Multifunctional polyelectrolyte-based coatings with high gas barrier properties

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Department of Applied Science & Technology

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- 53 technical & administrative staff
- 275 PhDs, post-docs & grant researchers

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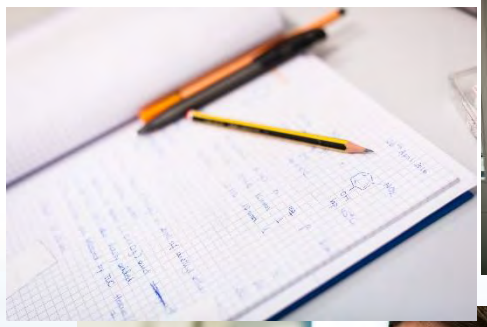
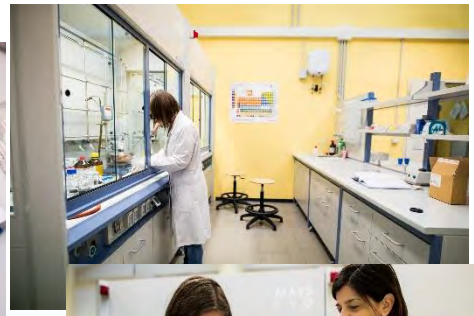
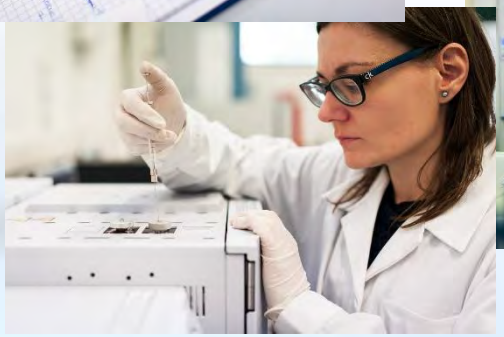
- **PROCESS ENGINEERING**
- **CONDENSED MATTER PHYSICS**
- **PARTICLE PHYSICS AND THEORETICAL PHYSICS**
- **ENERGY, ENVIRONMENT AND SAFETY ENGINEERING**
- **FOOD ENGINEERING**
- **….**

