An Overview of Polymer-based Electrolytes with High Ionic Mobility for advanced Li-solid state battery

Giuseppe Antonio ELIA

M. Falco, S. Porporato, Y. Zhang, M. Zhang, M. Gastaldi, F. Gambino, S. Saffirio, M. Milanesi, H. Darjazi, V. Sperati, A. Piovano, G. Meligrana, C. Gerbaldi

GAME Lab
Department of Applied Science and Technology
Politecnico di Torino, Italy

Group for applied materials and electrochemistry

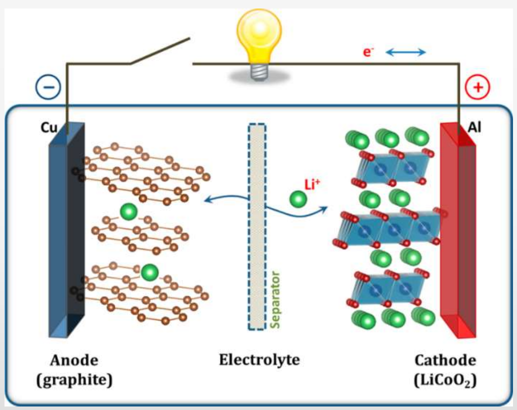
Politecnico di Torino 1859

giuseppe.elia@polito.it

Electrochemical energy storage role in decarbonizing EU by 2050

The mission
Be climate neutral by 2050
The route
A complete transition to renewables sources

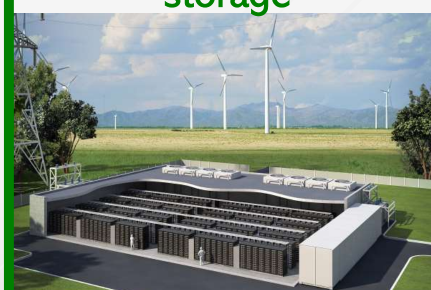
Battery technology plays a fundamental role



Electromobility

Ban of internal combustion engine (ICE) vehicles planned for 2030-2050 in most EU countries

Stationary energy storage



Use of cost-effective solutions for large-scale electricity storage derived from renewable resources

LIBs: characteristics and requirements for EVs

Rechargeable LIBs - intercalation chemistry

Development/optimisation of the1st generation electrodes on the market

- ✓ $LiCoO_2$ – 274 mAh/g (≈ 150 mAh/g with a cut-off voltage of 4.2 V), Co 60 wt. %
- ✓ Graphite – 372 mAh/g (LiC_6)
- ✓ Organic carbonate liquid electrolyte

Current LiB market: main application in portable electronic devices.

Emerging applications: EV & PHEV cars, smart grid energy storage

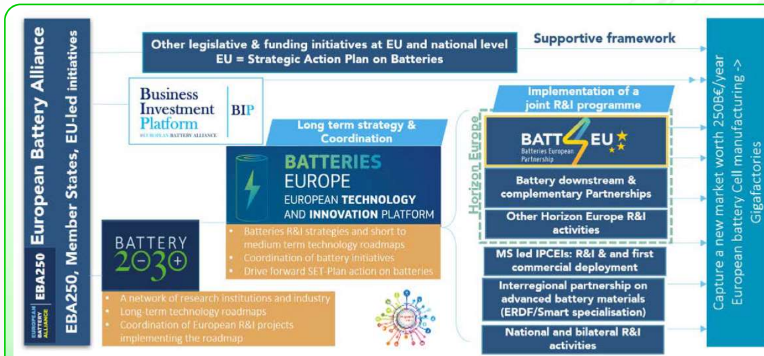
SEVERAL CHALLENGES

Challenge	Short description	Relevance
Cost	Improve cost competitiveness of battery active and passive materials	+++
Fast charging	3-5C fast charging in 10 min to 80 % SOC	+++
Sustainability	Reduce ecological and social footprint, ensure transparent value chain (battery passport)	+++
Energy density	High energy anodes with high loading and stable capacities of 1.200 mAh/g - High energy cathodes with high loading and stable capacities up to 300 mAh/g	++
Resilient sourcing of battery materials	Increase security of supply by enabling alternatives to Co-rich battery materials	++
Increase lifetime and cycle life	Improve cycle life of high voltage (2000+) and high-capacity batteries (3000+) to allow for viable 2nd life applications	+

- Low Cost
- High Energy Density
- High Power
- Safety
- Durability
- Sustainability

Towards all-solid-state: polymer-based electrolytes

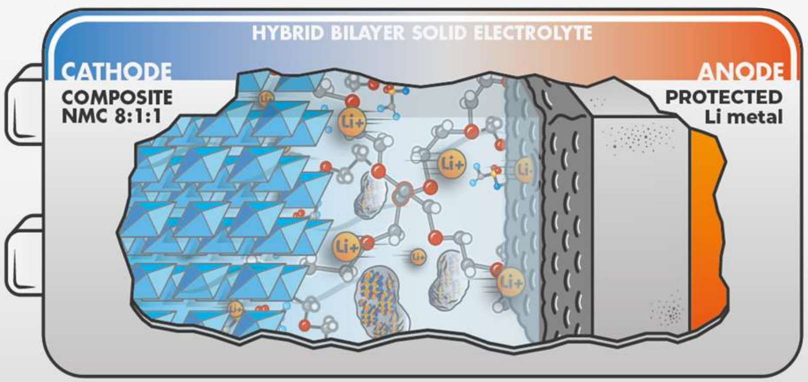
- ✓ Desirable **shapes and sizes**
- ✓ Light-weight (higher **energy density**)
- ✓ **Low cost** of fabrication
- ✓ Easy disposal at the end of life
- ✓ **Better safety**: no corrosive/explosive liquid leakage and less short-circuits
- ✓ … …

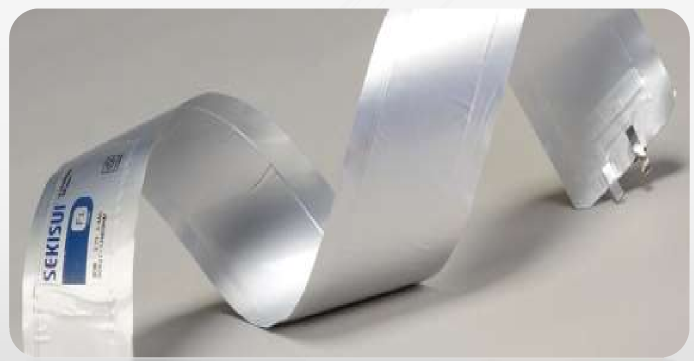


<u>Scheme of the EU Plan for "Batteries"</u>

energy density >350/400 Wh kg^{-1} & >1000 Wh L^{-1} for next-gen of Li-based batteries, **fast charge rates** above 10C as **2030 target**

