

Hybrid polymer/ceramic membranes: Towards a new concept of electrolytic separator for all-solid-state Li metal batteries

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LMP® (since 2011)



Use of **Li metal** as negative electrode

Easy **roll-to-roll** fabrication process

Low cost & eco-friendly



Solid Polymer Electrolyte made of **PEO** and **Li salt**

- high operating T° (80°C)

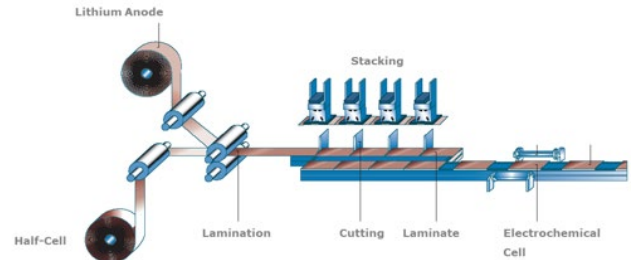
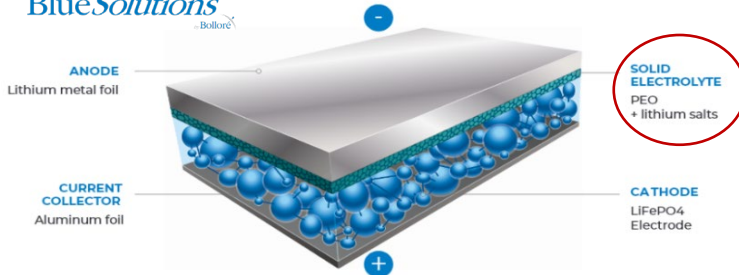
- use of **low potential positive** (LiFePO_4)

Next-gen solid electrolytes

- Operating at **ambient temperature**
- High voltage positive electrode ($>4\text{V vs. Li}^\circ$)

= **HIGH ENERGY DENSITY**

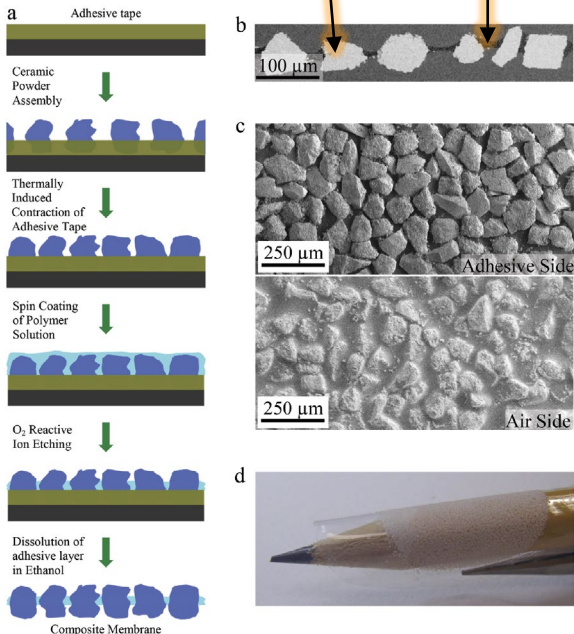
Blue Solutions
Bolloré



Assembly line of components (roll-to-roll)



Elaboration
multistep & complicated...

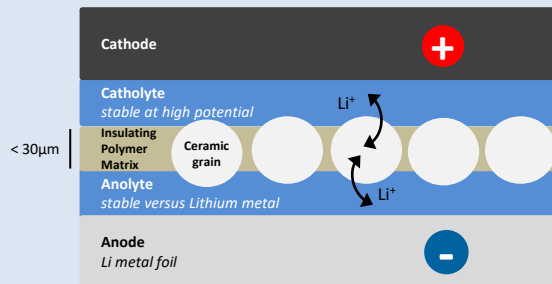


[1] Aetukuri, N. B. *et al.* Flexible Ion-Conducting Composite Membranes for Lithium Batteries. *Adv. Energy Mater.* **5**, 1–6 (2015)