CHemistry and Science of Polymers and Composites

Team @Alessandria site

Chemistry



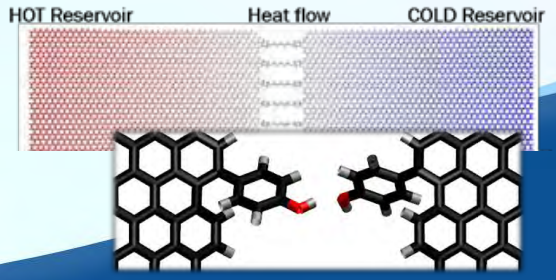
Properties

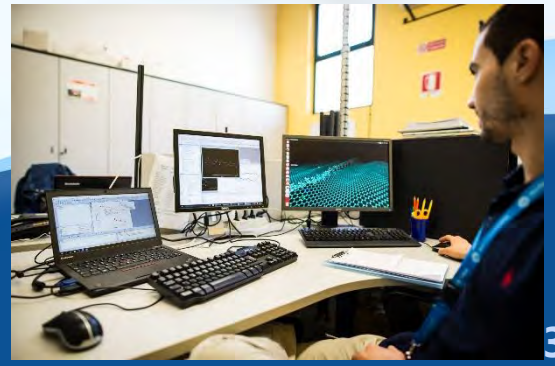




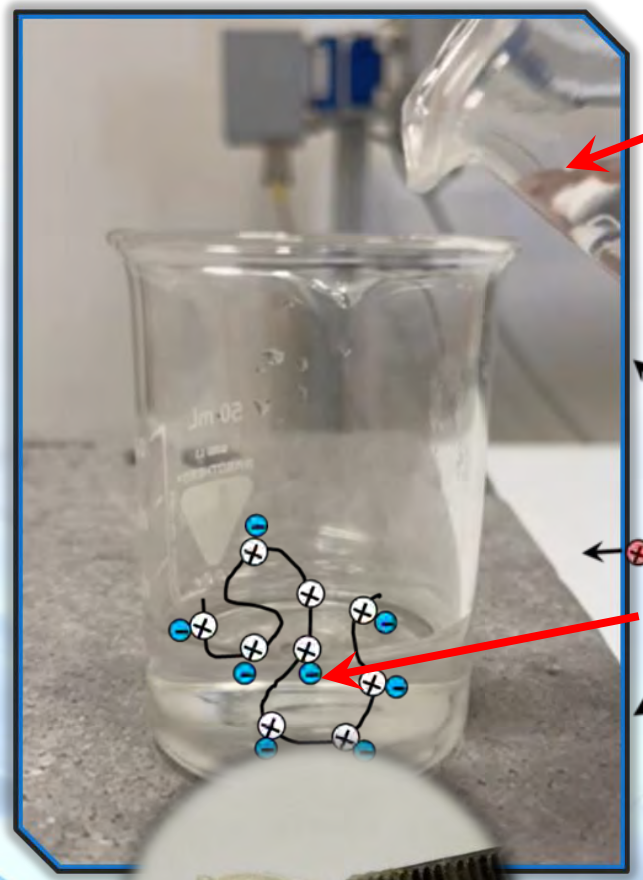

Processing

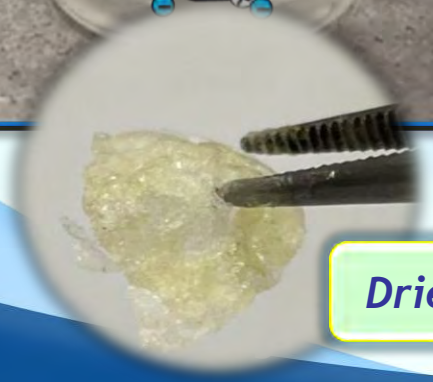

Modelling





Polyelectrolyte complexes - PECs

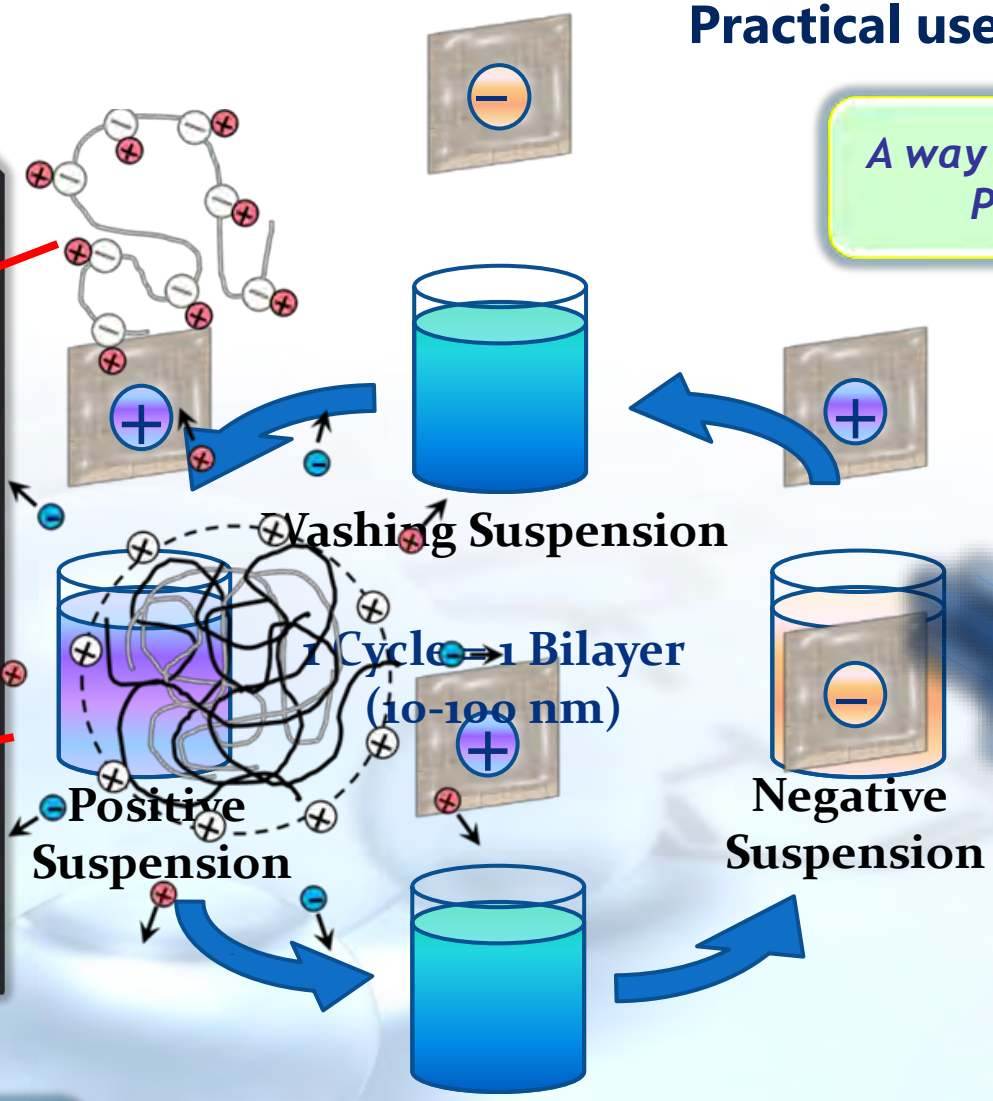


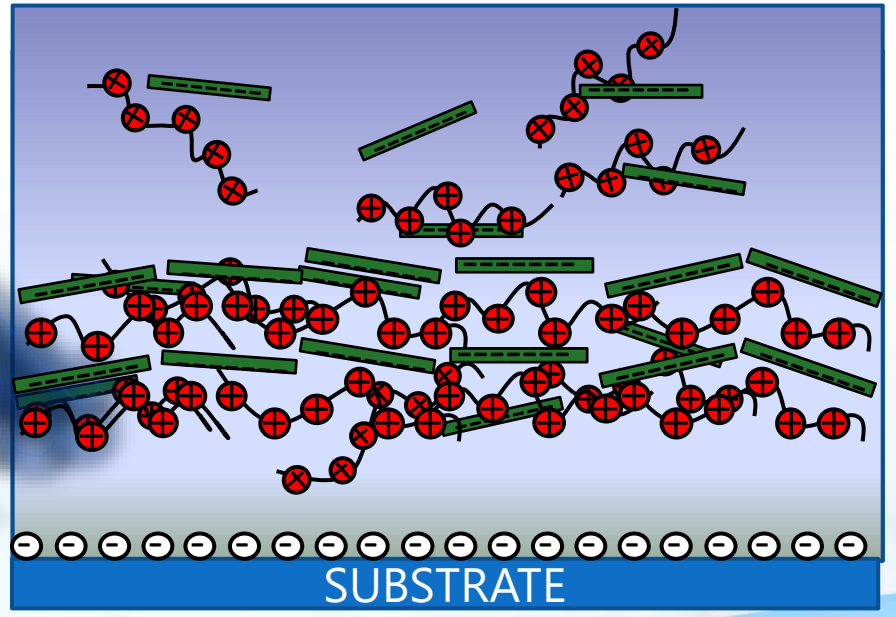


Dried PEC

Practical use of PECs – Layer by Layer assembly

A way to produce highly ordered and stratified PECs- based nanostructured coatings

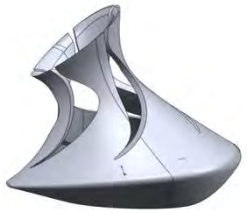


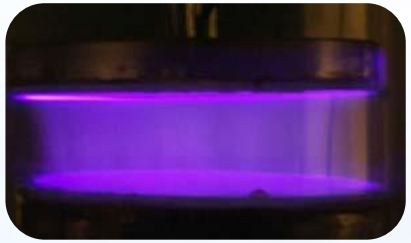
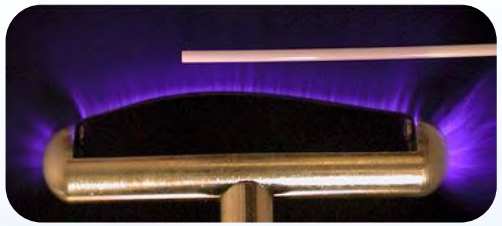


LbL key points

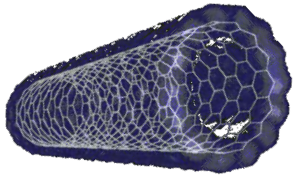
- Wide range of substrates (polymers, metals, textiles…)
- Simple and complex shapes
- Surfaces can be pre-treated using classical process (chemical activation, corona treatment, plasma etching…)
- The roughness, thickness and porosity of the film can be controlled adjusting experimental parameters.






