Progress beyond

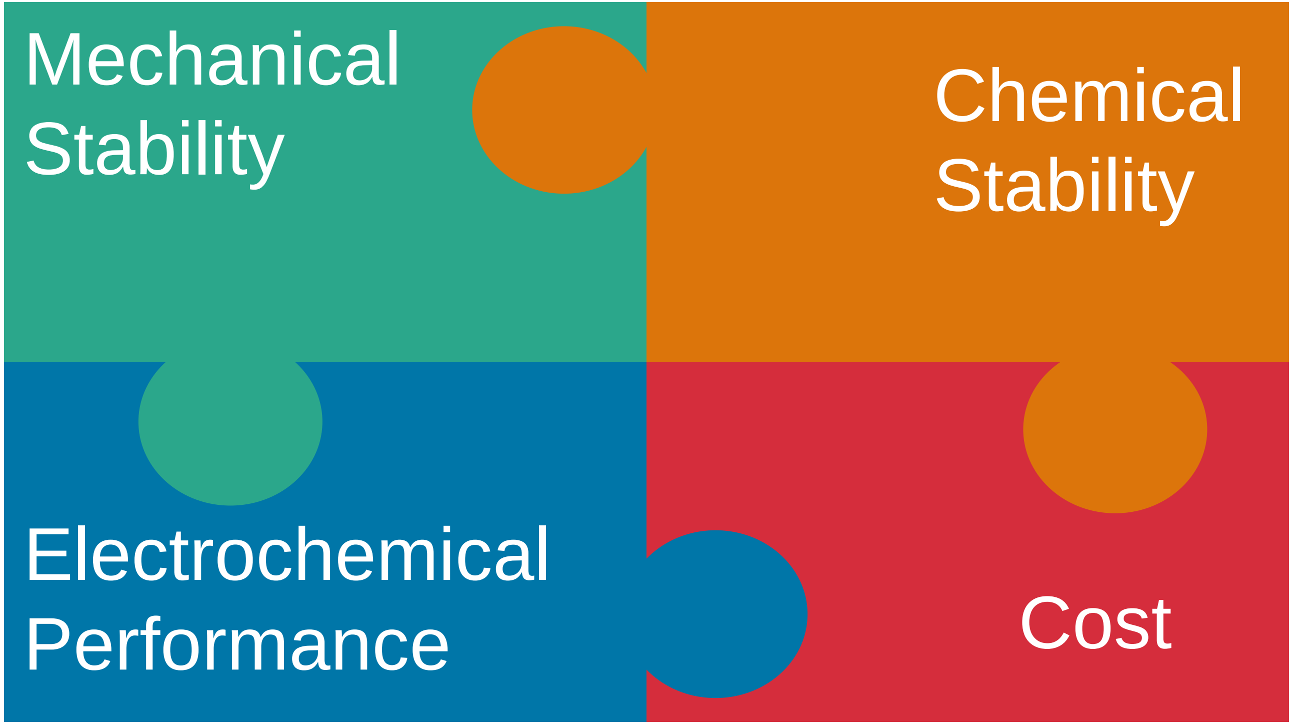
Research and Development on Polymers for H_2 Applications