[2] Aetukuri, N.B. *et al.* *ACS Appl. Energy Mater.* **3**, 12709–12715 (2020)

This PhD work

To elaborate this ceramic-based membrane thanks to a **one-step, dry & scalable process = EXTRUSION**



1/ Study the elaboration process of the composite material

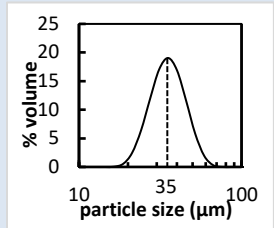
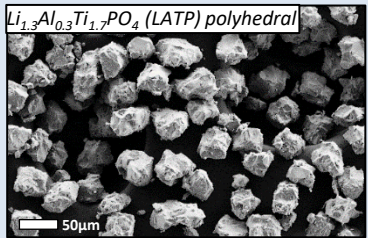
→ We need homogeneous and impermeable membranes

2/ Electrochemical study of interfaces between layers

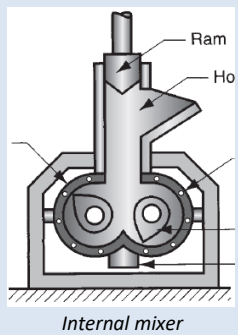
→ Optimization of the catholyte and the anolyte separately thanks to Electrochemical Impedance Spectroscopy (EIS)

Lab scale elaboration process of composite membranes

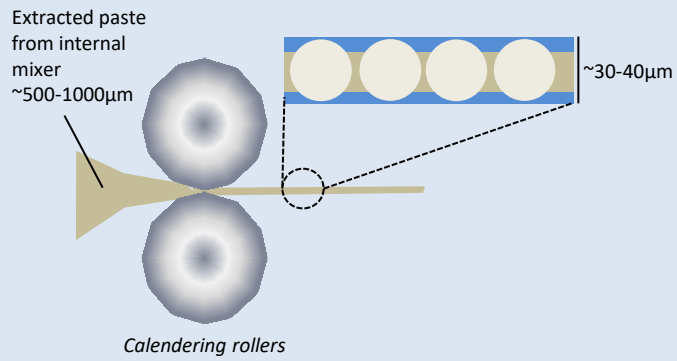
1 Internal blending at 130°C



- LATP particles**
- Monocrystalline grains**
- Narrow PSD thanks to sieving**
(diameter ~35µm +/- 15µm)
- Poly(ethylene) matrix**
industrial grade
- Extrudable**
- Insoluble** in solvent

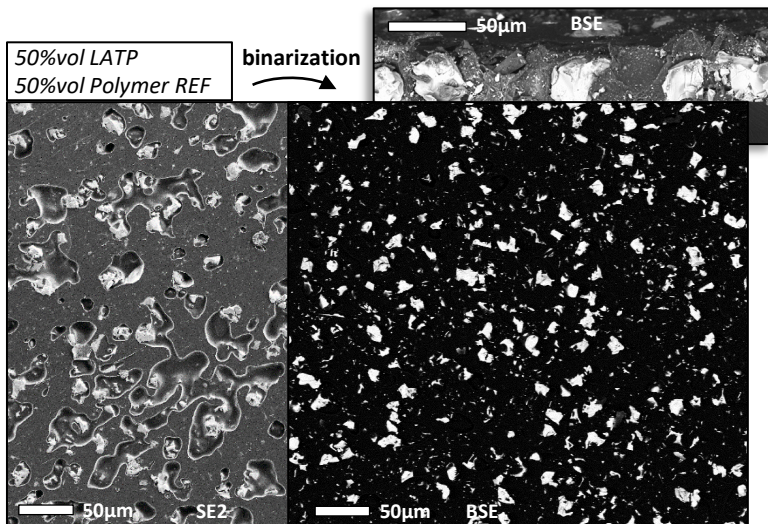


2 Calendering



- Optimization of the calendering parameters to produce a thin membrane with controlled characteristics
- Impermeability to solvent
 - Thickness
 - Fraction of apparent surface