Applications



Carbon Nanotubes

Metal nanoparticles

Bio-medical

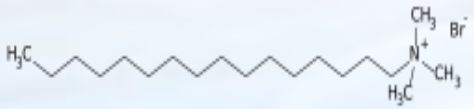
Anti-bacterial

Electrical properties

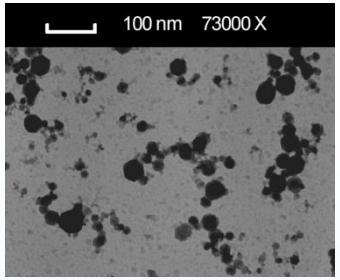
Gas barrier properties

Optical properties

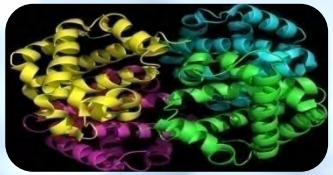
Flame retardancy



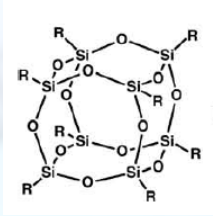
Surfactants



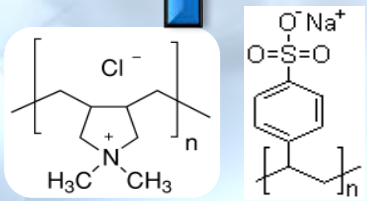
Ceramic nanoparticles



Bio-macromolecules



Organic-inorganic nanoparticles



Polyelectrolites

Plastics and packaging

Plastics

- Weight
- Optical properties
- Processability
- Mechanical properties
- Barrier properties

To achieve the best barrier properties a multi-material is needed

Possible solutions

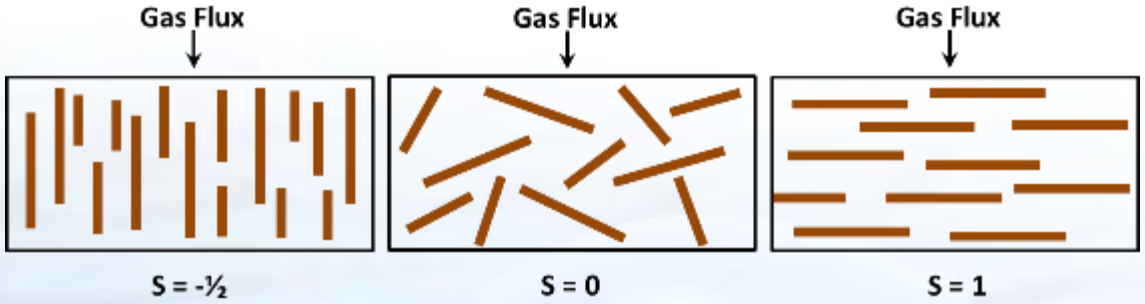
Nanostructured materials

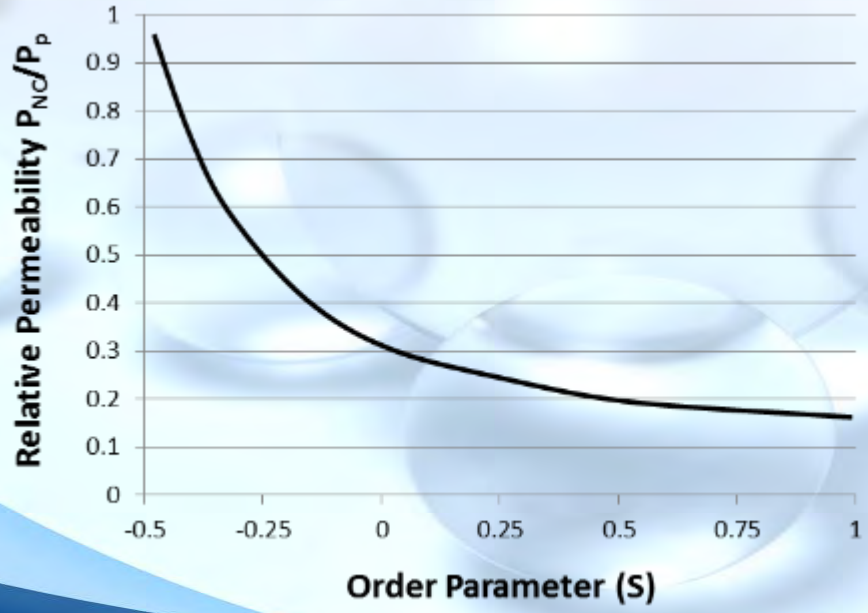
Layer by Layer Assembly

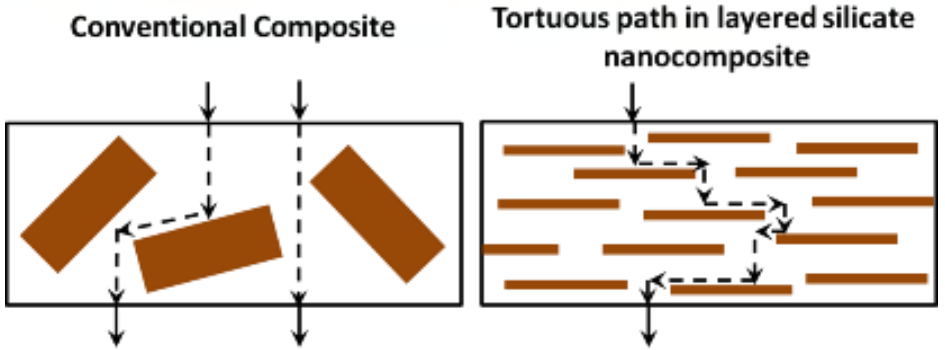
Nanometric coatings

Oxygen barrier effect

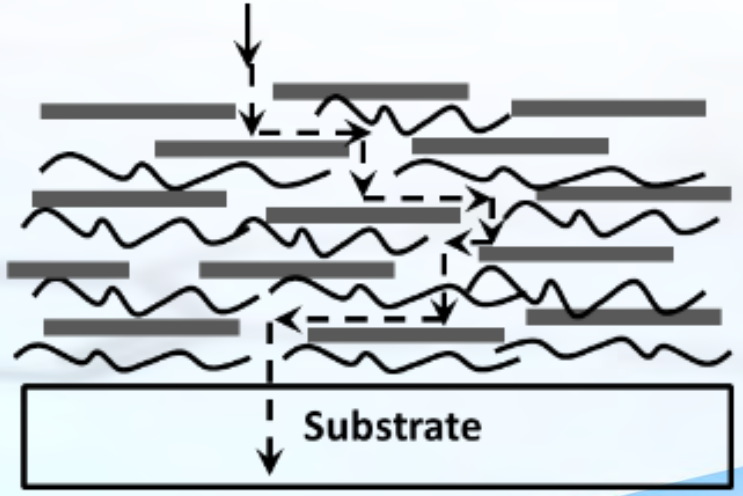
Relationship between LbL and polymer nanocomposites





