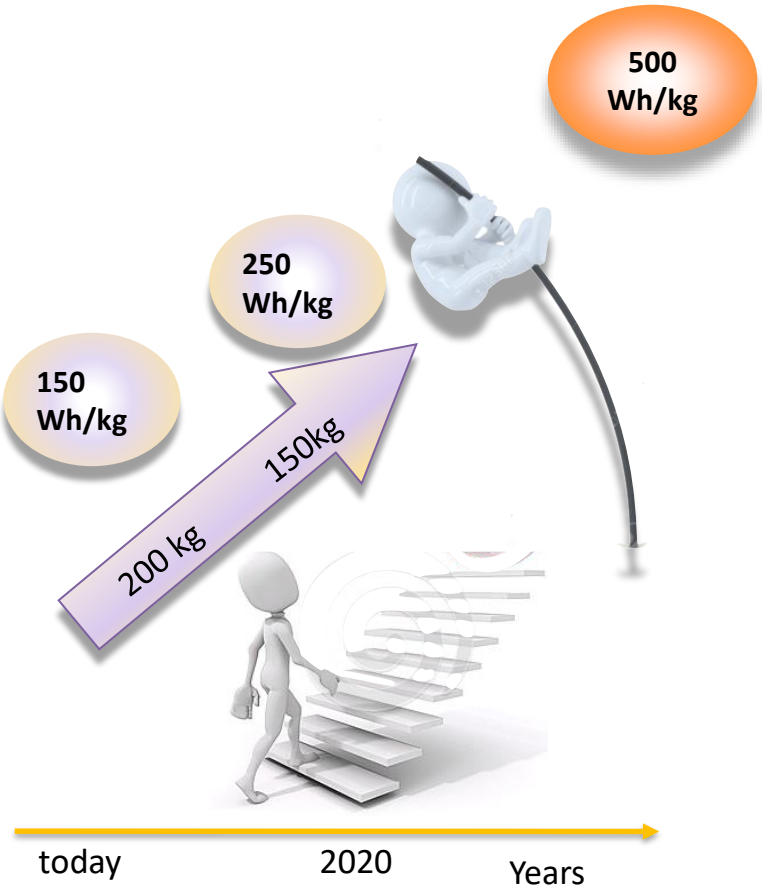
Enabling safe Lithium-metal anodes through composite polymer electrolytes

Julia Amici, Daniele Versaci, Claudia Torchio, Andrea Marchisio, Roberto Colombo, Federico Bella, Carlotta Francia and Silvia Bodoardo

Electrochemistry Group,
Department of Applied Science and Technology – Politecnico di Torino – c.so Duca degli Abruzzi, 24 – 10129 Torino – Italy

Challenges

Around 200 kg of actual Li-ion batteries are needed to reach no more than 200 km per single charge



→ Current Li-ion batteries are approaching the theoretical values;

→ There is still a need to improve the battery technology (fast charging, high voltage materials,…);

→ There is also the need for new technologies with higher theoretical capacity;

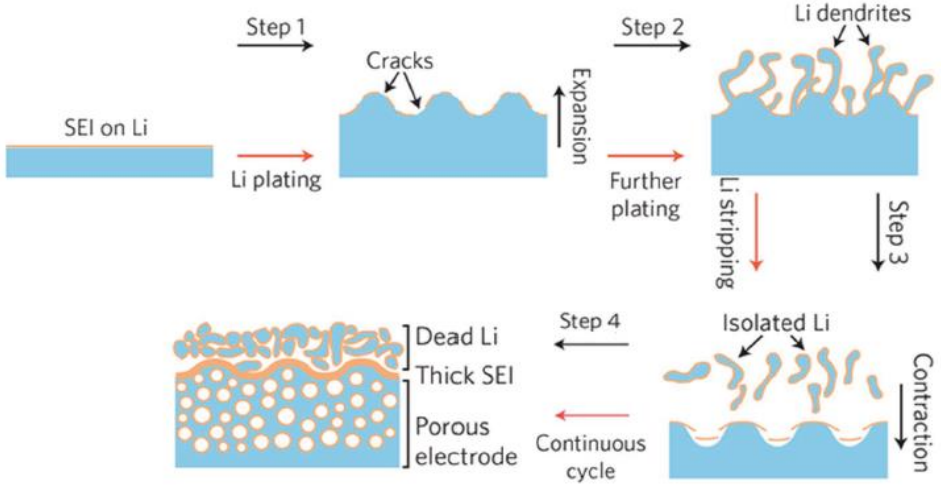
→ Reduction of weight and Increase of energy density is strongly required;

→ Development of inexpensive, thermally stable, long cycling and safe batteries.