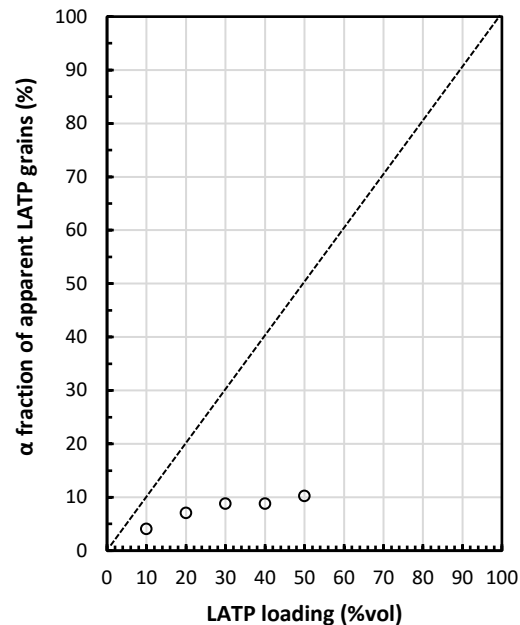
Morphology of the composite membrane



2/ Apparent surface fraction α of LTP grains $S_{mbn} = \alpha S_{tot}$

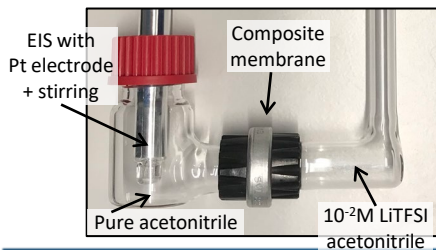
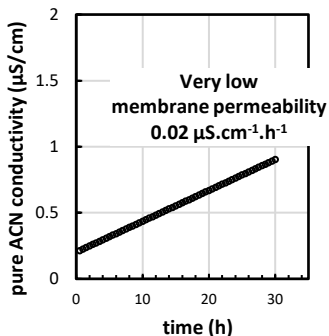
→ α is not proportional to LTP loading (%vol)

α fraction of apparent surface vs. LTP loading (from BSE image binarization)



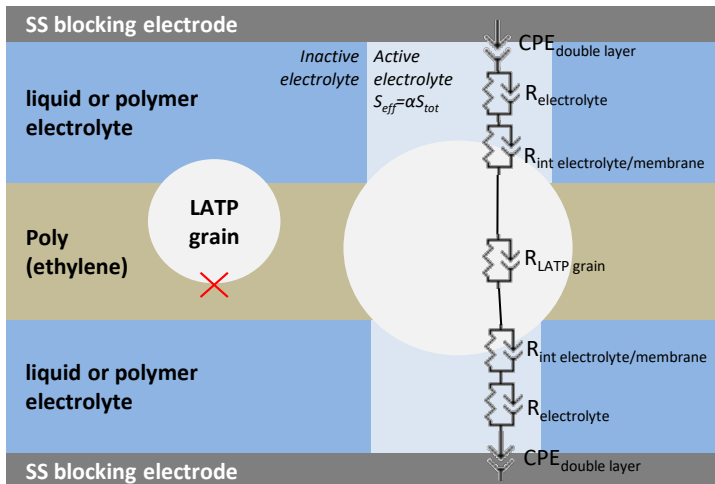
1/ Surface roughness (air bubbles trapped)

→ impermeable to liquid electrolyte?

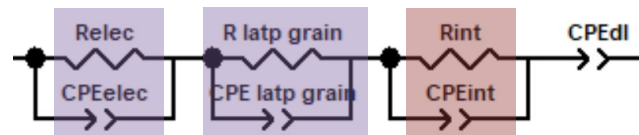


Ionic charge transport and transfer through a multilayer system

Scheme of the Li^+ percolating pathway through the multilayer



Equivalent Circuit Model (ECM)



High frequencies \leftrightarrow ionic bulk conduction

Middle frequencies \leftrightarrow ionic charge transfer

$$R_{tot} = (2 * R_{elec} + R_{LAMP\ grain}) + R_{int}$$

How to study such electrolytic system thanks to EIS?