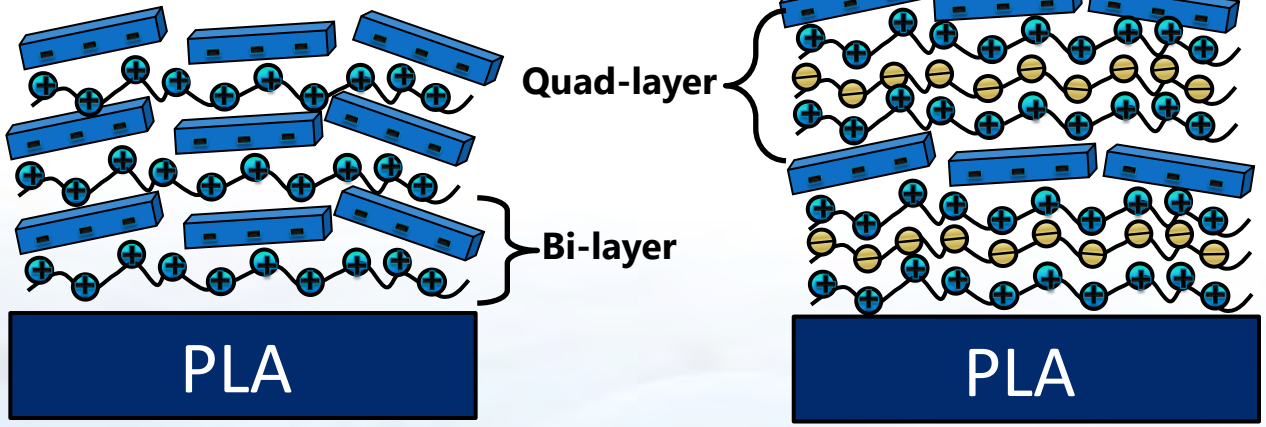


LbL nanostructured coating with maximized clay barrie effect

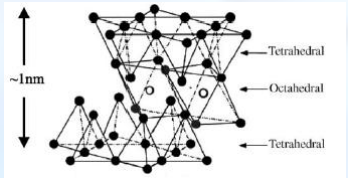


Prog. Polym. Sci. 28 (2003) 1539–1641

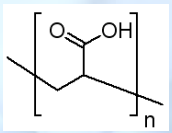
Oxygen barrier on PLA



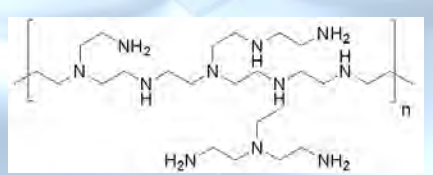
Anionic Clay:
Sodium Montmorrilonite



Anionic polymer:
Poly(acrylic acid)



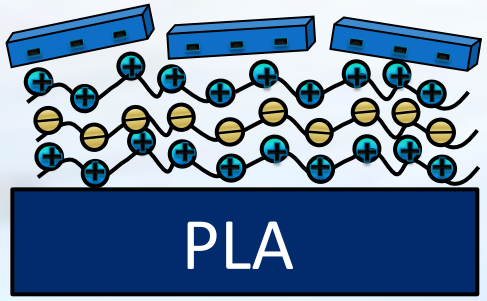
Cationic polymer:
Branched Polyethylenimine



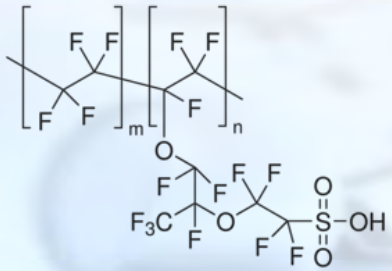
	Permeability [cc mm/m^2 day atm] (@ 0%RH, 23°C)	Reduction%
PLA	14.5	-
PLA nanocomposite (3% C20A)	13.7	-3
PLA nanocomposite (5% C20A)	11.3	-20
PLA 20 BL	9.4	-33
PLA 40 BL	3.5	-75
PLA 60 BL	2.2	-86
PLA 4 QL	9.7	-31
PLA 6 QL	0.5	-95

Nafion-based coatings

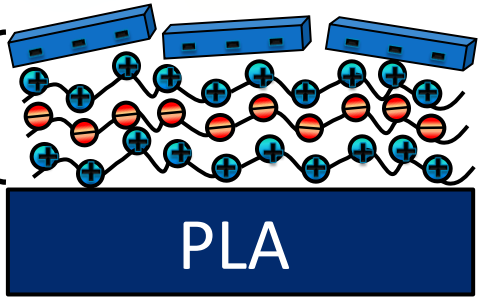
In dry conditions the Quad-layer architecture provides the best barrier properties which are almost completely lost in humid conditions



Anionic polymer:
Nafion

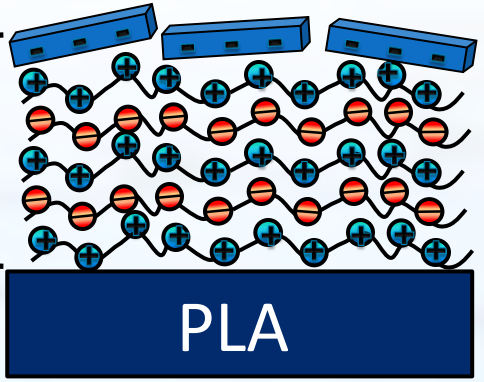


Quad-layer Architecture



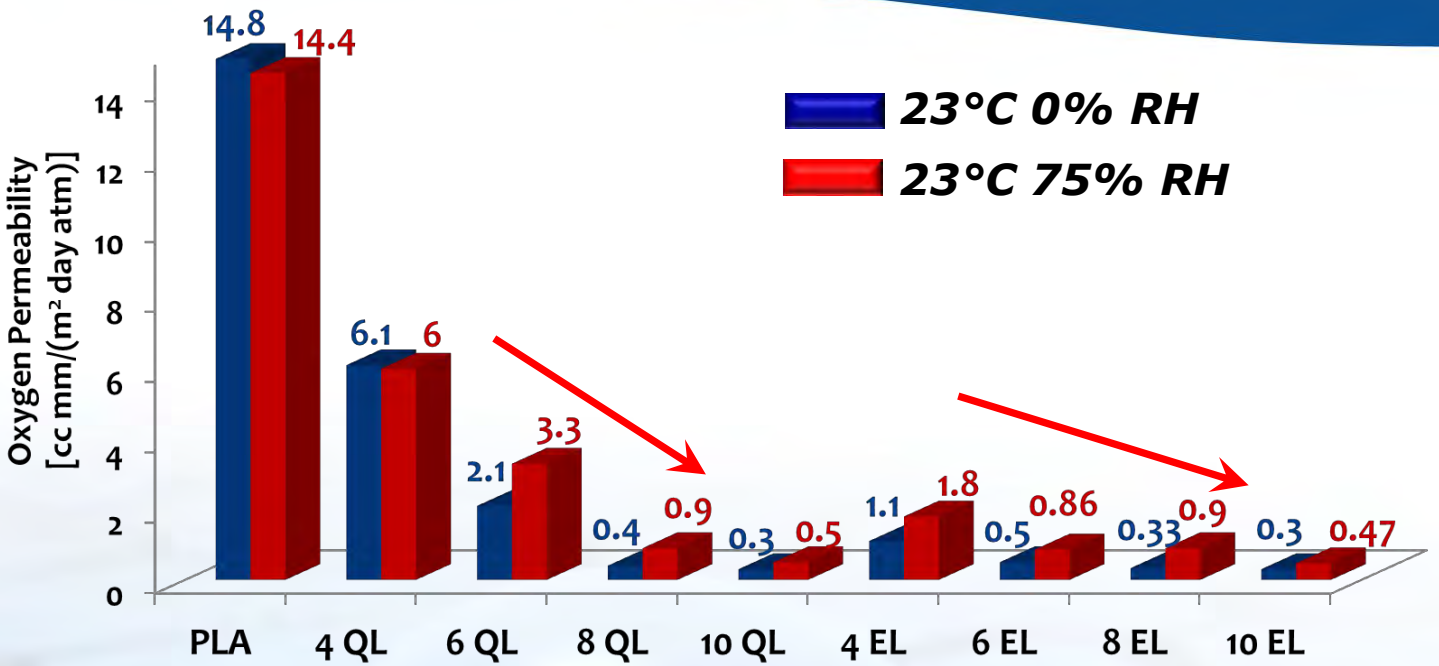
4, 6 Quad-layers (QL)