Claudio Oldani and Daniele Facchi

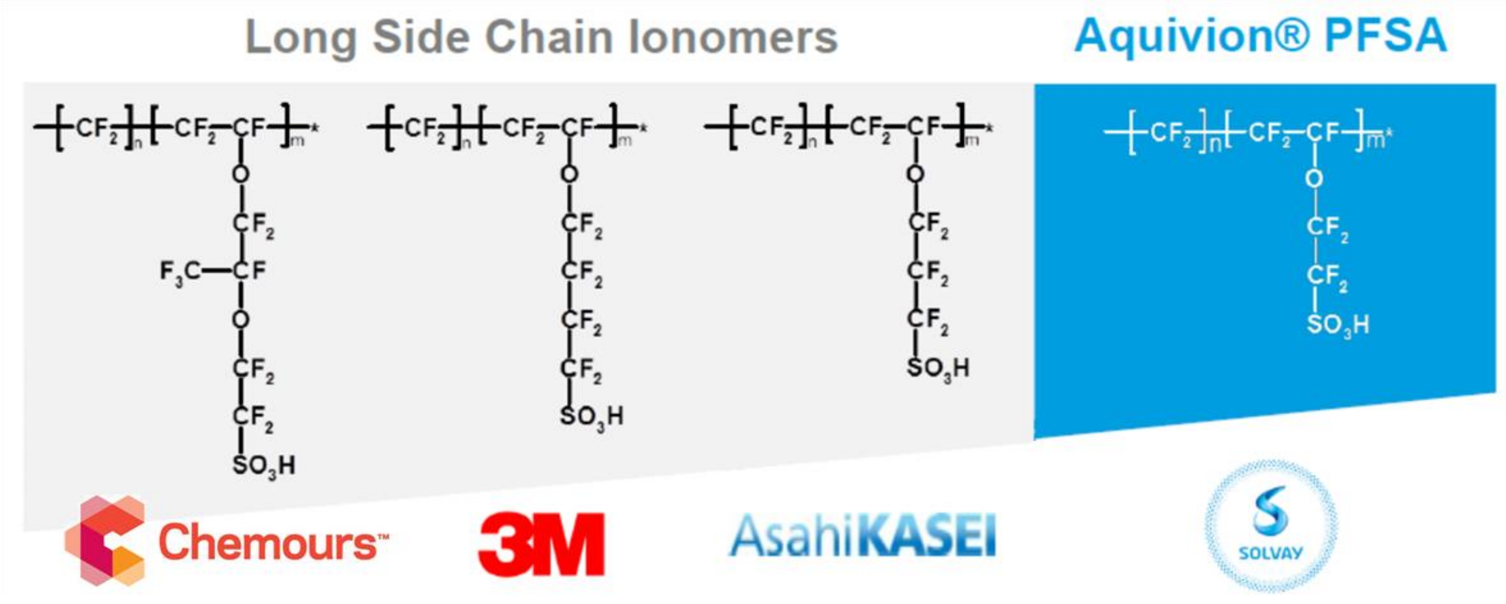
Solvay Specialty Polymers
R&D Center, Viale Lombardia 20, Bollate (MI)

March 10, 2021

The Blueprint for Material Development

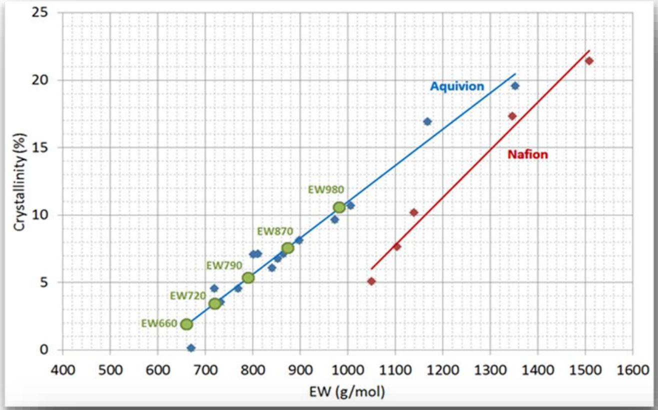


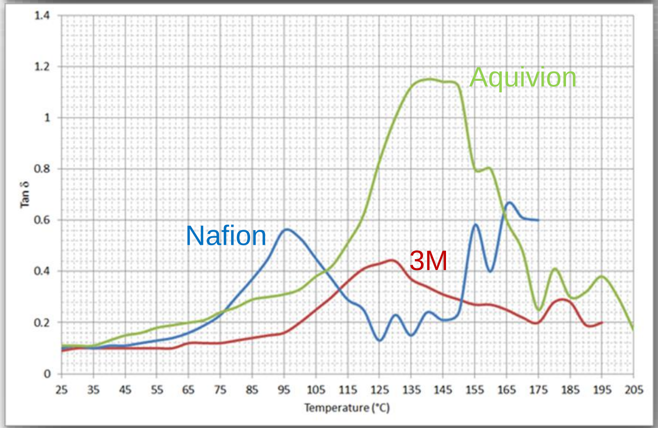
Aquivion® Ionomer: Chemical Structure

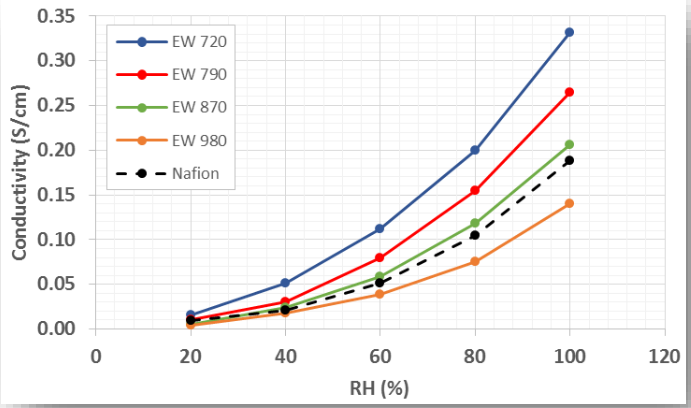


Aquivion® is the shortest side chain perfluorosulfonic acid ionomer available on the market