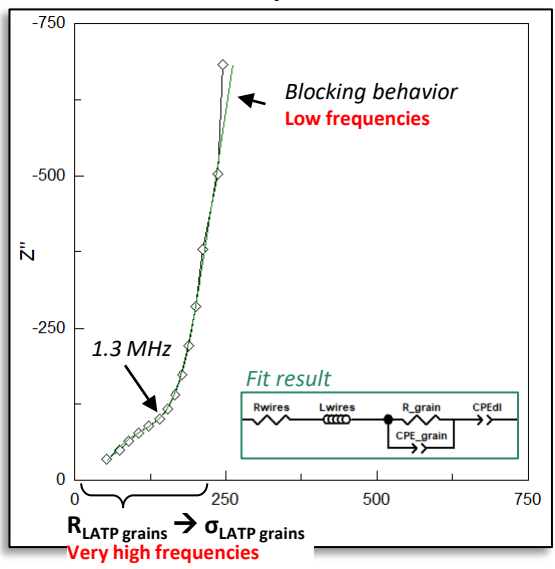
- Study of **intrinsic conduction properties** of each layer
 - R_{elec} (easy to do)
 - $R_{LAMP\ grain}$ (tricky to do)
- Study the **charge transfer resistance** $R_{int\ elec/mbn}$ in multilayer systems
 → Which parameters drives R_{int} ?

Membrane conductivity $R_{LATP\ grains}$

Conventional methods **DOESN'T WORK** (gold coating, Cu or SS electrode)...

- We developed our own **flexible composite blocking electrode** made of
- **Ketjen Black (carbon)** for e^- conduction
 - **Poly(ethylene)** for flexibility

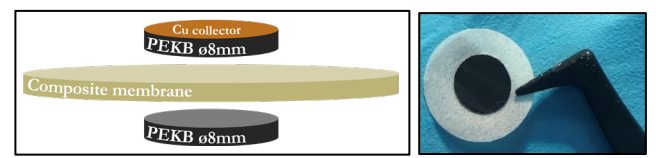
Impedance spectra of a 50%vol LATP-based membrane at $-40^\circ C$ from 7MHz to 80kHz



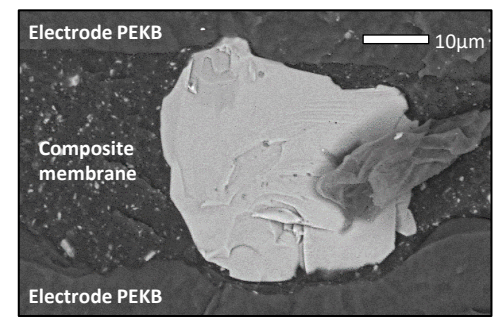
PE / KB (10%vol) coated on Cu current collector