Li POLYMER-BASED BATTERY

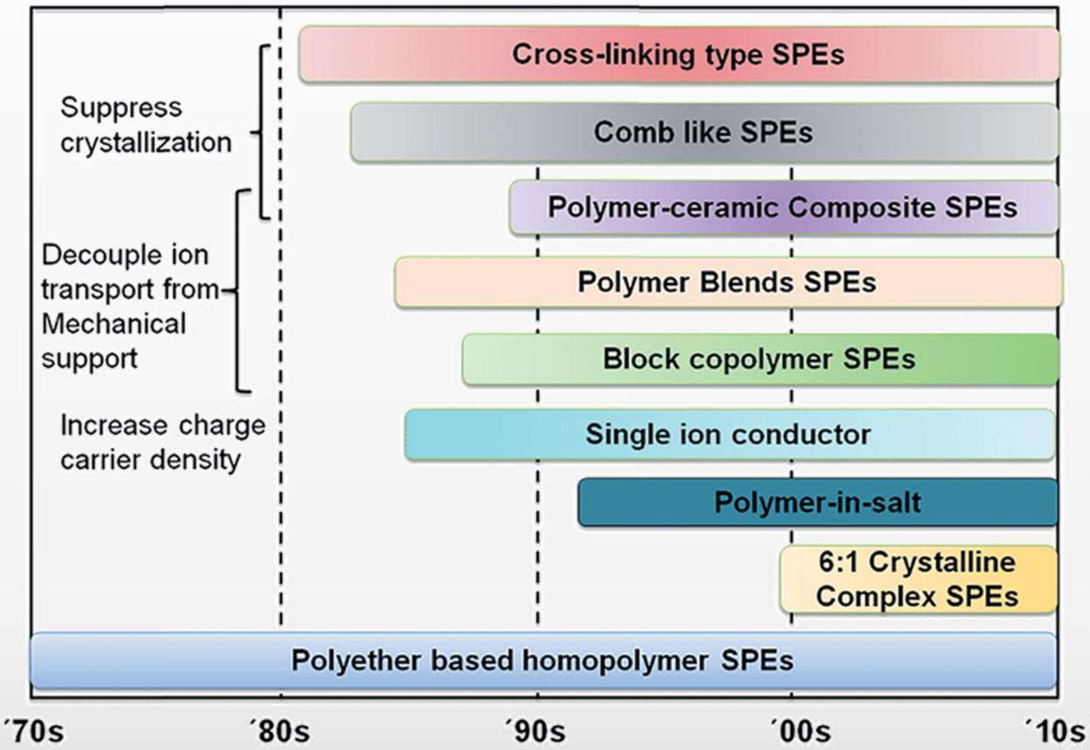




- Safe
- High energy
- Thin
- Flexible
- Leak-free

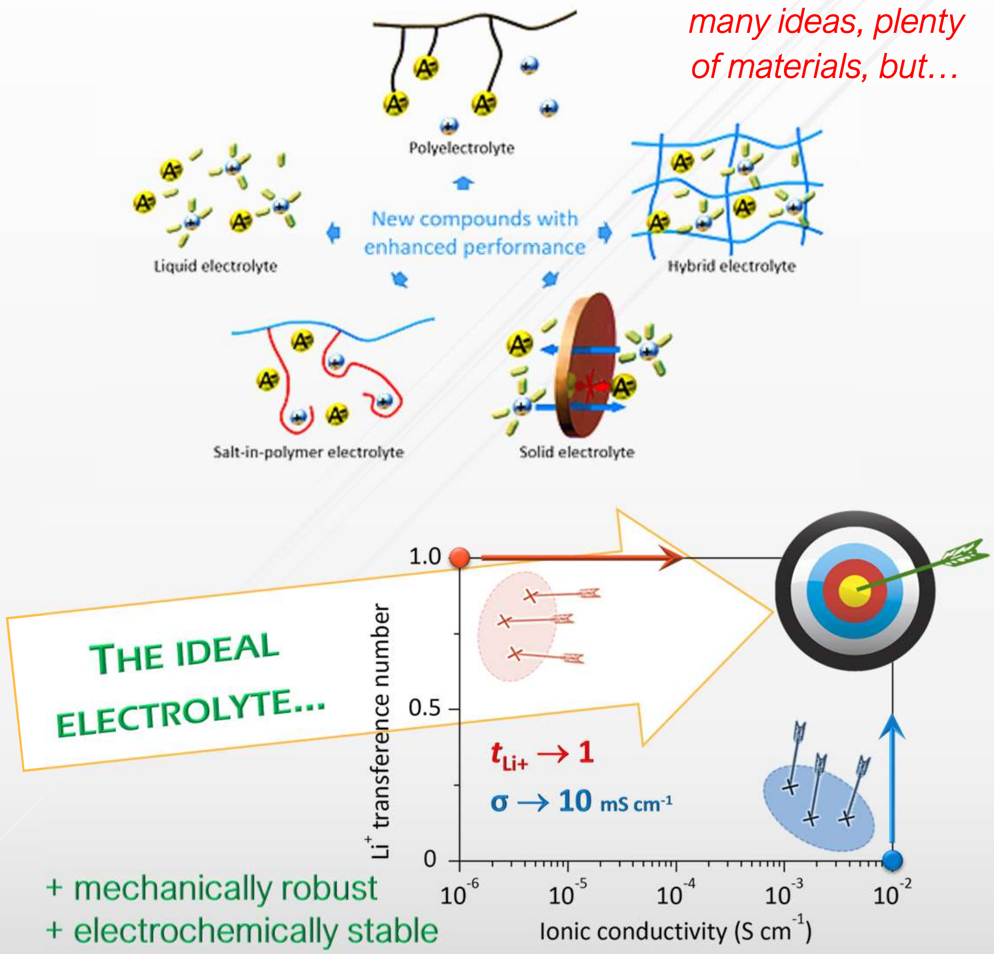
Polymer-based electrolytes: requirements & characteristics

"non comprehensive" summary of solid polymer electrolyte development in the last decades



S. Cheng et al., *RSC Advances* 5 (2015) 48793

many ideas, plenty of materials, but…



+ mechanically robust
+ electrochemically stable

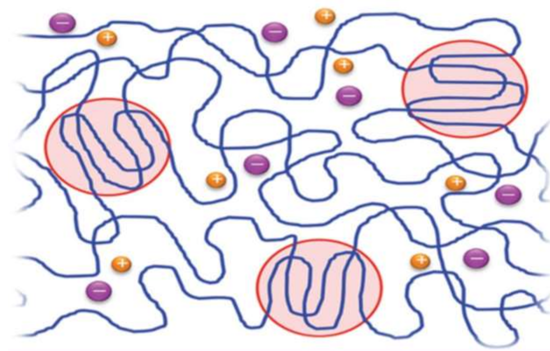
Polymer-based electrolytes: requirements & characteristics

Requirements

- High **ionic conductivity** @RT (>1 mS cm^{-1})
- Li^{+} ion **transference number** (~1)
- High **thermal, chemical and electrochemical stability**
- High mechanical **robustness** (> 150 MPa)
- Excellent **compatibility** with electrode materials
- Easy **disposal** at the end of battery life

Li^{+} conduction in ether-polymers by "hopping" on (EO) coordination sites

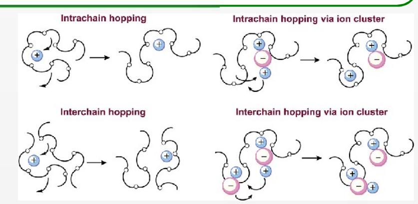
M. Armand et al., 1979



P.V. Wright et al., 1973

Most common polymer electrolyte: poly(ethylene) oxide (PEO)

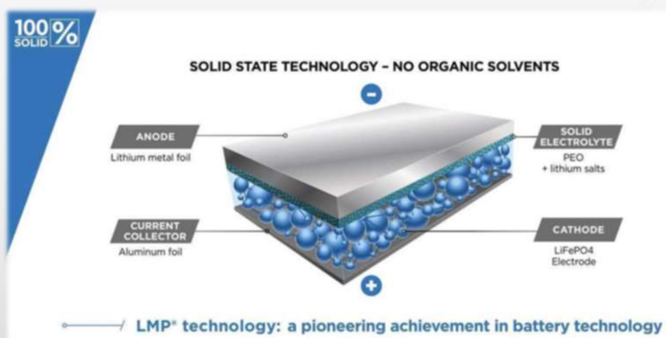
…**it works** only in the amorphous state (i.e., above melting T > **60 °C**)