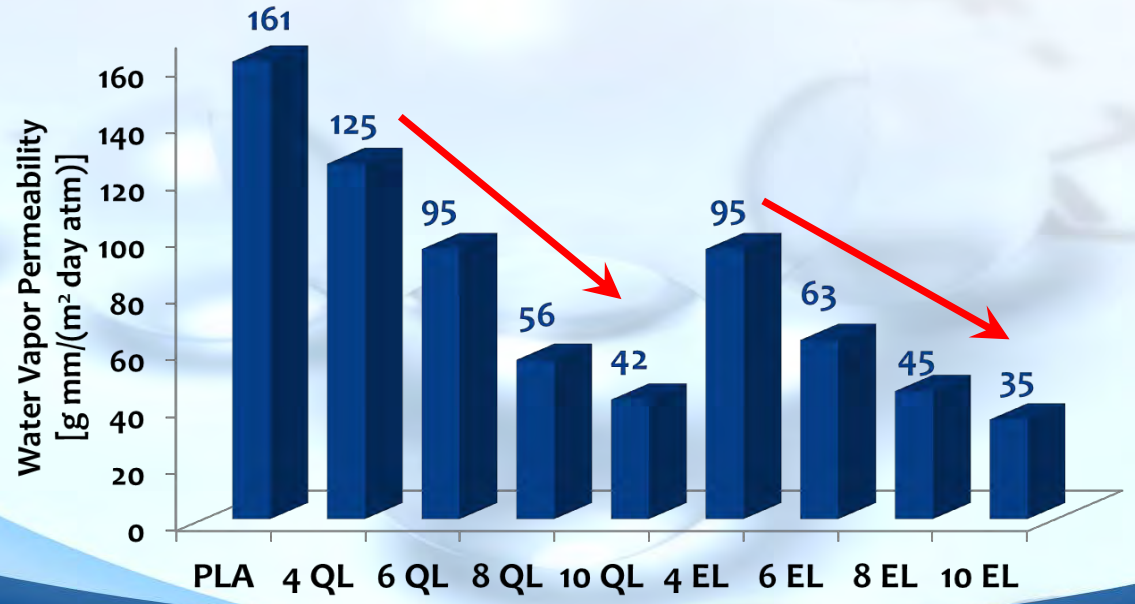
Esa-layer Architecture

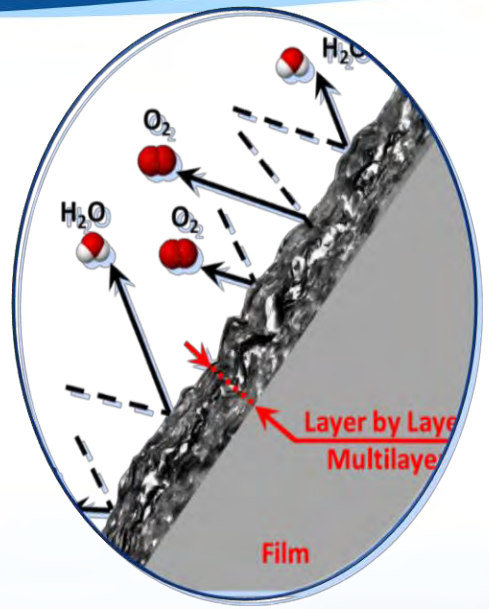


4, 6 Esa-layers (EL)

Nafion-based architectures



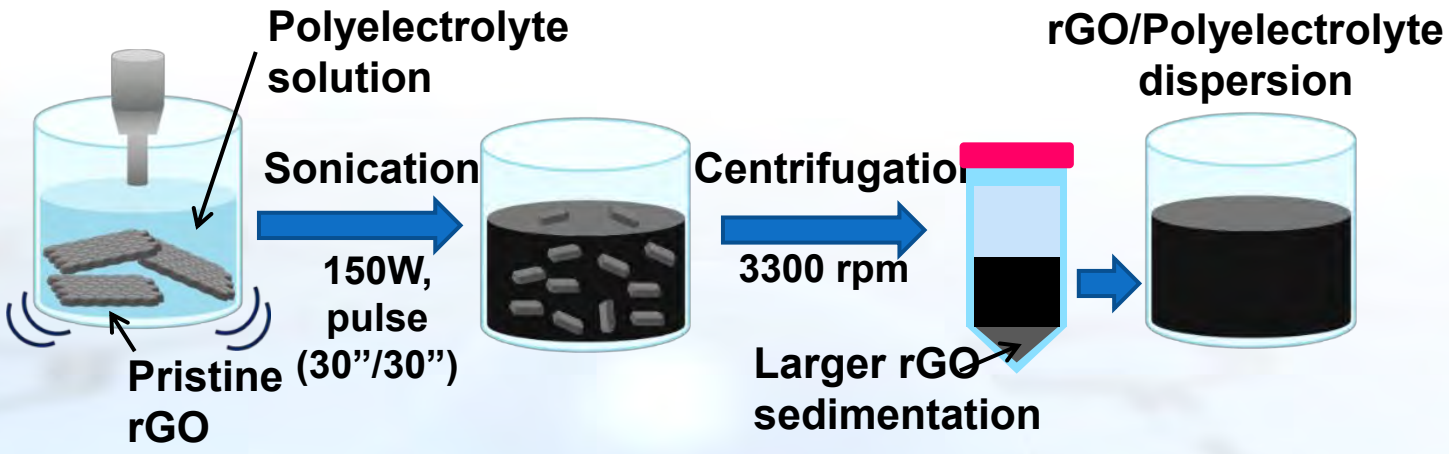




Nafion layers increase the hydrophobicity of the coating and help in maintaining the gas barrier properties in humid conditions

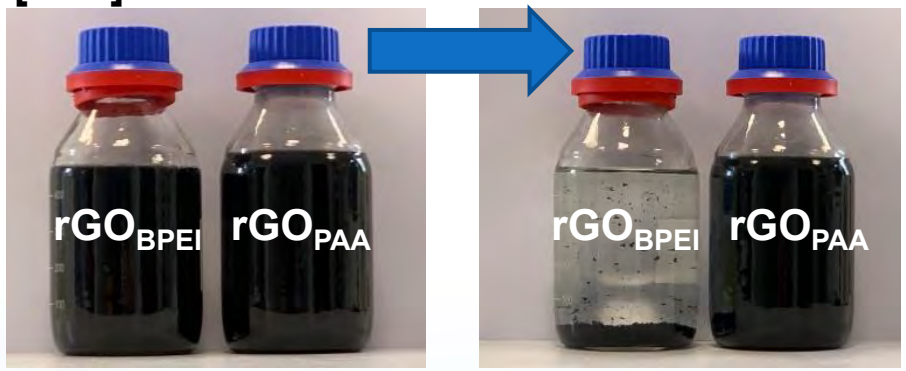
Graphene-based coatings

Liquid phase dispersion of graphene related materials mediated by polyelectrolytes:



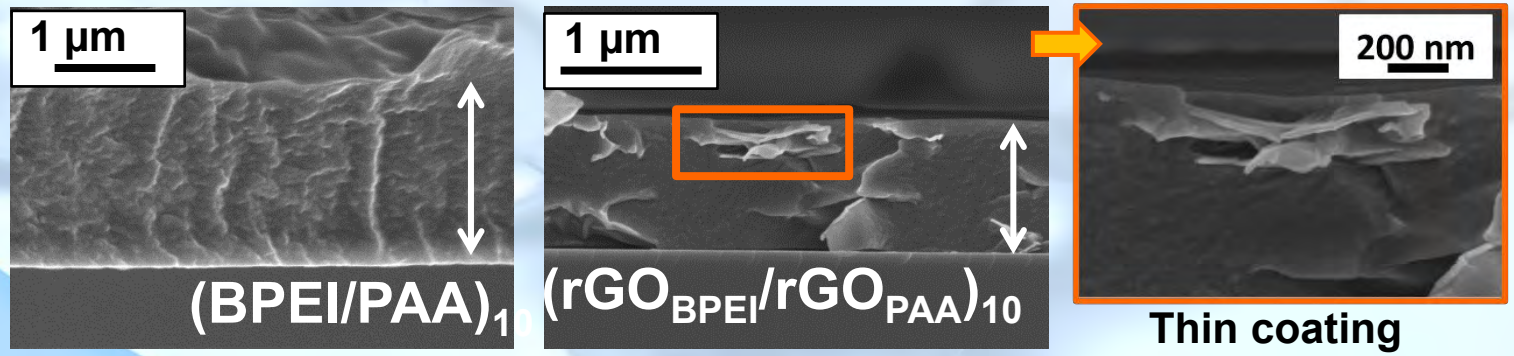
[rGO] in PAA 0.002 wt%

[rGO] in BPEI 0.004 wt%



3 month

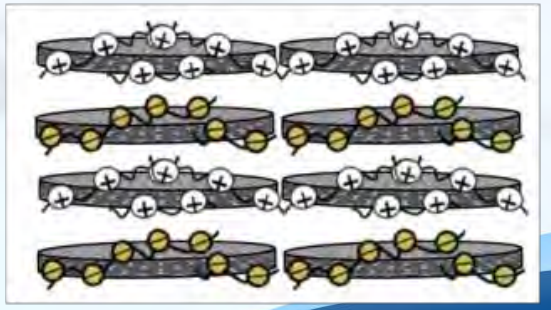
12 months



1.2 ± 0.3 µm

1.0 ± 0.1 µm

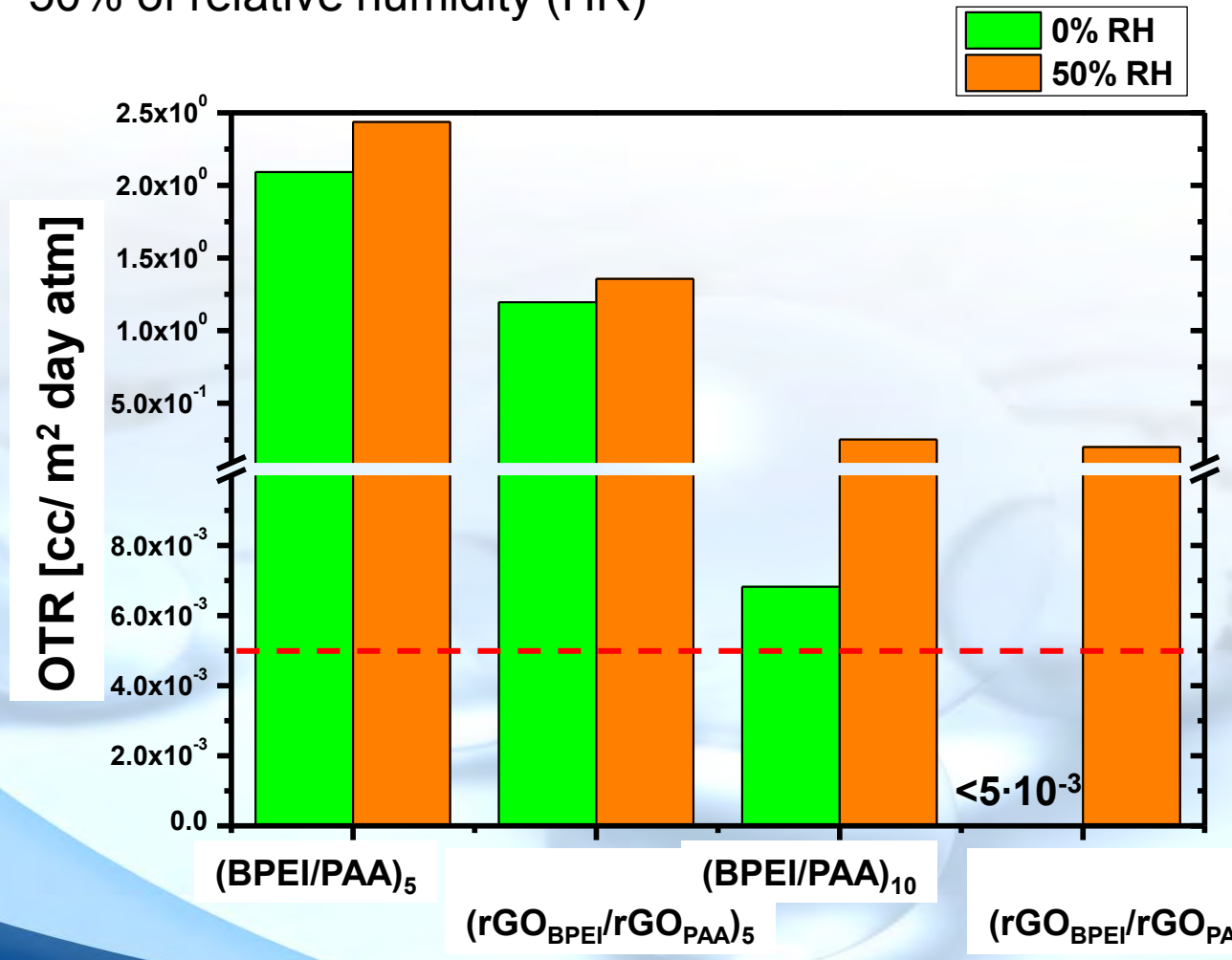
Thin coating embedding rGO nanoplates



L. Maddalena et al., ACS Appl. Mater. Interfaces 2021, 13, 43301−43313

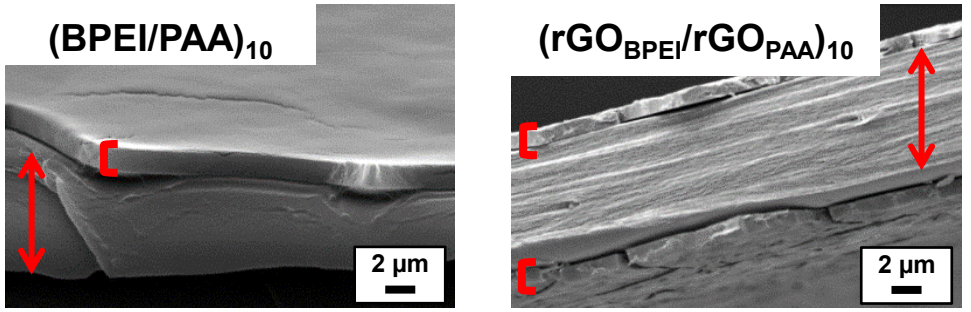
Gas barrier properties

Oxygen Transmission Rate (OTR) on 5 and 10 BL assembled on PET 10 μm thick film in at 23°C, 0% and 50% of relative humidity (HR)