Aquivion® Ionomer: Main Properties

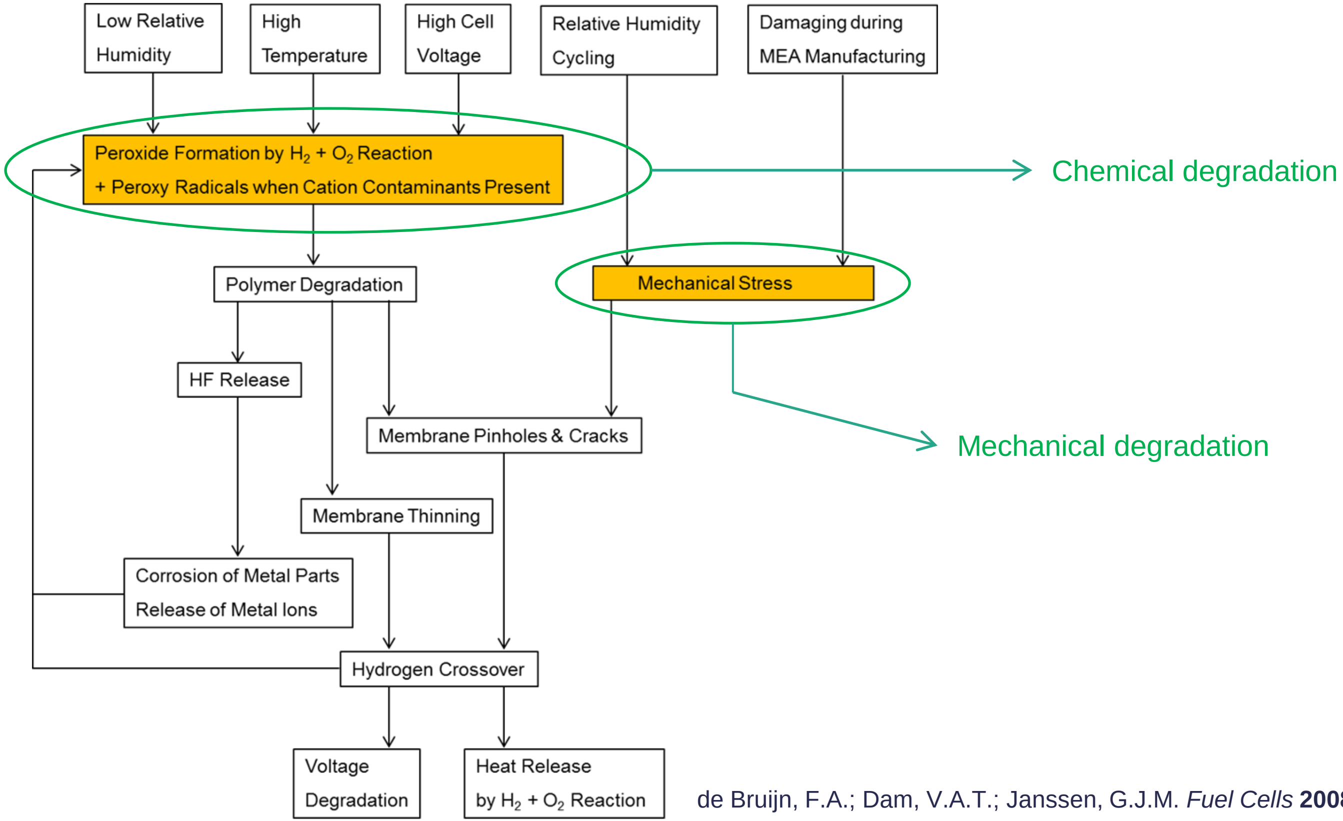






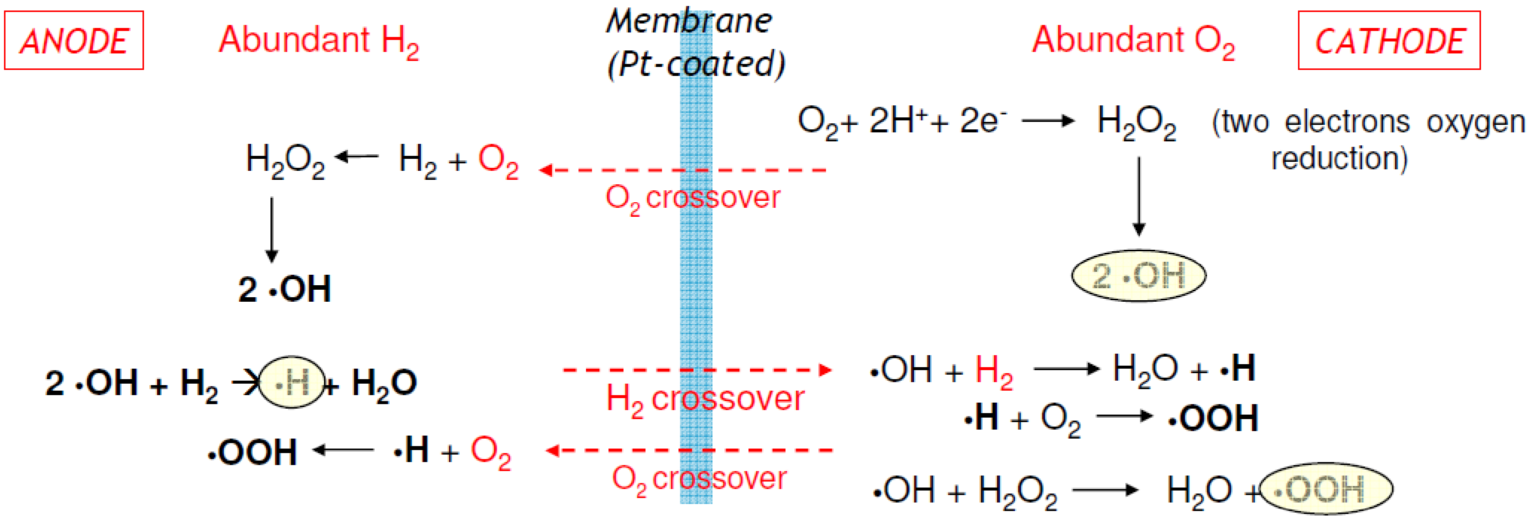
The presence of the shorter side-chain induces higher Tg and higher crystallinity