Already industrialized

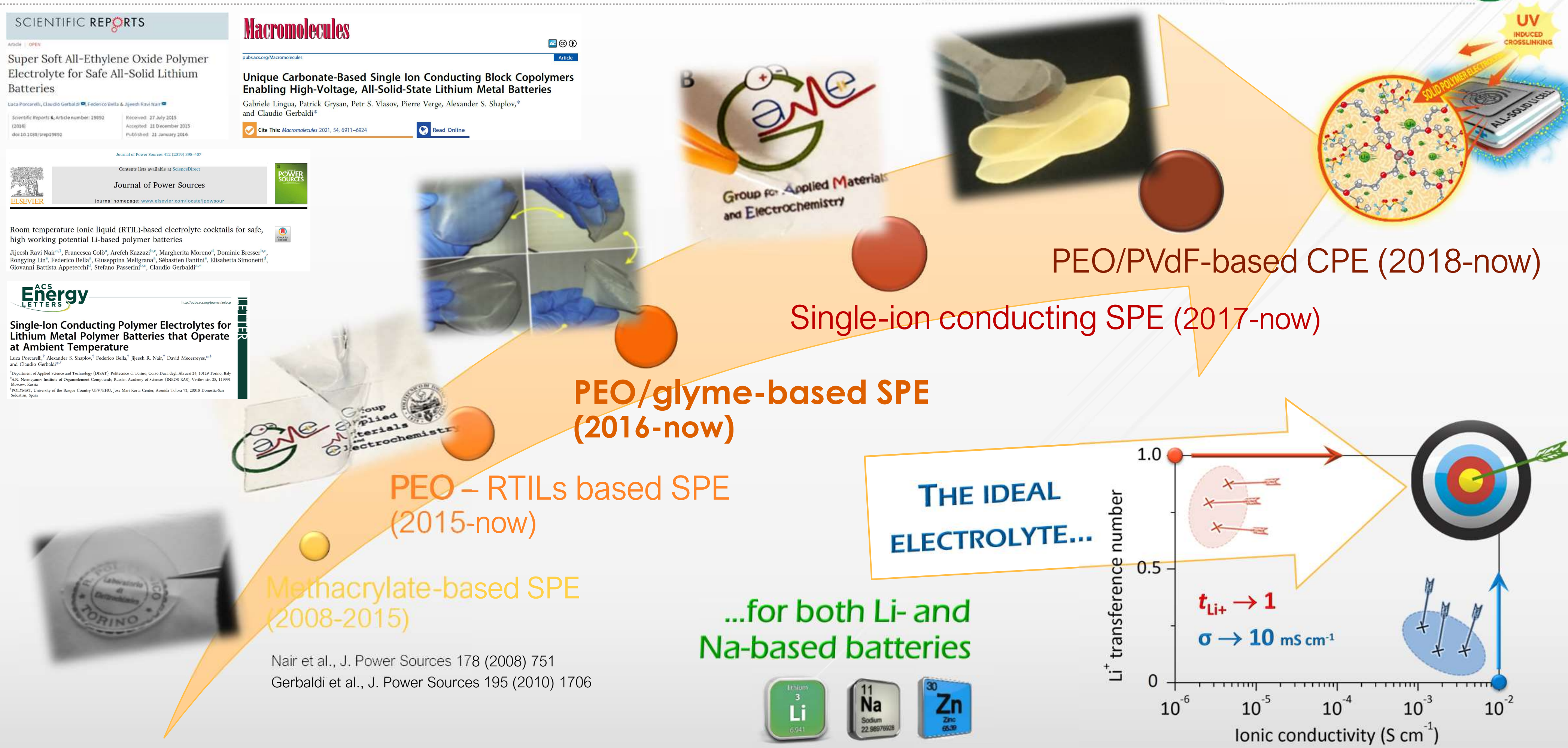
Bolloré Bluebus

EV BlueCar in Torino



- Crystallinity suppression by plasticizers, fillers, grafting, cross-linking, etc.
- Produced by solvent casting (time/energy consuming, hard to remove traces of solvent from the final membrane)

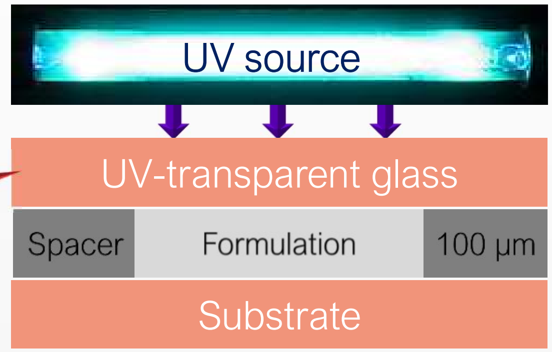
UV-cured polymer-based electrolytes @ Game Lab



UV-induced free radical polymerization

Polymerization/crosslinking triggered by light radiation

(pre-)polymer formulation
- Radical initiator
- Functional monomer(s)
- Lithium salt
- Additives?



UV-curing set-up

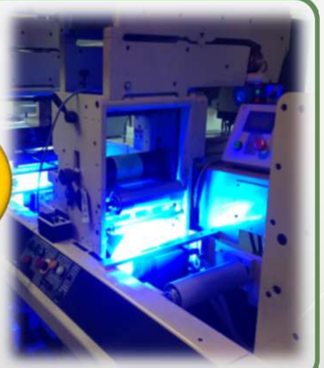
3 min

Crosslinked polymer electrolyte membrane
- Self-standing
- Elastic
- Ready to use

J.V. Crivello et al., Chem. Mater. 26 (2014) 533
J. Lalevée et al., Polym. Chem. 6 (2015) 3895

- ✓ Fast, **single step** preparation
- ✓ **Cost effective**
- ✓ **No solvents**
- ✓ No catalysts
- ✓ Energy saving
- ✓ Transferable to the **industrial scale**

GREEN and UP SCALABLE PROCESS



European Commission > Horizon 2020 > Innovation Radar >

Discover
Great EU-funded Innovations

European Commission

INNOVATION

Solvent-free process for (composite) polymer electrolyte membranes

KEY INNOVATOR

Politecnico di Torino

Market Maturity: **Tech Ready**
These are innovations that are progressing on technology development process (e.g. pilots, prototypes, demonstration). Learn more →

Market Creation Potential
This innovation was assessed by the JRC's Market Creation Potential indicator framework as addressing the needs of **existing markets and existing customers**. Learn more →

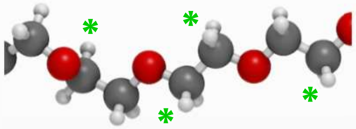
Go to Market needs
Needs that, if addressed, can increase the chances this innovation gets to (or closer to) the market incude:
- Prepare for Market entry
- Scale-up market opportunities

The EU-funded Research **Project**

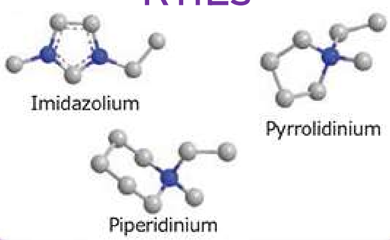
This innovation was developed under the Horizon 2020 project **Si-DRIVE** with an end date of 31/01/2023
- Read more about this project on **CORDIS** →
- Details of this project on the **Horizon 2020 dashboard** →