Instrumental lower detection limit

SEM on composites cross-section



Permeability of the coatings at 50% RH

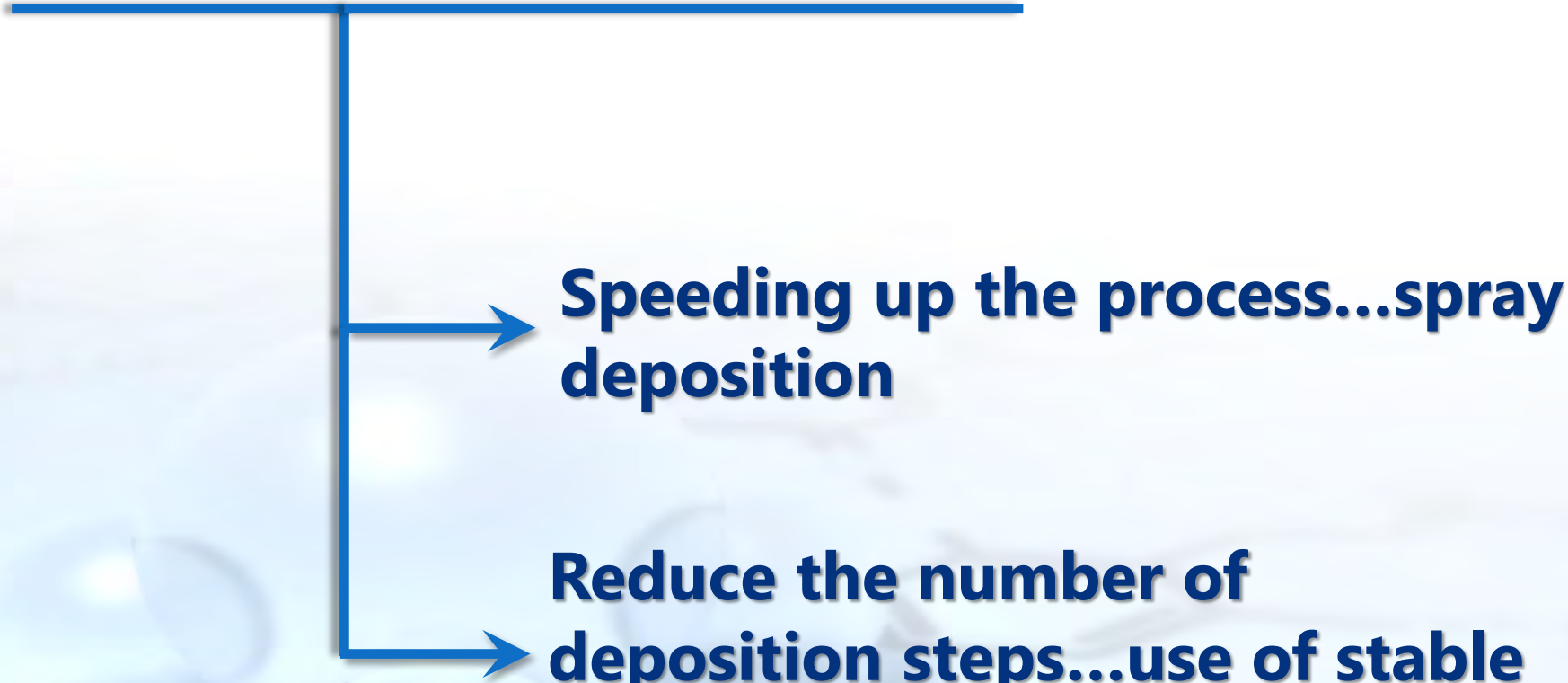
$$P_{composite} = \left(\frac{\phi_{PET}}{P_{PET}} + \frac{\phi_{coating}}{P_{coating}} \right)^{-1}$$

P coating [cc mm/m² day atm], in 50%RH

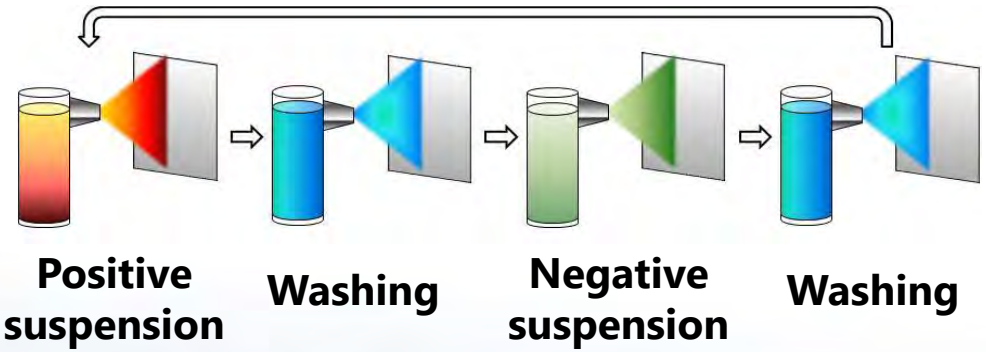
(BPEI/PAA)₁₀	**1.8· 10⁻³**
(rGO_BPEI/rGO_PAA)₁₀	3.7· 10⁻⁴

A.P. Roberts et al., Journal of Membrane Science, 208, 2002, 75-88.