Julia Amici
julia.amici@polito.it

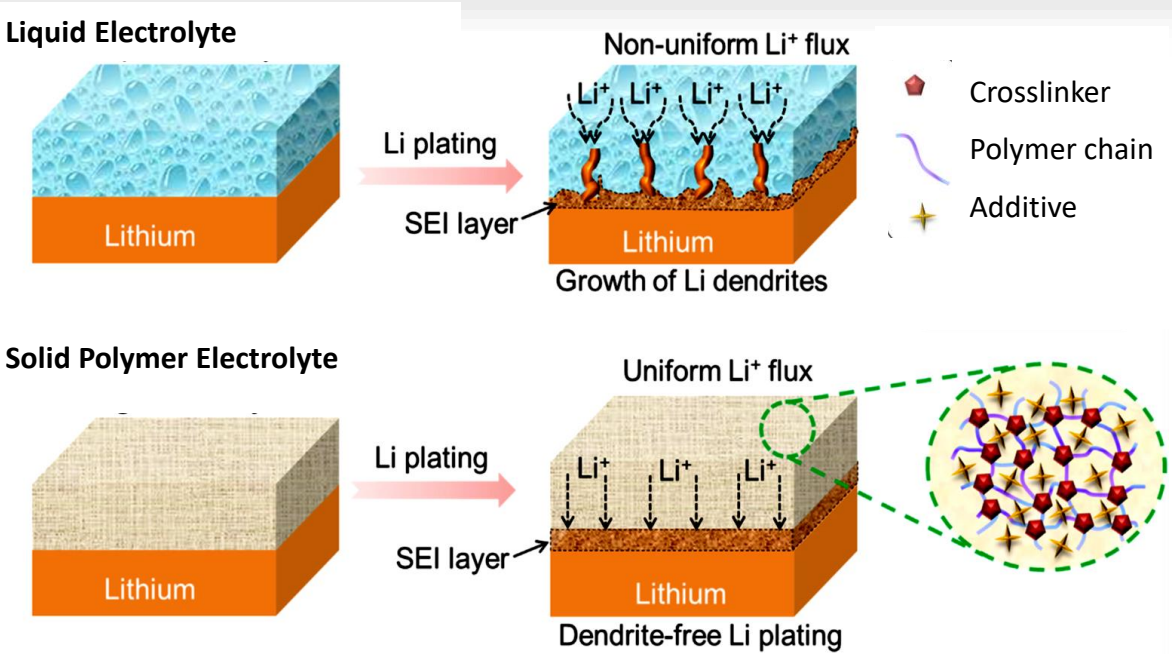
Metallic Li

- ☺ High specific capacity of 3860 mA h g^{-1} and low potential of −3.040 V versus standard hydrogen electrode (SHE).
- ☹ Very high reactivity:
  - ➢ Formation of dendrite -> short circuit
  - ➢ Dendrite breaking -> dead lithium
  - ➢ Continuous SEI formation -> electrolyte consumption



Julia Amici
julia.amici@polito.it

Composite Polymer Electrolyte



T. Chen et al., Nano Energy, 2018, 54, 17–25

Various additives can be used to enhance **ionic conductivities**:

→ Lithium salts

→ Conventional liquid electrolytes (swelling)

→ Ionic liquids

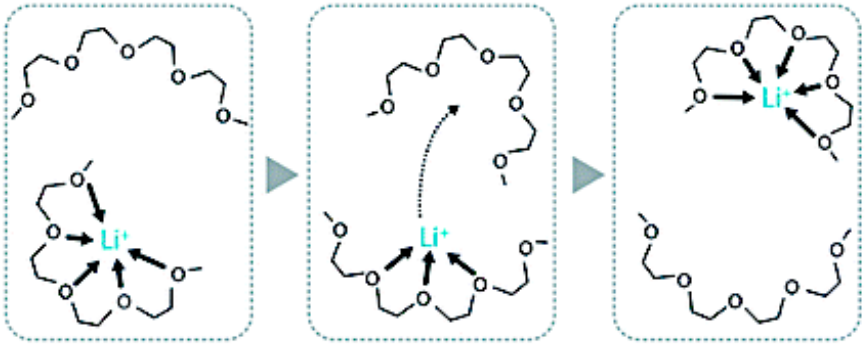
Various additives can be used to enhance **mechanical properties and/or for additional properties**:

→ Inorganic fillers, ceramic materials, nanosponges,…

Julia Amici
julia.amici@polito.it

Composite Polymer Electrolyte

How does it work?

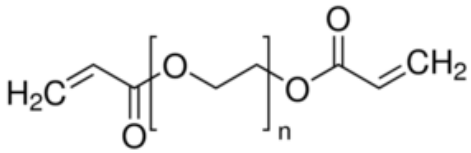


Schematic drawing of Li^+ transport assisted by the segmental motion of the polymeric chains.

Alberto Varzi, Rinaldo Raccichini, Stefano Passerini, Bruno Scrosati, J. Mater. Chem. A, 2016, 4, 17251-17259

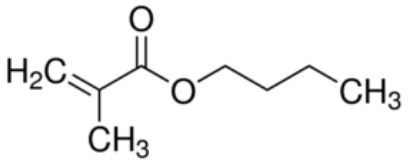
Choice of chemicals

PEGDA 575 (Cross-linking agent)



→ ether-bond-rich cross-linking agent
→ good compatibility with ether-based liquid electrolyte
→ the long chain of –C-O-C- → quick and efficient Li^+ transportation (chain segmental motion)

Butyl Methacrylate



→ good compatibility with ether-based liquid electrolyte
→ C=O functional group

Additive

Julia Amici
julia.amici@polito.it

Synthesis

Technique:

→ thermo-initiated radical polymerization: (to incorpore high amounts of inorganic additives without interference)

→ solvent-free (more environmental friendly, avoid traces of solvents inside the cell)

- Buthyl methacrylate (monomer) + Benzoyl peroxide (thermo-initiator) + Polyethylene glycol diacrylate (Crosslinker) + eventual additive
- 3 different heating steps : 30 min @ 80°C, 20h @ 45°C and 2h @ 100°C
- Carried out in controlled atmosphere (O_2<0,5ppm) to avoid oxygen inhibition
- Preparation of a precursor solution then casted on glass slide