UV-crosslinked PEO-based electrolytes with G4 or RTILs

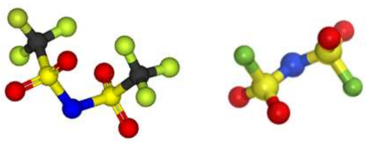
Polymer: PEO



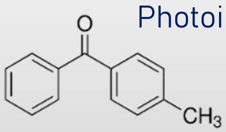
RTILs



Salt: Li^{+} $TFSI^{-}$/ FSI^{-}



Photoinitiator: Me-BP



CROSSLINKED PEO-based SPE

H** abstraction mechanism by Me-BP

MIX @50 °C

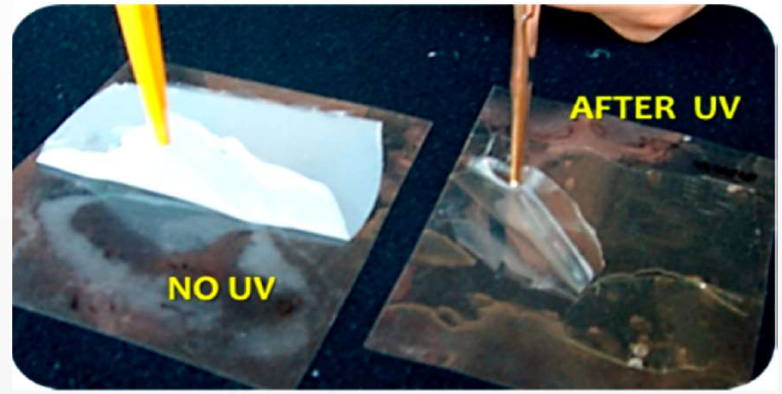
Hot Press

NO Solvent
carbonate free

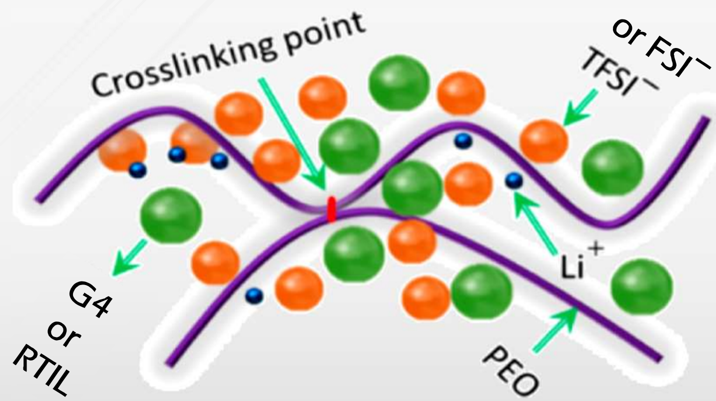
Polymer electrolytes can be finely tuned by various plasticisers/ additives/fillers (glymes, RTILs, ceramics, etc.)

patent WO 2015/104727 A1
J.R. Nair et al., *ACS Appl. Mater. Interf*. 7 (2015) 12961
L. Porcarelli et al., *Scientific Reports* 6 (2016) 19892

THERMOSET MATERIAL

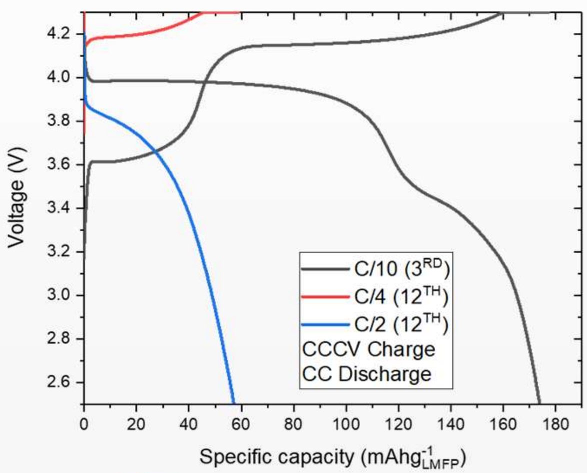


UV-induced PEO amorphisation

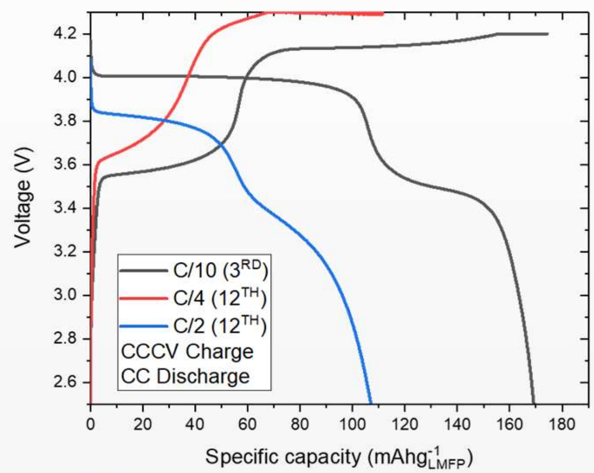


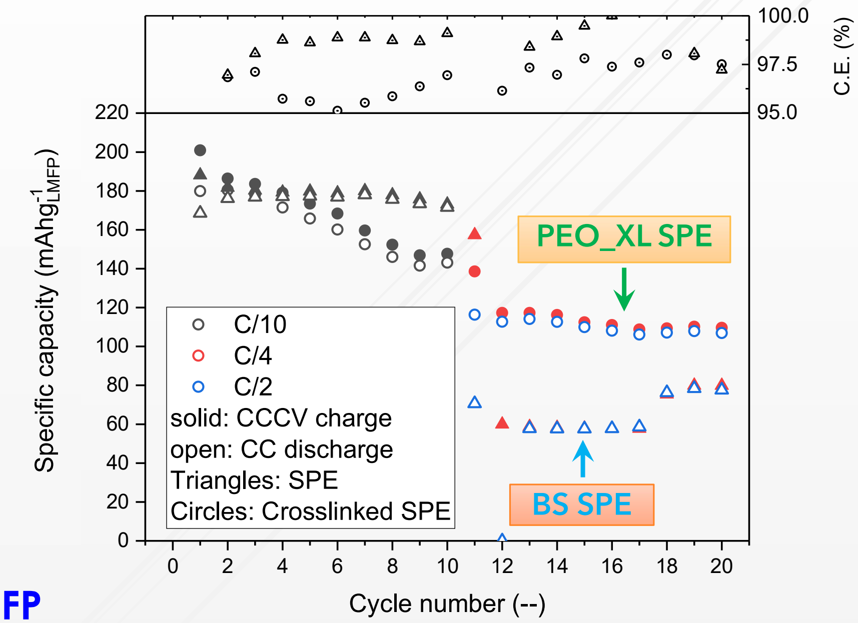
Crosslinked PEO + SICPE: Li metal cell cycling at 25 °C

BlueSolutions (BS) SPE



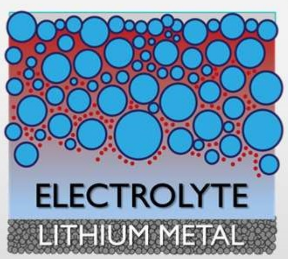
Crosslinked PEO_XL SPE





PSIONIC

Ready for scale-up by solvent-free extrusion



COMPOSITE CATHODE (CATHOLYTE with SICPE)