allowing the increasing of the acid loading.

Degradation Conditions & Effects



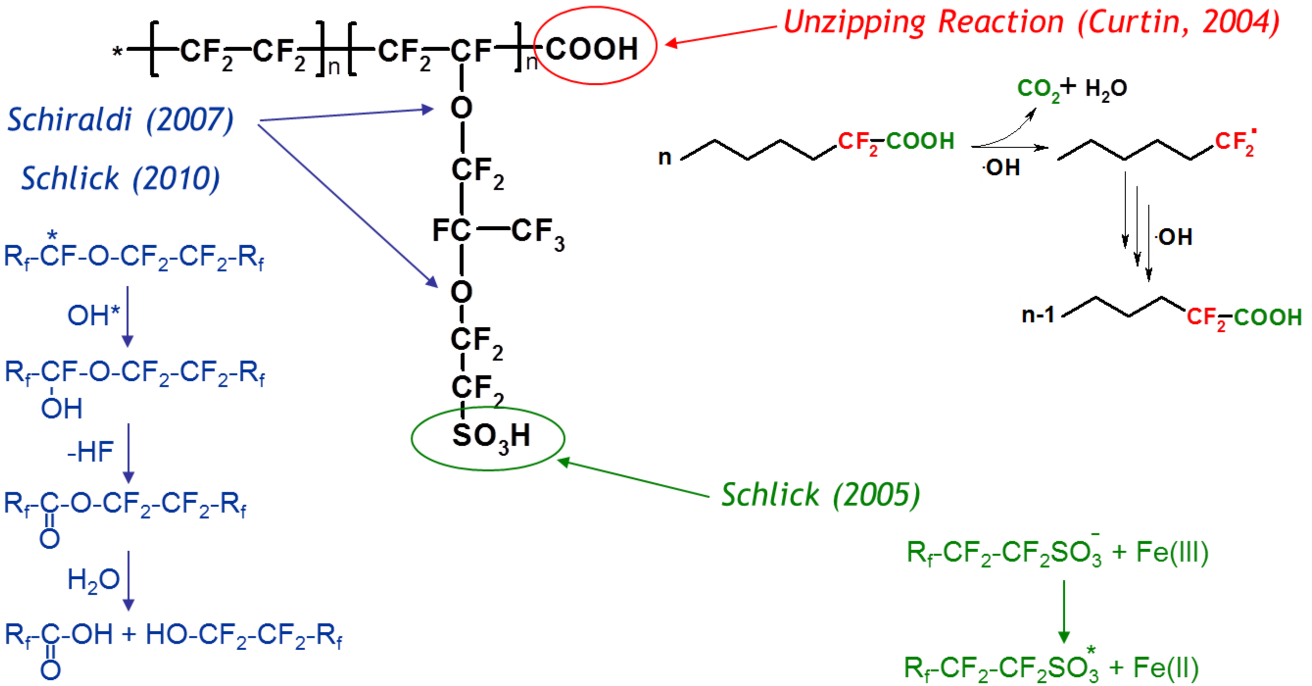
de Bruijn, F.A.; Dam, V.A.T.; Janssen, G.J.M. *Fuel Cells* **2008**, 3-22.

