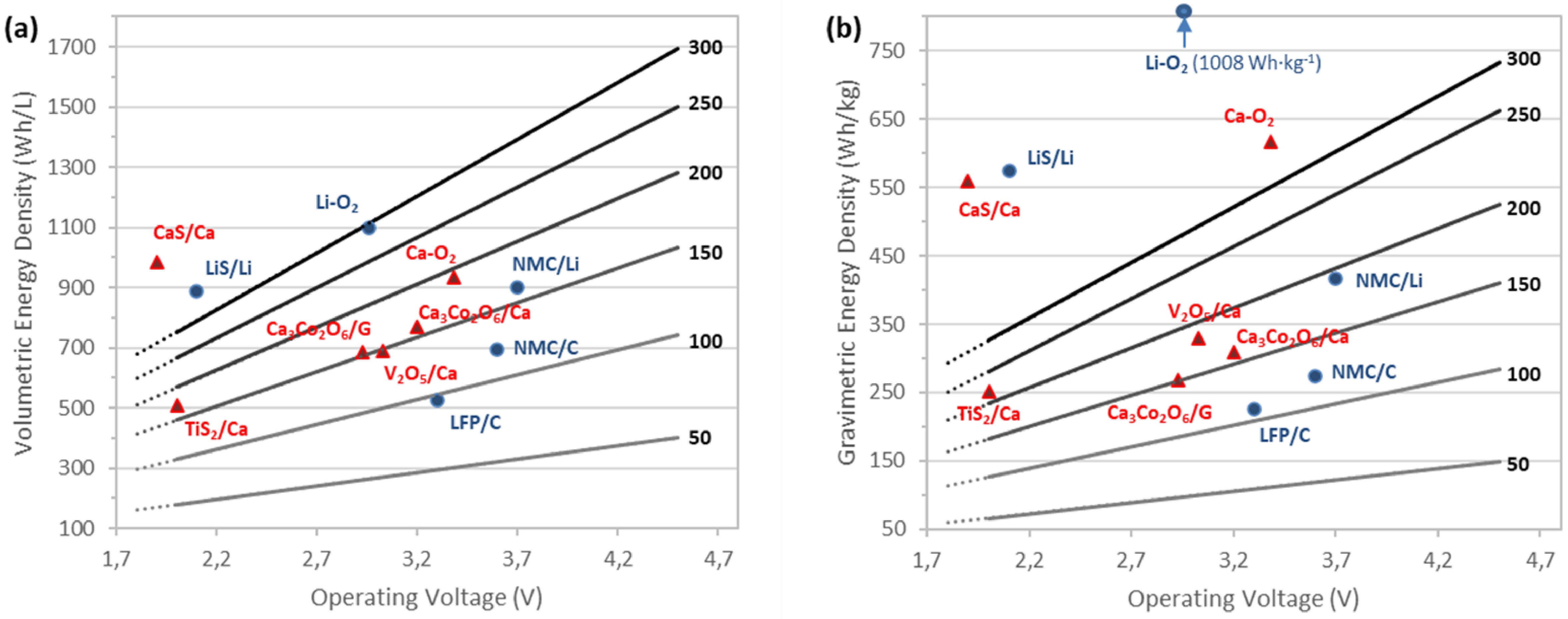
Techno-economic modelling of Ca batteries



Volumetric (a) and gravimetric (b) energy densities for Li based batteries (blue circles) and Ca battery technologies (red triangles). The straight lines are calculated energy densities of hypothetical Ca metal batteries as a function of operation potential and cathode specific capacities (on the right of each line).

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Features of Ca-batteries from the techno-economic analysis and OUTLOOK

Combinations of 3.0 V / 250 $mAh \cdot g^{-1}$ or 3.5 V / 200 $mAh \cdot g^{-1}$ can yield **gravimetric energy densities** above the 400 $Wh \cdot kg^{-1}$ targeted by the Strategic Energy Technology (SET) Plan for year 2030, and high **volumetric energy densities** >1000 $Wh \cdot L^{-1}$, even higher than any of the estimated sulfur-cathode-based battery technologies and exceeding the 750 $Wh \cdot L^{-1}$ target in the SET Plan.

In terms of **power density**, expecting that 2C current rates are feasible without energy loss, most of the Ca metal-based batteries estimated here could achieve > 1500 $W \cdot L^{-1}$ and >700 $W \cdot kg^{-1}$ (SET Plan targets).

Ca-based batteries may disclose remarkable innovations and technological breakthrough, either from a fundamental science point of view or from an application perspective!

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Thanks for your attention!

Electric vehicles powered by **solid-polymer electrolyte lithium batteries**:

Li | Li^+-polymer | $LiFePO_4$