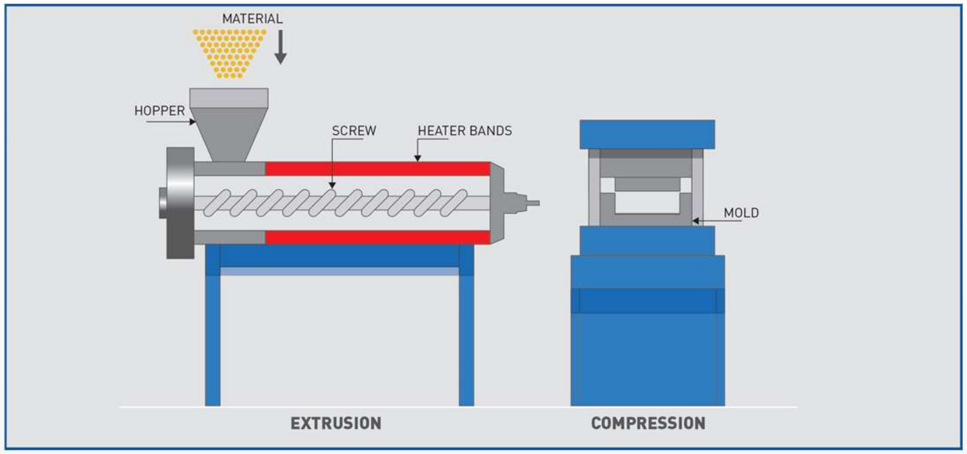
CROSSLINKED PEO-G4

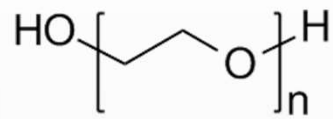
ANODE

- Stable cycling with **LMFP cathode** (loading 5.6 mg cm^{-2}) in solid-state configuration
- Higher performance vs. LMP® BS cell at 25 °C up to C/2 rate
- **MILESTONE** for **Gen1 solid-state cells** achieved

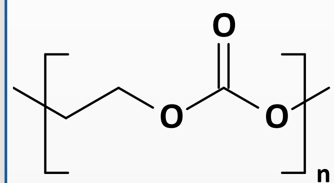
Galvanostatic test up to 4.6V, in Li metal cell with Li/PEO_XL/NMC+SICPE configuration at 25 °C.

Polycarbonate blends with PEO by solvent-free extrusion

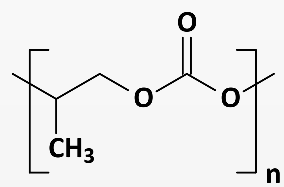




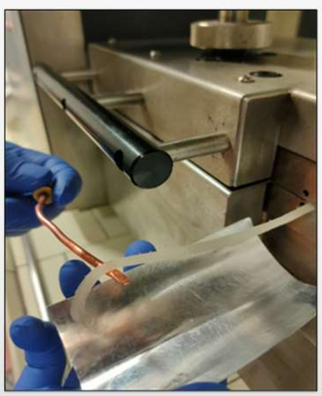
Poly(ethylene oxide) (PEO)



Poly(ethylene carbonate) (PEC)



Poly(propylene carbonate) (PPC)



- Solvent-free process characterised by good scalability potential
- Polycarbonates are expected to improve mechanical properties and electrochemical stability

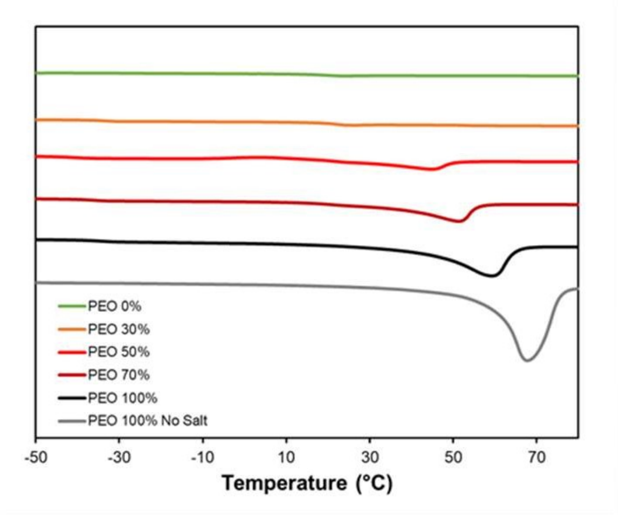
Gambino et al. / Manuscript in preparation

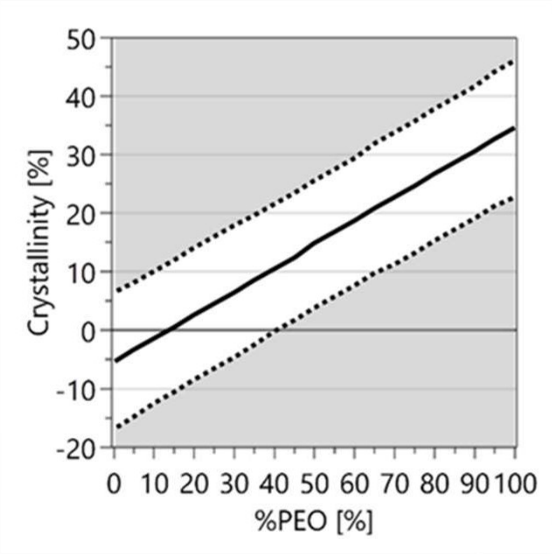
Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the composite crystallinity

Crystallinity obtained by thermal analysis (DSC) of the samples for the different PEO-PPC and PEO-PEC mixtures

Li salts LiTFSI with a fixed amount of [EO]:[Li] 20:1





- The addition of polycarbonates reduces the PEO crystallinity
- The reduced crystallinity is expected to guarantee improved ionic mobility

Gambino et al. / Manuscript in preparation

Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the composite crystallinity

Crystallinity obtained by thermal analysis (DSC) of the samples for the different PEO-PPC and PEO-PEC mixtures

Li salts LiTFSI with a fixed amount of [EO]:[Li] 20:1

PC (%)	**PEO 4M /PEC formulations**			**PEO 4M /PPC formulations**			**PEO 400k /PEC formulations**			**PEO 400k /PPC formulations**		
	T_g PEO (°C)	T_g PEC (°C)	Crystallinity (%)	T_g PEO (°C)	T_g PPC (°C)	Crystallinity (%)	T_g PEO (°C)	T_g PEC (°C)	Crystallinity (%)	T_g PEO (°C)	T_g PPC (°C)	Crystallinity (%)
0	-30	-	35	-30	-	35	-32	-	33	-32	-	33
30	-33	22	33	-34	37	19	-33	25	24	-34	36	22
50	-36	-	1	-31	40	9	-33	23	8	-31	39	11
70	-36	23	0	-33	40	0	-33	21	0	-32	40	0
100	-	21	0	-	26	0	-	21	0	-	26	0

- The addition of polycarbonates reduces the PEO crystallinity
- The reduced crystallinity is expected to guarantee improved ionic mobility