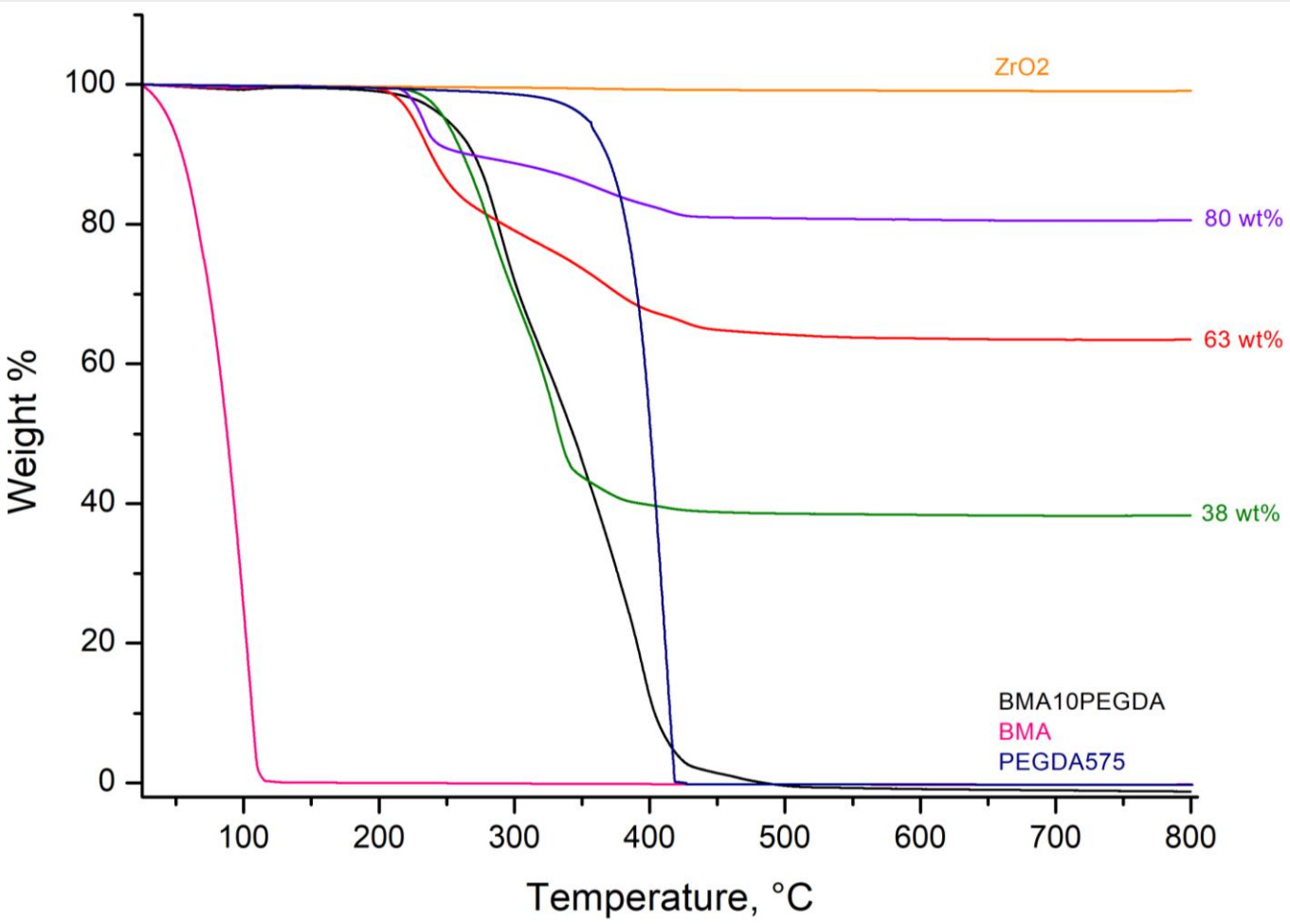
Julia Amici
julia.amici@polito.it

First Example

- Application: metallic Li-ion cells
- Additive: commercial monoclinic ZrO_2 nanoparticles
- Scope : enhance mechanical properties to allow smoother Li plating and stripping

Julia Amici
julia.amici@polito.it

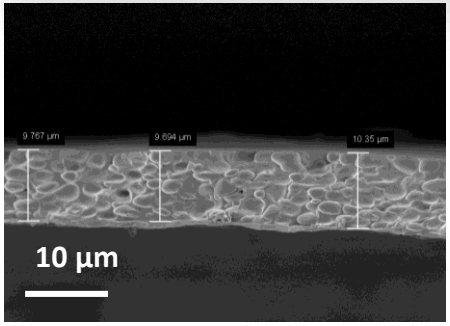
Characterization

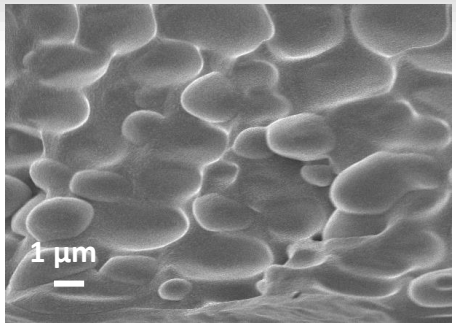


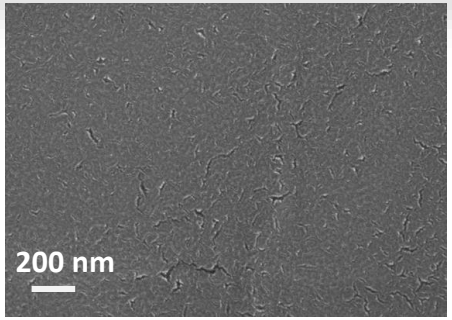
TGA: from 25 to 800 °C, 10 °C/min, in air