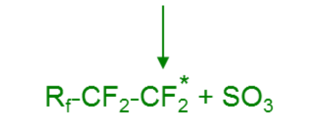
Where Do the Radicals Come From?



- H_2O_2 can be generated at the cathode side by electrochemical reaction and on the anode side as a consequence of O_2 crossover.
- Traces of metals (but also Pt catalyst surface!!) can promote HO* generation.
- HO* plays a pivotal role in producing H* and HOO* radicals both at cathode and anode side.

Proposed Sites of Degradation

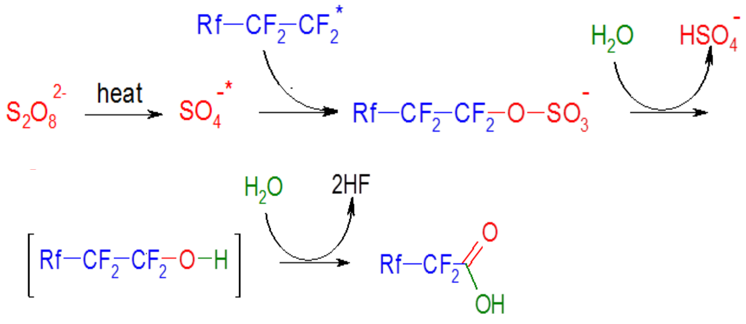




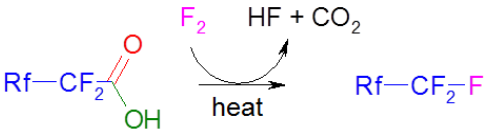
Curtin, D.E.; Lousenberg, R.D.; Henry, T.J.; Tangeman, P.C.; Tisack, M.E. *J. Power Sources* **2004**, *131*, 41-48
Kadirov, M.K.; Bosnjakovic, A.; Schlick, S. *J. Phys. Chem. B* **2005**, *109*, 7664-7670
Zhou, C.; Guerra, M.A.; Qiu, Z.-M.; Zawodzinski, T.A.; Schiraldi, D.A. *Macromolecules* **2007**, *40*, 8695-8707
Danilczuk, M.; Perkowski, A.J.; Schlick, S. *Macromolecules* **2010**, *43*, 3352-3358