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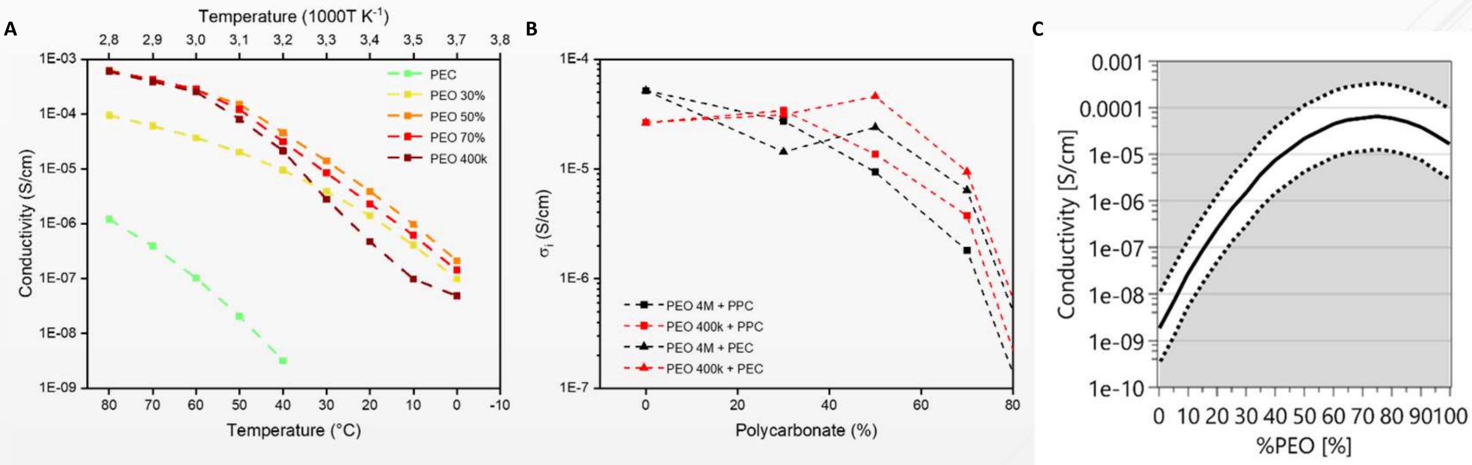
Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the ionic conductivity

Ionic conductivity value at 40°C for the different PEO-PPC and PEO-PEC mixtures

Li salts LiTFSI with a fixed amount of [EO]:[Li] 20:1



- The addition of polycarbonate does not substantially affect the ionic until a threshold of 50%
- The drop in conductivity suggests the 50% as the maximum threshold for the composite

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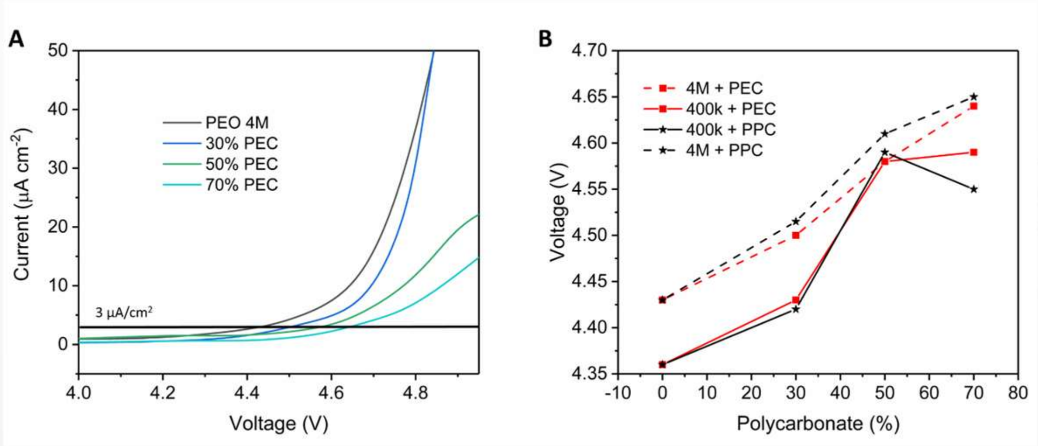
Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the electrochemical window stability (EWS)

EWS value at 40°C for the different PEO-PPC and PEO-PEC mixtures

Li salts LiTFSI with a fixed amount of [EO]:[Li] 20:1



- The addition of polycarbonate evidences an increase of the EWS
- The stability increase is most likely associated by the superior stability of polycarbonate with respect to PEO polymer

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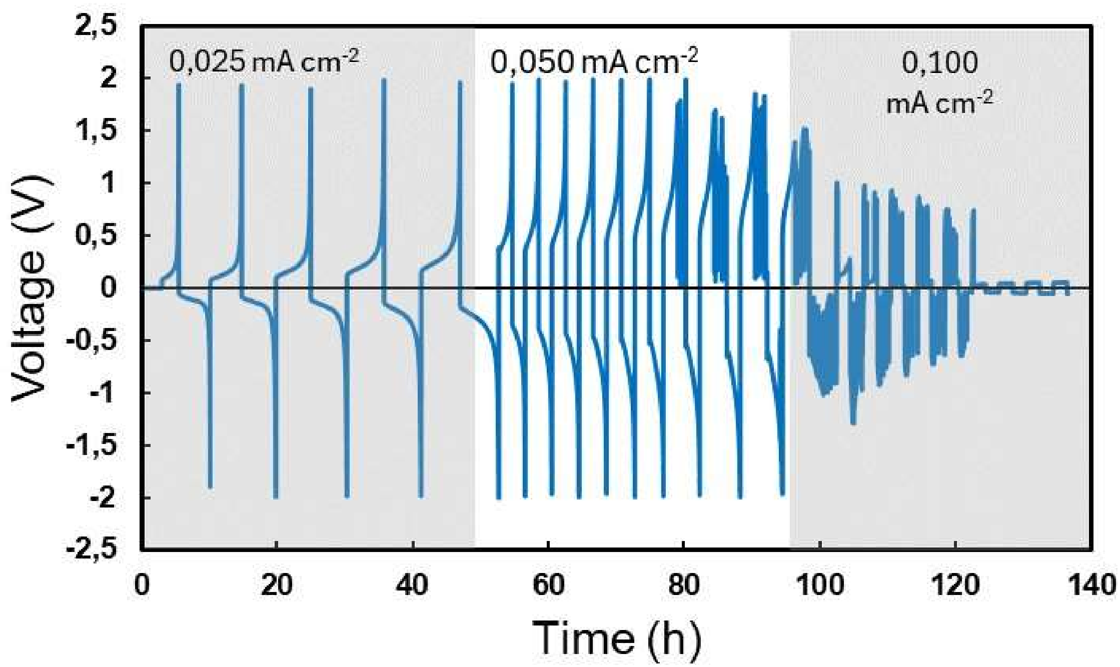
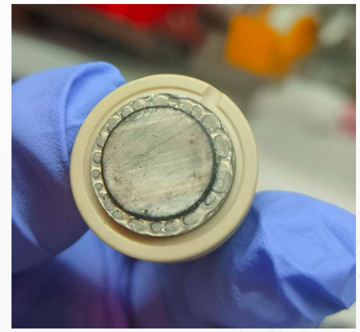
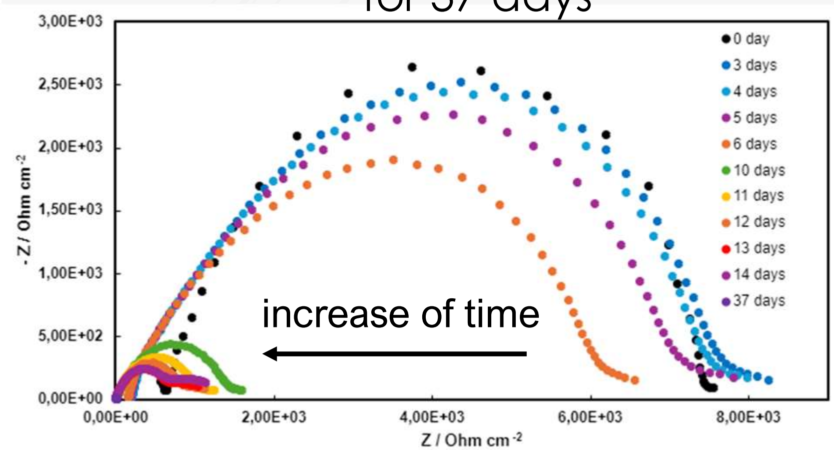
PEO:PEC 1:1 – Lithium Plating and Stripping