Julia Amici
julia.amici@polito.it

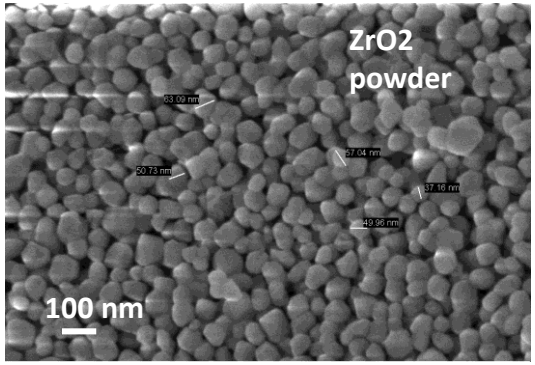
Characterization



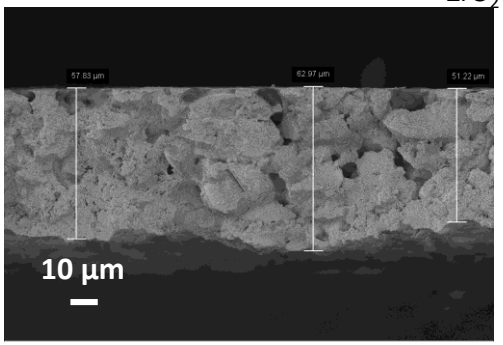


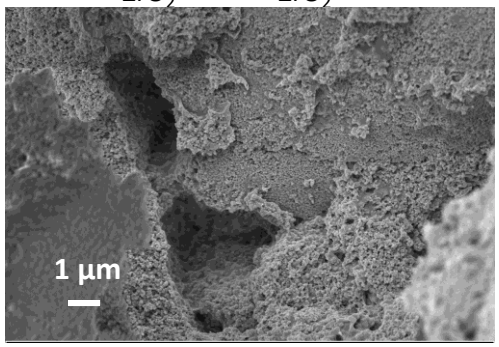


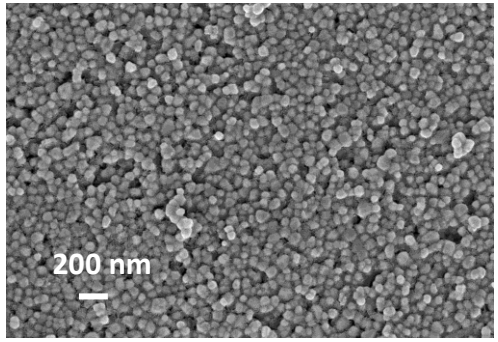
FESEM



No additive | 38 wt% ZrO_2 | 63 wt% ZrO_2 | 80 wt% ZrO_2

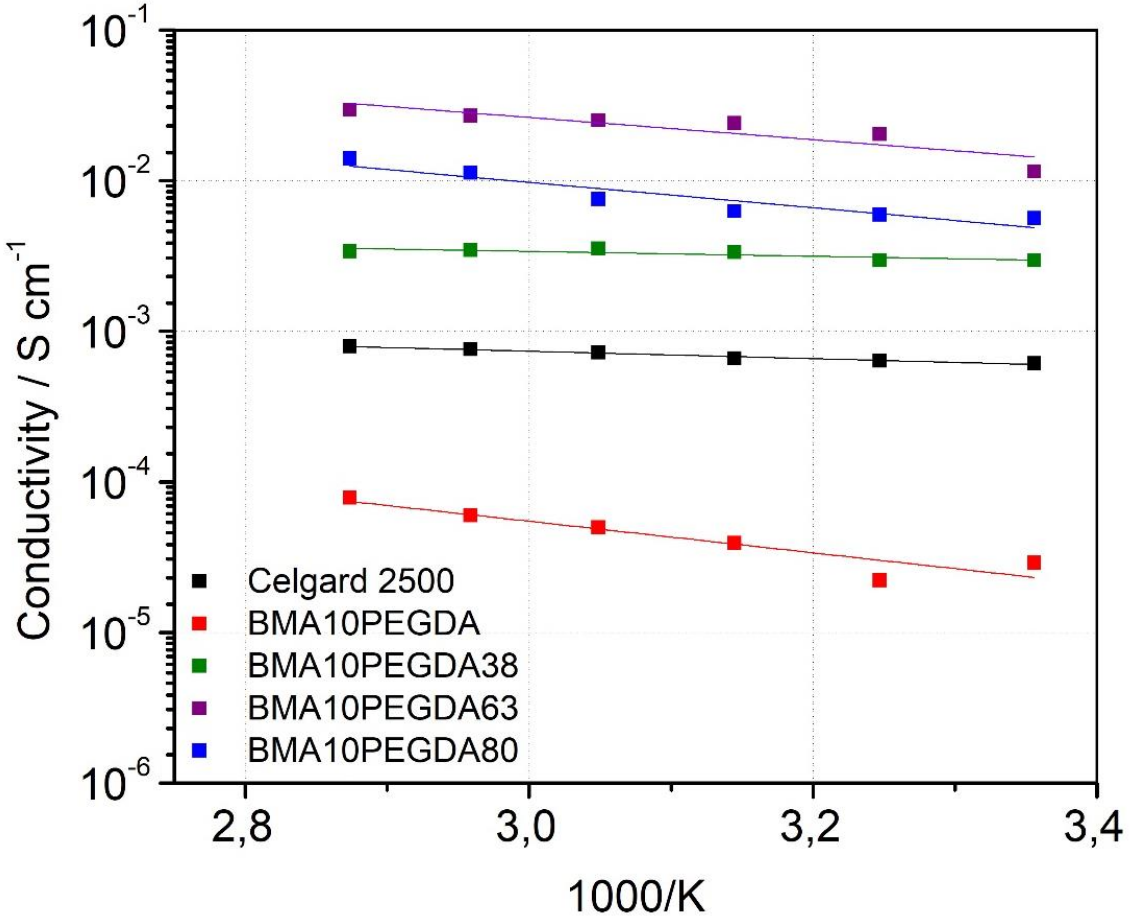






Julia Amici
julia.amici@polito.it

Characterization



→ By EIS measurements (between 100 kHz and 1 Hz at OCV);

→ On SS/CGPE/SS symmetrical cells;

→ Between 25 and 70 °C;

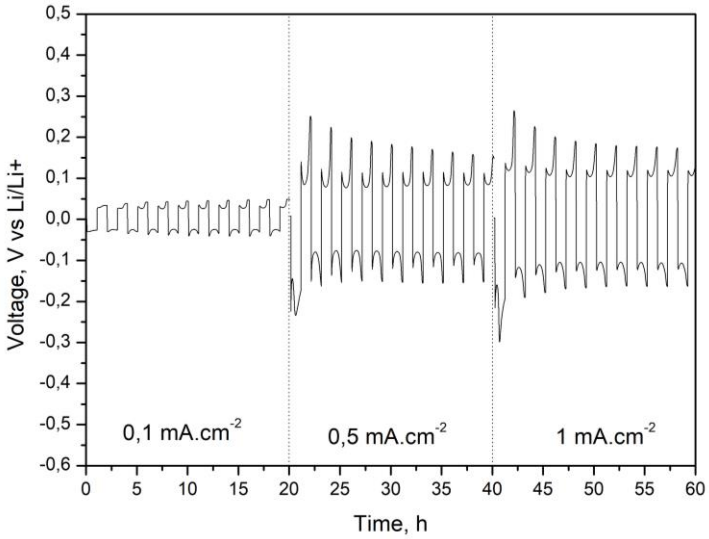
→The ionic conductivity was calculated at each temperature following the equation:

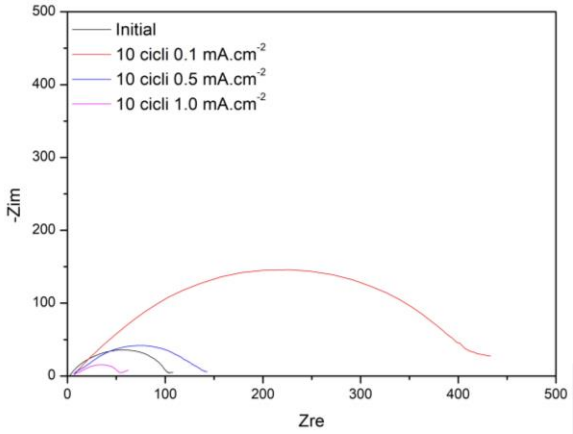
$\sigma = (l/A)\ (1/R_{\Omega})$

where l is the membrane thickness, A is the membrane surface area and R_{Ω} is the resistance value at the high-frequency intercept

Julia Amici
julia.amici@polito.it

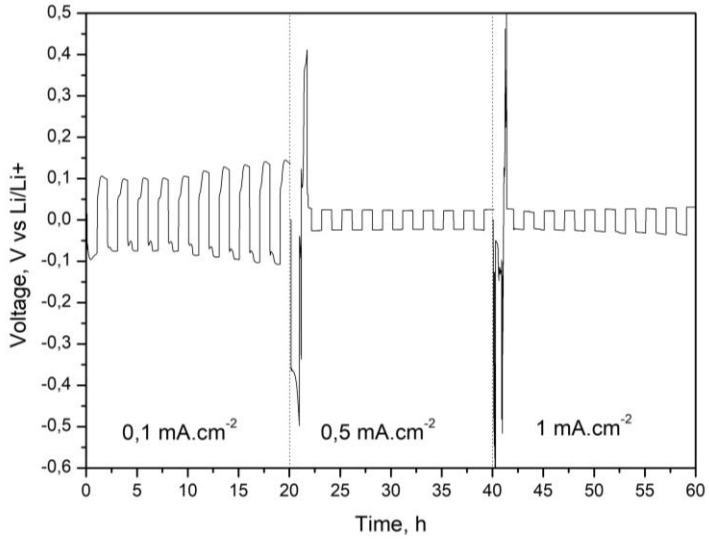
Li Plating/Stripping

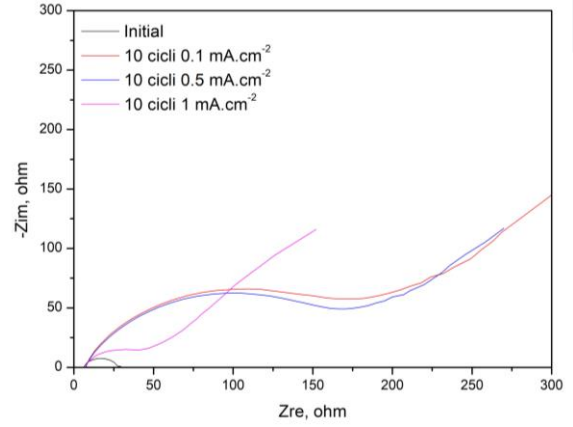




Standard

Li Plating /Stripping:
Li/CGPE/Li cells
Current density: 0.1 mA.cm^{-2}
Discharge capacity: 0.1 mAh.cm^{-2}