Symmetrical setup PEKB/mbn/PEKB in coin cell

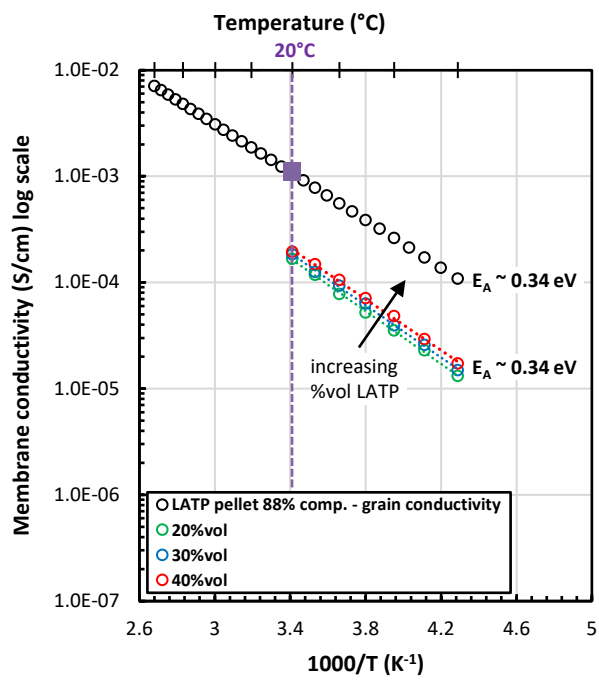


Coin cell cross-section (SEM, BSE) → good contacts



Membrane conductivity $R_{LATP\ grains}$

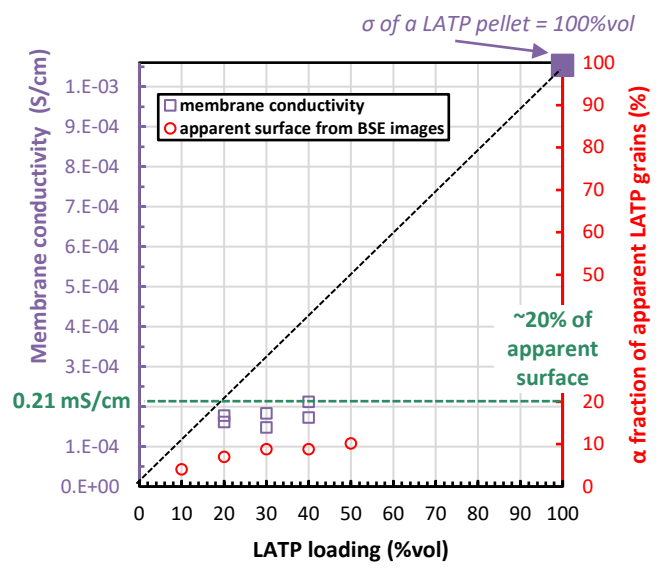
Ionic conductivity of membranes as a function of T^o



- E_A are in good agreement with LTP [3]

[3] Cretnin, M. & Fabry, P., J. Eur. Ceram. Soc. 19, 2931-2940 (1999).

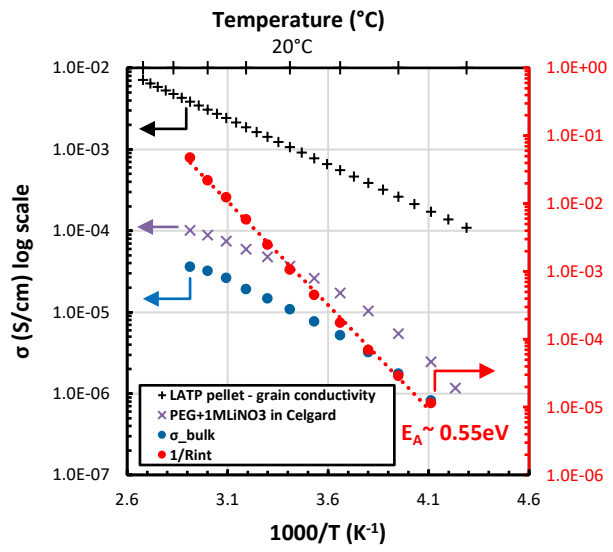
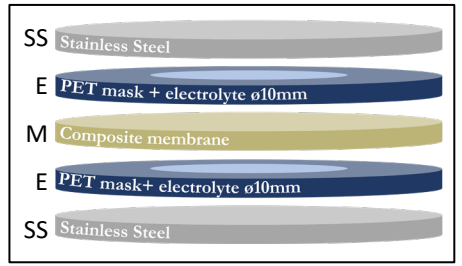
$\sigma_{LTP\ grains}$ at 20^oC
 compared to **α fraction of apparent LTP grains**
 as function of the LTP loading (%vol)



- $\sigma_{LTP\ grains}$ is **not proportional** to the ceramic loading (%vol)
- $\sigma_{LTP\ grains}$ is **well correlated** to SEM binarized images