After the experiment of stability a gel-like compund was found inside the cell

Stability over time of Li/PEO:PEC/Li for 37 days

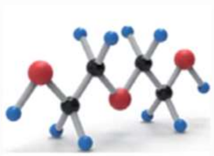


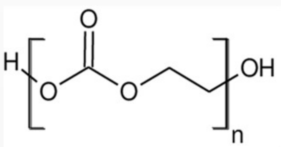
40°C Several spikes already present at low current. while short-circuiting at 0.050 mA cm^{-2}

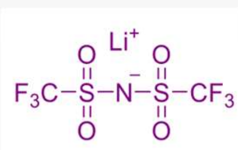
B. Sun et al. / Solid State Ionics 262 (2014) 738–742

Gastaldi et al. / Manuscript in preparation

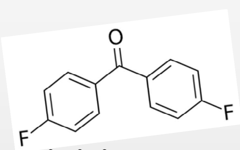
UV-Curing of PEO and PCs





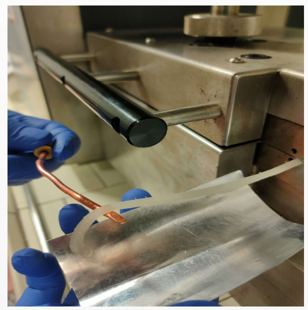


Li+ TFSI-
[EO]:[Li] 20:1



Photoiniziator: 4.4' difluorobenzophenone

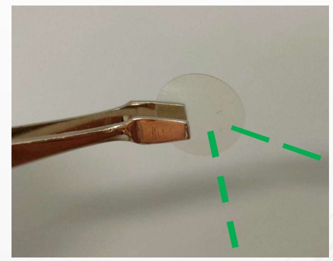
Extrusion
140 °C



Blended polymer

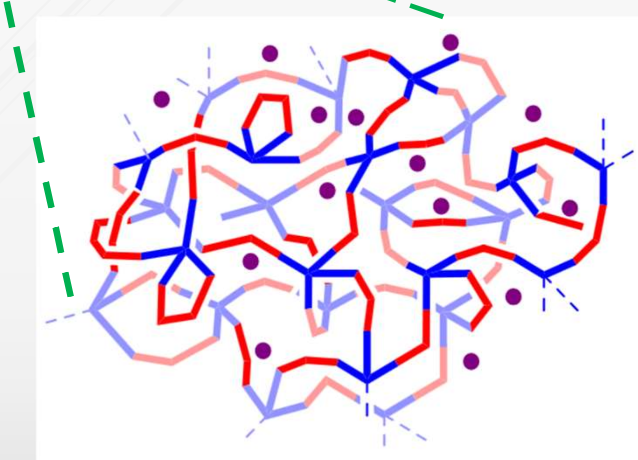
Hot press (10 bar)

\+



Crosslinked polymer electrolyte membrane

- Self-standing
- Elastic
- Ready to use
- Thickness up 60 µm



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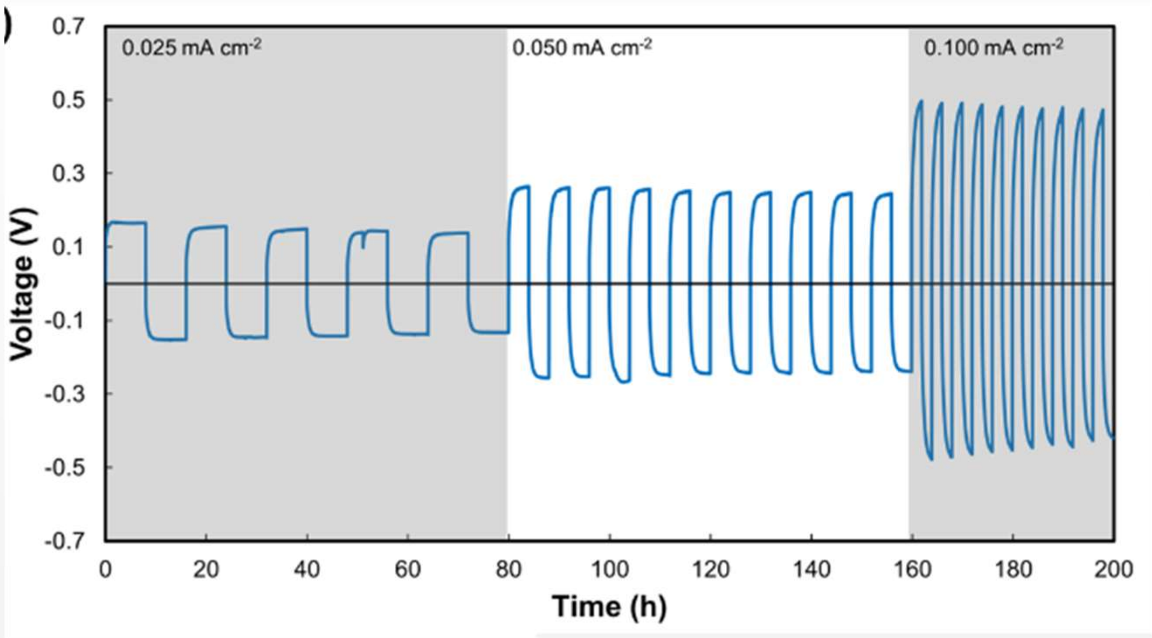
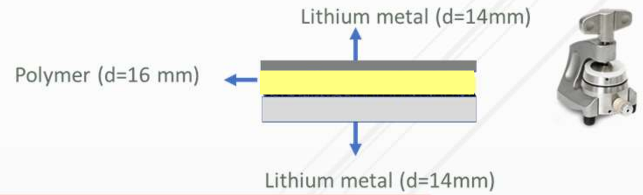
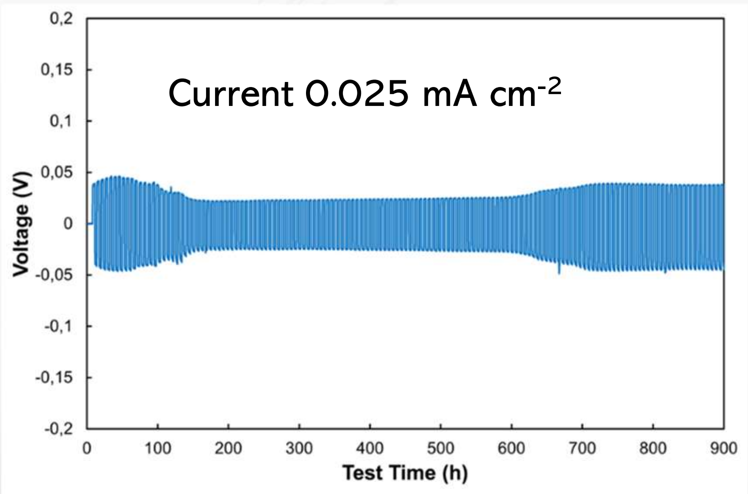
Compatibility vs. Li metal