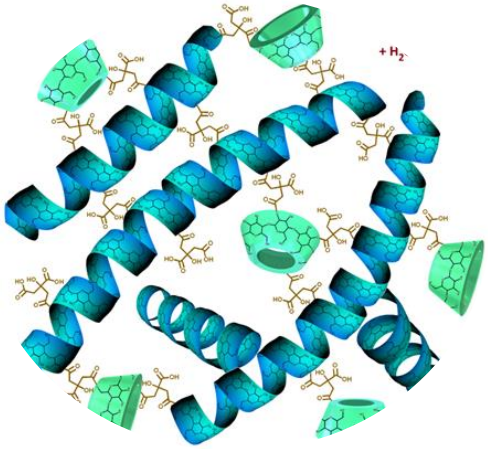




CGPE with 63 wt% ZrO_2

Julia Amici
julia.amici@polito.it

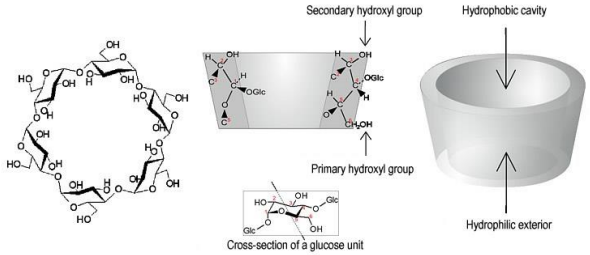
Second Example



- Application: Li-O_2 cells

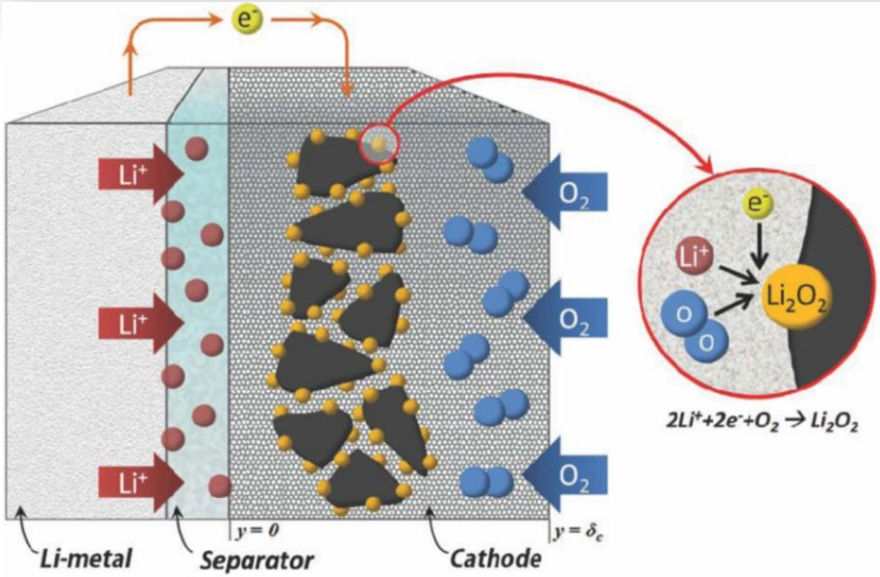
- Additive: dextrin-based nanosponges

- Scope : limit O_2 cross-over and consequent Li oxidation



Julia Amici
julia.amici@polito.it

Challenges



Yun Wang and Sung Chan Cho, J. Electrochem. Soc. 2013 volume 160, issue 10, A1847-A1855

ORR:

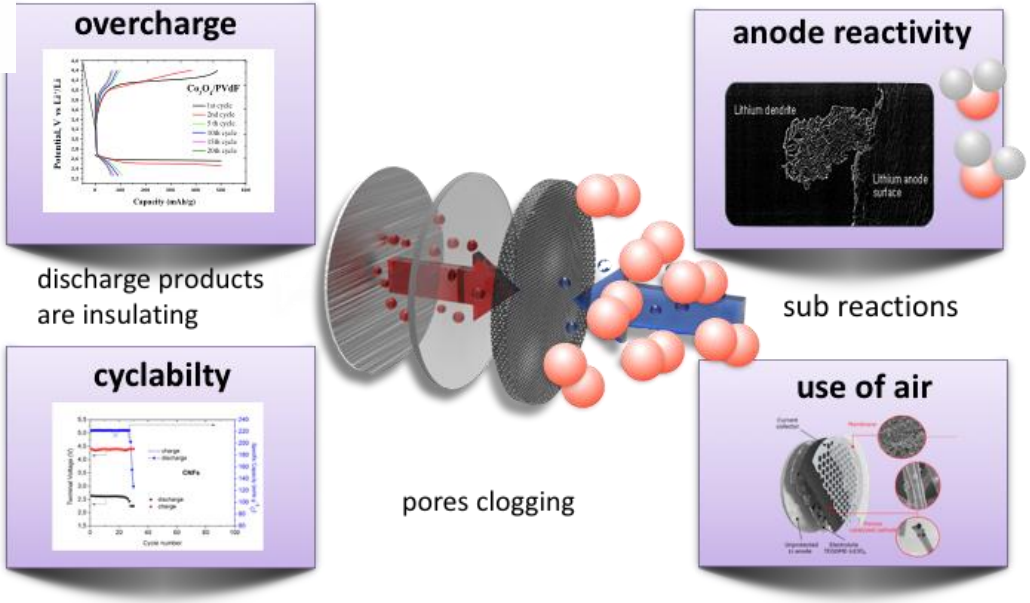
$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- + Li^+ \rightarrow LiO_2$$

$$LiO_2 \rightarrow Li_2O_2 + O_2$$

OER:

$$Li_2O_2 \rightarrow 2Li^+ + O_2 + e^-$$

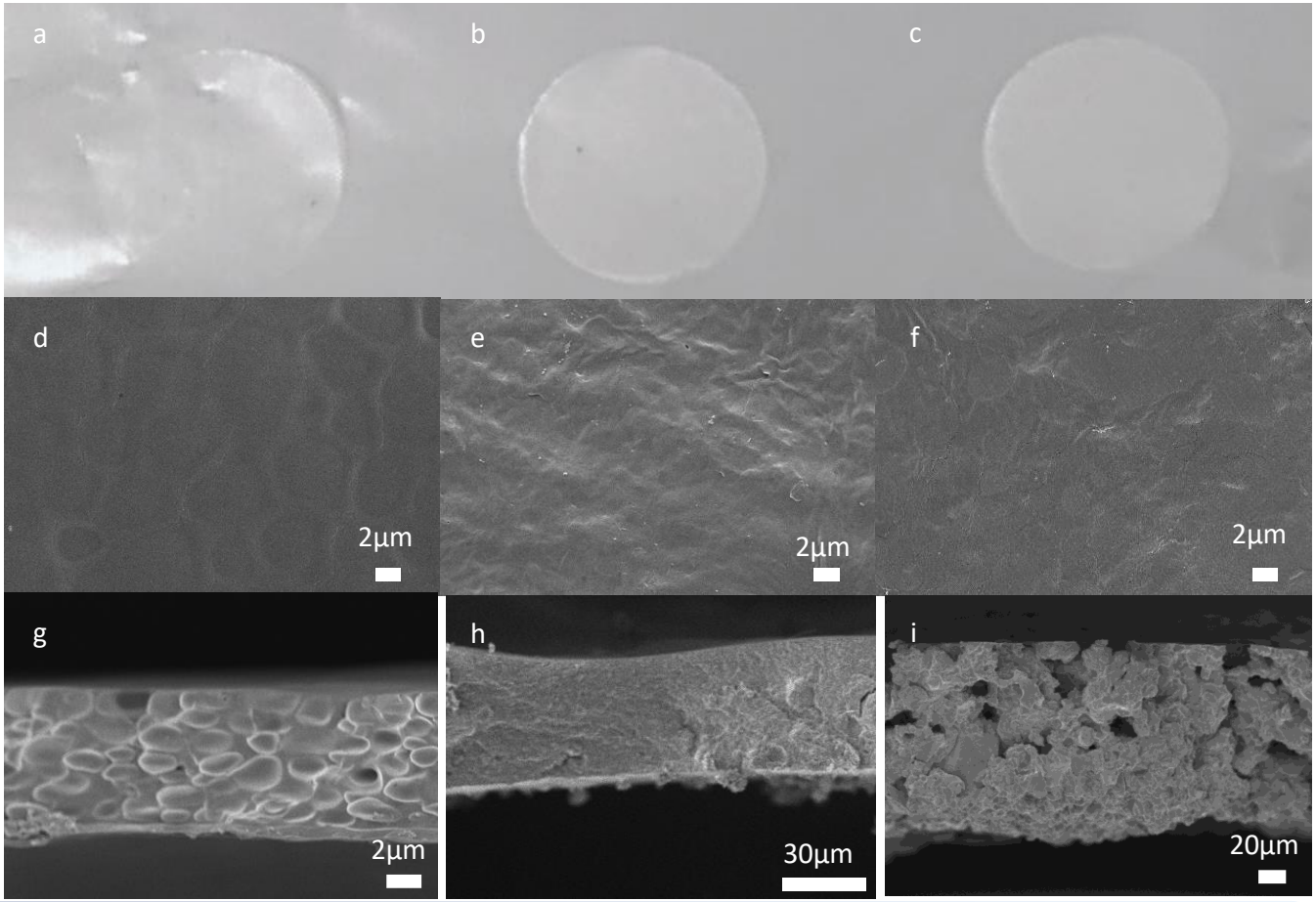


Julia Amici
julia.amici@polito.it

Characterization

FESEM

BMA10PEGDA (0%wt)	BMA10PEGDA5NS (5%wt)	BMA10PEGDA10NS (10%wt)

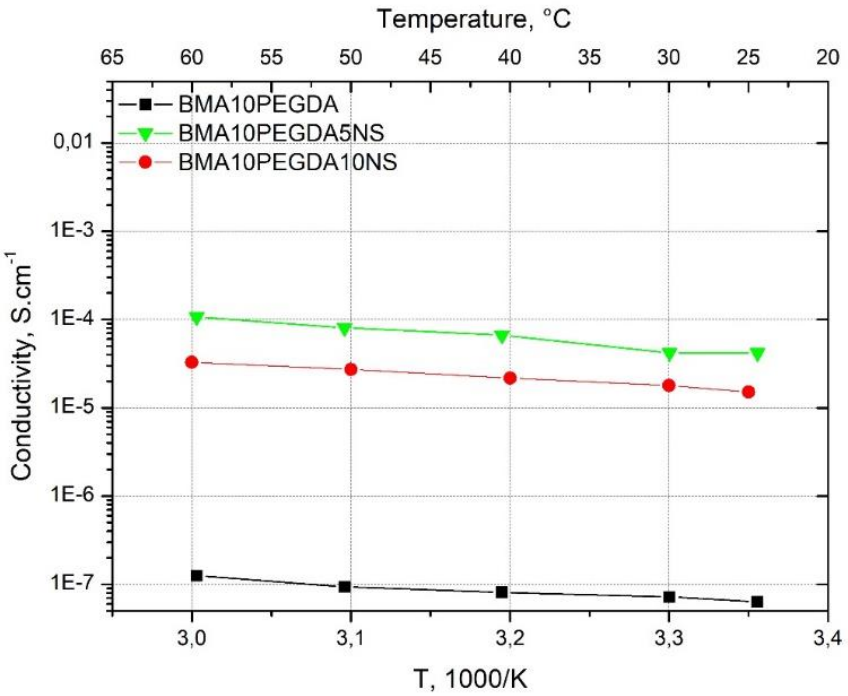


Julia Amici
julia.amici@polito.it

Characterization

Liquid Electrolyte Uptake

BMA10PEGDA	BMA10PEGDA5NS	BMA10PEGDA10NS
40%	110%	100%



→ By EIS measurements (between 100 kHz and 1 Hz at OCV);

→ On SS/CGPE/SS symmetrical cells;

→ Between 25 and 70 °C;

→The ionic conductivity was calculated at each temperature following the equation:

$\sigma = (l/A)\,(1/R_{\Omega})$

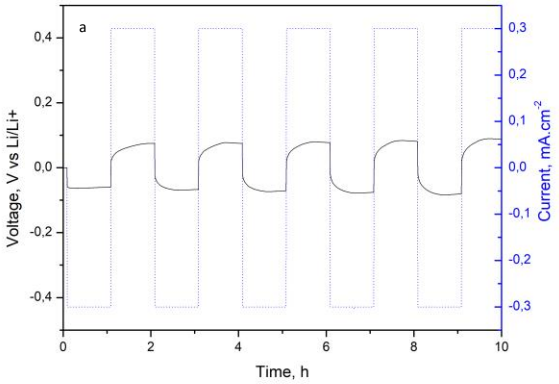
where l is the membrane thickness, A is the membrane surface area and R_{Ω} is the resistance value at the high-frequency intercept

Tipologia membrana	KP [Barrer]	KP [g/(m²*24h)]
BMA10PEGDA+DMSO	0,030	5,99
BMA10PEGDA5NS+DMSO	0,006	1,02