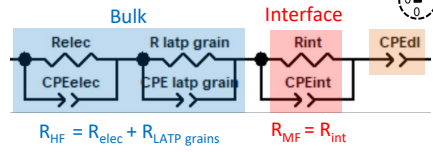
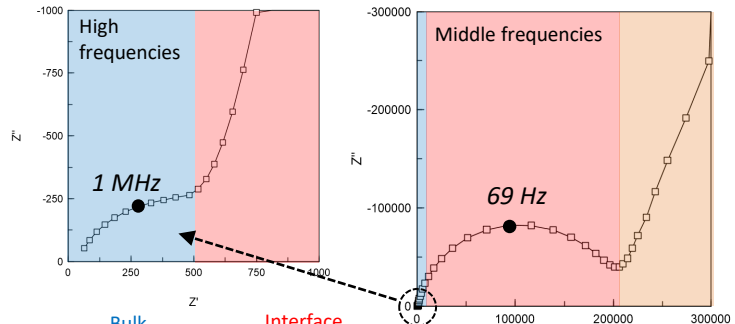
Charge transfer resistance $R_{int\ elec/mbn}$

SS/multilayer/SS (SSEMESS) setup in coin cell



Charge transfer resistance (1/Ω.cm²)

Impedance spectra at 20°C from 7MHz to 100mHz
 M = LATP 40%vol / PE ref
 E = PEGDME + 1M LiNO₃ in Celgard separator



- σ_{bulk} has a VTF behavior similar to σ_{elec}

Because the LATP has a much higher conductivity than the liquid elec

- $\alpha = \frac{\sigma_{bulk}}{\sigma_{elec}} = 20-30\%$ for a 40%vol LATP loading

- R_{MF} has a consistent activation energy for charge transfer [4][5]

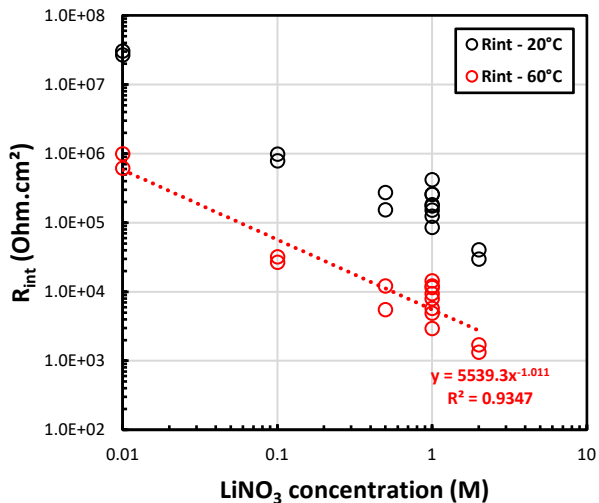
→ What are the determining parameters of R_{int} ?

Charge transfer resistance R_{int} – Tips for improvement

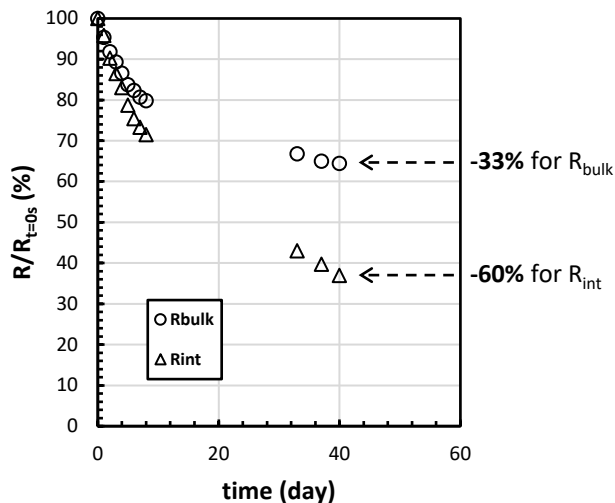
R_{int} as a function of $LiNO_3$ concentration at 20°C and 60°C

$M = LAMP\ 40\%vol / PE\ ref$

$E = PEGDME + xM\ LiNO_3$ in Celgard separator



Evolution of R_{bulk} and R_{int} with time after thermal treatment at 40°C



- Increase the **concentration of Li salt** [5]
- Change the **nature of the salt and solvent** [5] → best $R_{int} \sim 10^4\ Ohm.cm^2$ at 40°C
- **Thermal treatment** → stabilization of the electrolyte / LAMP grains interface
- **Chemical treatment** of the interface → reduce E_A