Capacity fixed to 0.25 mAh cm^{-2}



At low currents the plating/stripping of Li showed low overpotential



70°C

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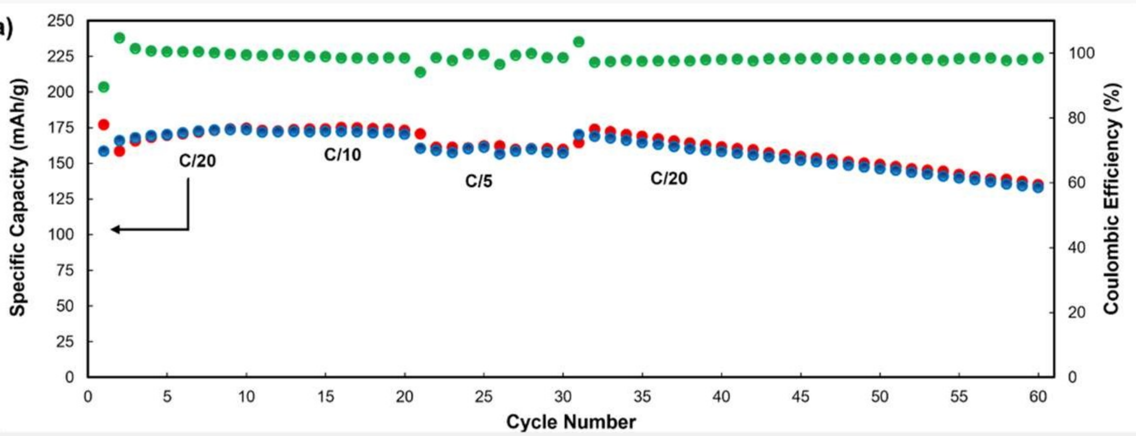
Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the cycling performance in Li-cells

Electrochemical performances at 70°C for the different PEO-PEC 1:1 mixtures against $LiFePO_4$

Li salts LiTFSI with a fixed amount of [EO]:[Li] 20:1



70°C

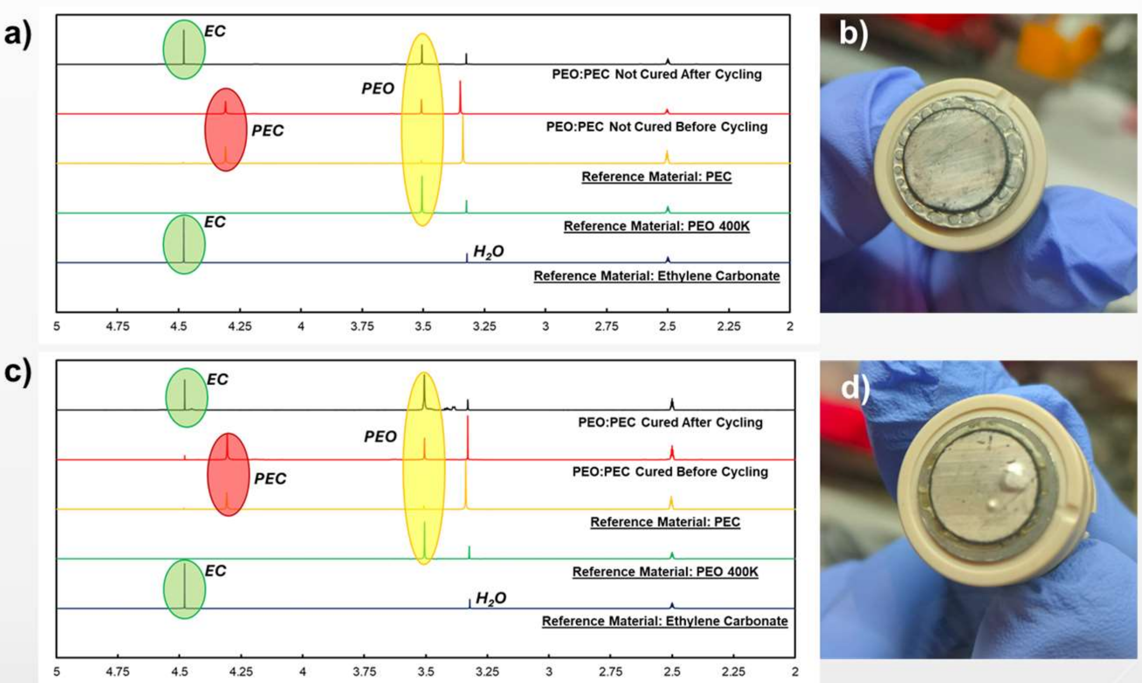
Catholyte electrode provided by Blue Solution with loading of 12 mg cm^{-2}

- The obtained electrolyte shows good electrochemical behaviour in Li-metal cells
- The good coulombic efficiency evidences excellent interfacial stability

Gastaldi et al. / Manuscript in preparation

Polycarbonate blends with PEO by solvent-free extrusion

Evaluation of the electrolyte degradation mechanism



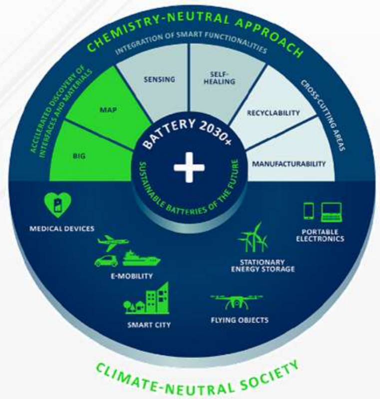
- The increased stability is not associated with reduced degradation of the PEC
- The stability is most likely associated with the improved mechanical stability associated with the cross-linking of the membrane

Gastaldi et al. / Manuscript in preparation

Concluding remarks & perspectives

A holistic approach to next-gen batteries

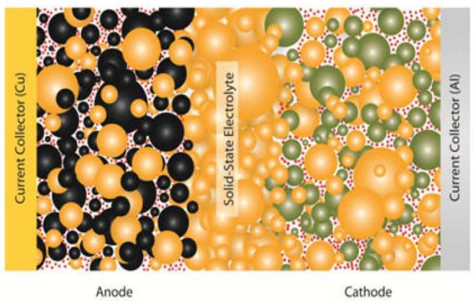
https://battery2030.eu/



…higher capacities @higher rates @lower cost

2020 · 2022 · 2024 · 2030

GEN 4a → All-solid-state Li-ion battery

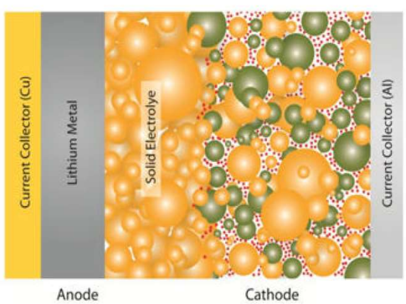


e.g., NMC/Si

<325 Wh kg^{-1}

1000 Wh L^{-1}

GEN 4b → All-solid-state Li metal battery



e.g., NMC/Li

>400 Wh kg^{-1}

>1200 Wh L^{-1}

fast charge rates above 10C

Truly solid polymer and "hybrid" electrolytes amongst most promising solutions

- Understanding **conduction mechanisms**
- Understanding **Li dendrites propagation**
- Assessment of **interfaces** impact
- **Optimisation** of materials/preparation

…improved safety

Acknowledgements

Horizon Europe – PSIONIC

High voltage, room temperature single-ion polymer electrolyte for safer all-solid-state lithium metal batteries (GA 101069703)

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Together
Everyone
Achieves
More

Thank you !

Acknowledgements

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