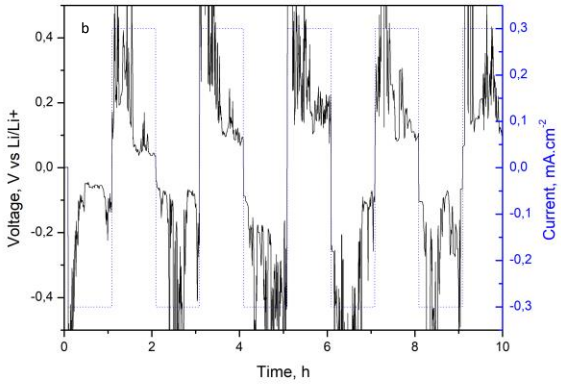
Julia Amici
julia.amici@polito.it

Li Plating/Stripping

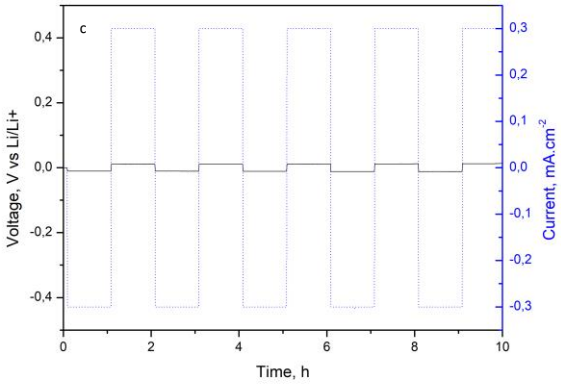
Li Plating /Stripping:
Li/CGPE/Li cells
Current density: 0.3 $mA.cm^{-2}$
Discharge capacity: 0.3 $mAh.cm^{-2}$



STANDARD



BMA10PEGDA



BMA10PEGDA5NS

Julia Amici
julia.amici@polito.it

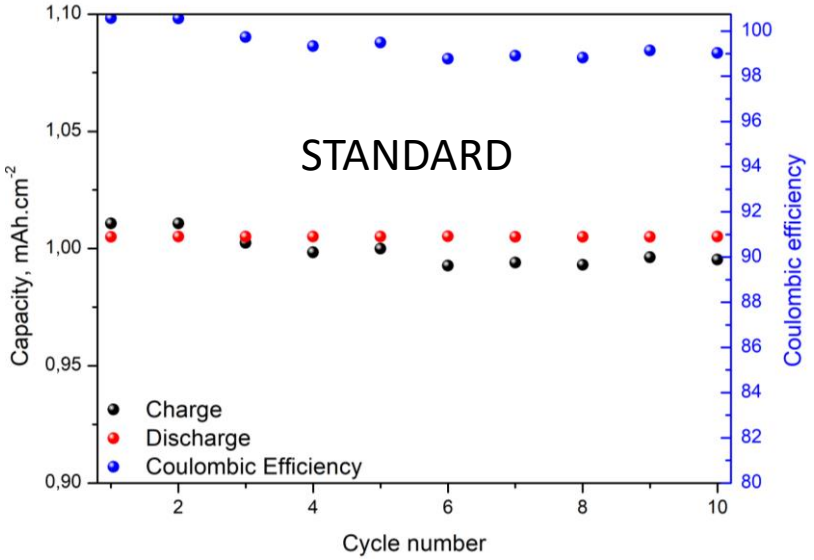
Cycling

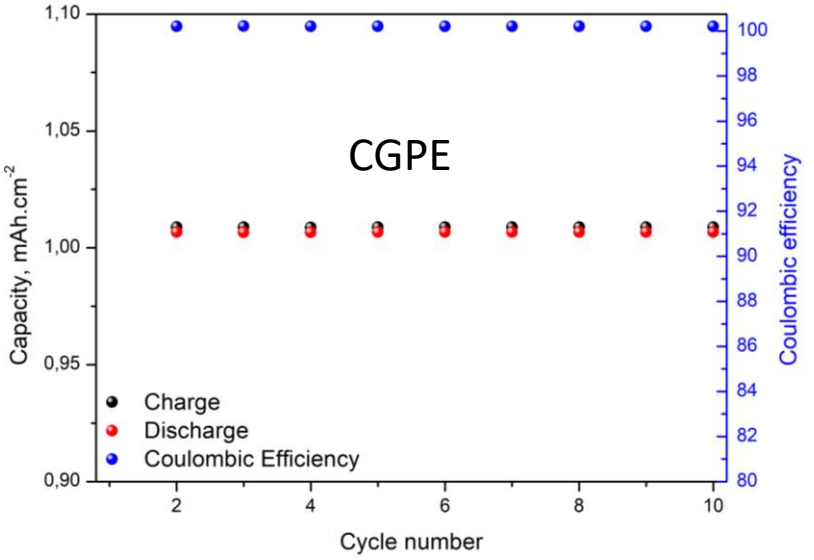
- Air cathode: Commercial Gas Diffusion Layer (Sigraget: GDL-24BC).
- Electrolyte: 0.5 M LiTFSI in DMSO over glass fiber separator (STANDARD) or CGPE.
- Anode: metallic lithium foil (0.2 mm thick, Chemetall).

→ In EL-Cell:

- Applied current density: 0.025 mA / cm^2,
- Voltage cutoff interval: 2.25-4.4V,
- Time cutoff interval: 40h discharge, 40h charge.
- O_2 flow 3 ml / min.

→ Cells rested 6h at OCV prior to measurement.





Julia Amici
julia.amici@polito.it

Conclusions

Technology:	Metallic Li-ion	Li-Air
Issue:	Metallic Lithium reactivity	

- ✓ Methacrylate based thermally cured electrolyte
- ✓ Liquid electrolyte uptake
- ✓ High amounts of ZrO_2 incorporation to block dendrites formation
- ✓ Very stabilizing effects on Li plating and stripping process

- ✓ Methacrylate based thermally cured electrolyte
- ✓ Nanosponge incorporation blocking O_2 cross-over
- ✓ Encouraging results in cell

Preparation and characterization of a new versatile polymer matrix allowing:

- the addition of a wide range of organic and inorganic additives up to really high ratio.
- eventual activation with small amount of liquid electrolyte (outstanding room-temperature conductivities).

→ Safer metallic Li cells for a wide range of technology

Julia Amici
julia.amici@polito.it

The Electrochemistry Group

Julia Amici
julia.amici@polito.it

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Julia Amici
julia.amici@polito.it