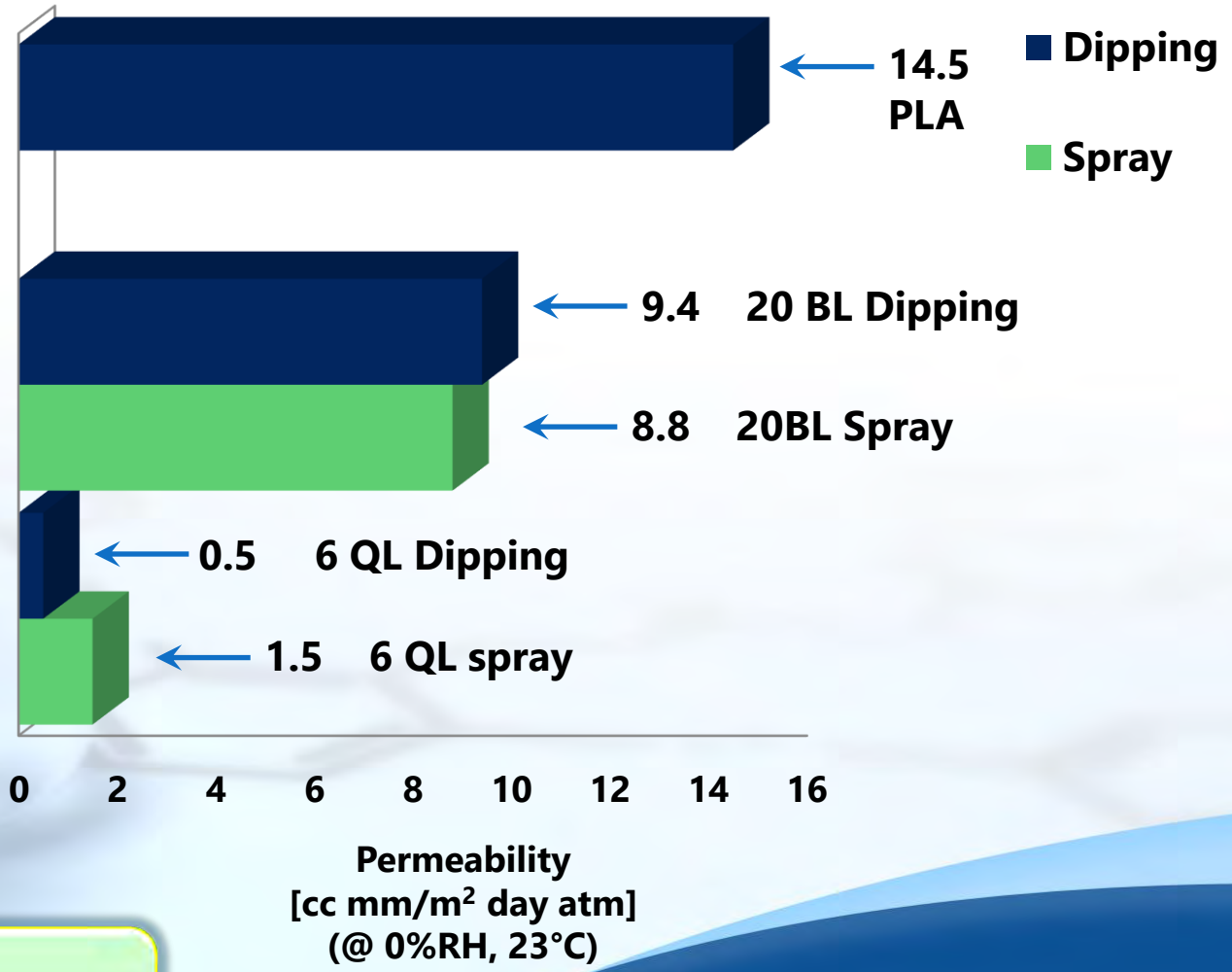
Can we improve LbL gas barrier coatings ?



Oxygen barrier spray

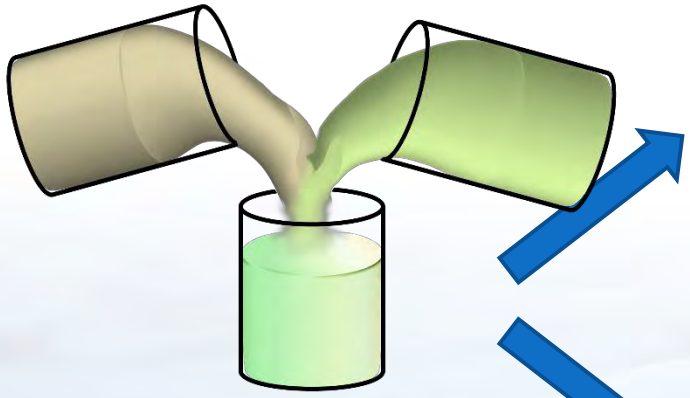


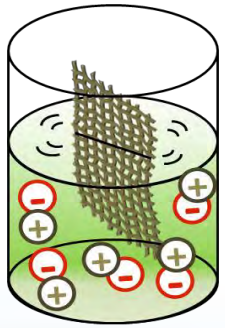
- ✔ Time for 1 Bi-layer <1 min
- ✔ Suspension concentration theoretically constant
- ✔ Possibility to treat only one side
- ✘ New deposition technique



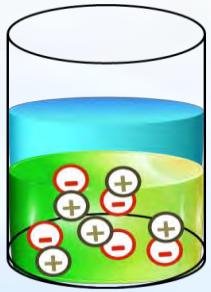
Spray-based LbL can

Practical use of PECs – Water soluble and compacted PECs

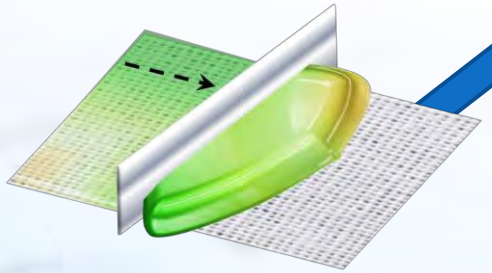




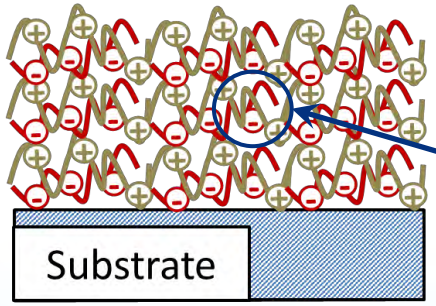
Conventional dipping



Compaction by centrifugal force



Direct PECs deposition



LbL-like assembly

PECs formed under controlled conditions

- ❑ *Concentration*
- ❑ *Charge density*
- ❑ *pH*
- ❑ *Ionic strength*
- ❑ ….

✓ Can achieve LbL-like structures

✓ Few steps deposition approach

✓ Enable different deposition procedures

✗ Constraints on PECs formation

✗ Viscosity might impact deposition

Conclusions

- ***Layer by layer assembly has been successfully applied on PLA and PET films for oxygen barrier properties***
- ***The treatments have been performed using both conventional dipping and spray techniques***
- ***Coatings built up via conventional dipping turned out to have the best barrier properties***
- ***Sprayed coatings showed promising results in terms of barrier properties and treatment time***

Thank you for your kind attention

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