Conclusion

- Elaboration of composite poly(ethylene)/LATP membranes
 - ✓ Scalable, one step, low-cost and eco-friendly **extrusion process**
 - ✓ Thin membranes **~30 μm**
 - ✓ Membranes are impermeable, non soluble & has good mechanical properties
 - ✓ High ionic conductivity **2.10⁻⁴ S/cm** at 20°C and **t⁺ = 1**
- **R_{int} is the limiting factor** of the total resistance in multilayer systems → BUT it can be **improved**

Perspectives

- Reduce the composite membrane thickness to **~15 μm**
- Li/Li symmetrical cell + Li metal battery cycling
 - ✓ study of dendritic growth
 - ✓ effective t⁺ in multilayer systems

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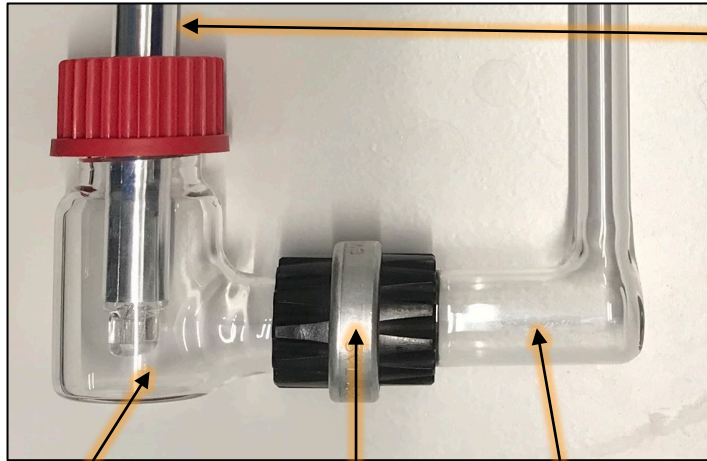
Université de Grenoble Alpes, Massif de Belledonne

Thank you.



No pinhole within the membrane ? → Permeability cell

Permeability cell setup at 20°C in dry room



2 Pt electrodes for each compartment

Recording impedance of each solutions over time

Compartment 1

10^{-2} M LiTFSI + Acetonitrile
at $t = 0$ s

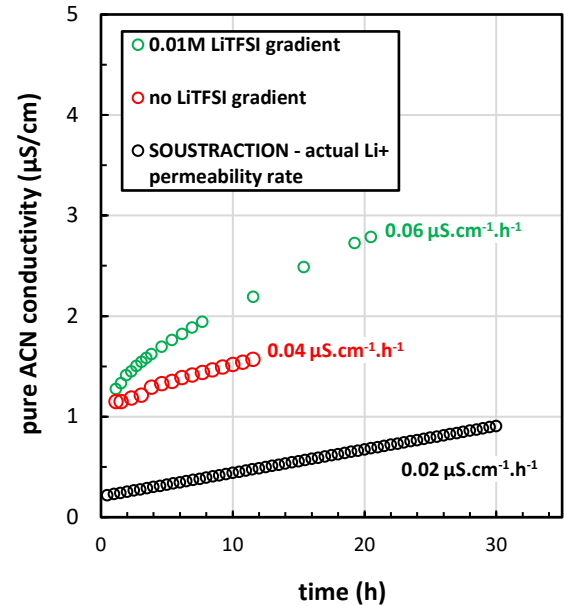
Magnetic stirring

Compartment 2

Pure Acetonitrile at $t = 0$ s
Magnetic stirring

Junction

$\varnothing 22$ mm composite membrane



Li salt	Solvent <i>anolyte/catholyte</i>	R_{int} at 40°C (Ohm.cm ²)
LiNO ₃ 2M	PEGDME 240g/mol	6.10 ³
	TEGDME	1.10 ⁴
LiTFSI 2M	PEGDME 240g/mol	1.10 ⁶
	PC	1.10 ⁵
	LP30	1.10 ³