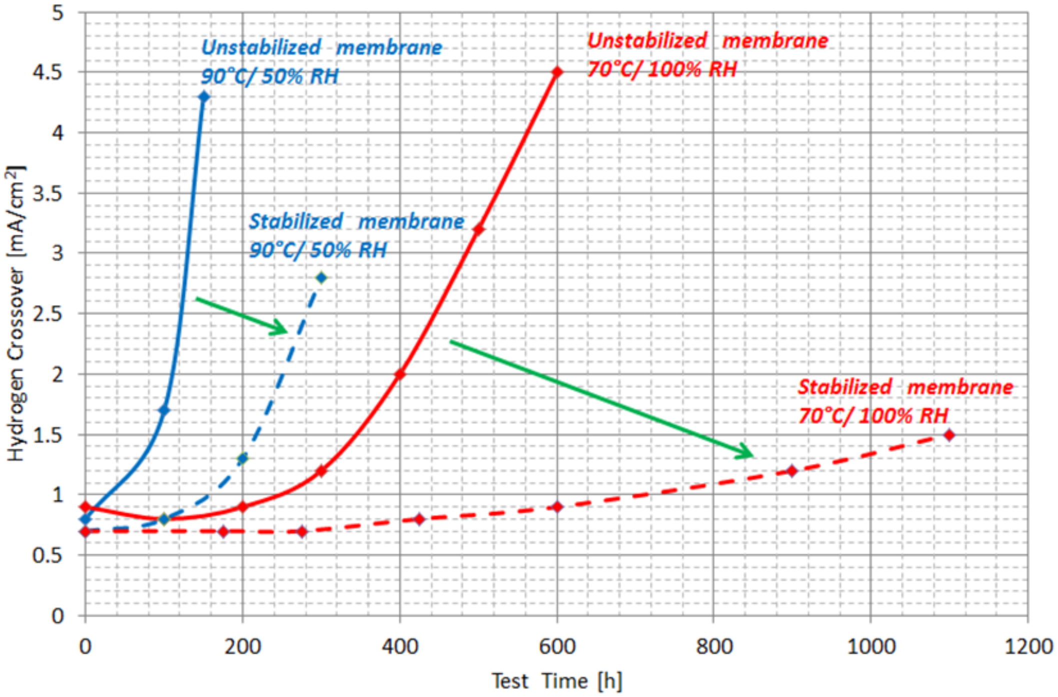
Chemical Stabilization

Carboxylic Acid Formation



Carboxylic Acid Removal (aka Stabilization)





Application in Water Electrolysis

SOLVAY

Electrohypem HPEM2GAS NEPTUNE

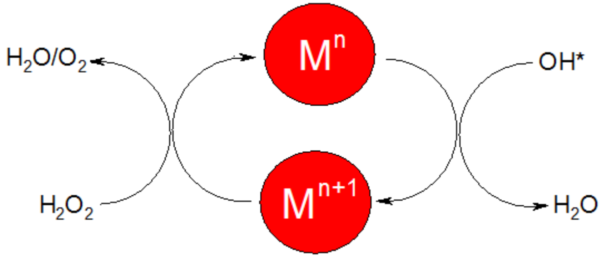
Electrohypem (2012-2015) HPEM2GAS (2016-2019) Neptune (2018-present)

120 μm 90 μm 50 μm membrane

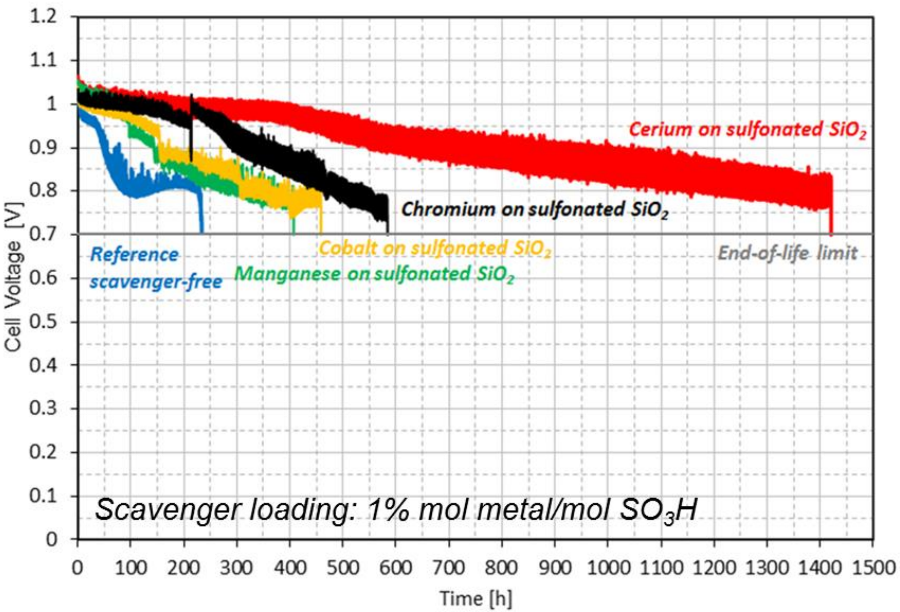
Membrane thickness must be the trade-off between the high current density and the low H_2 crossover.

In order to reduce membrane thickness while keeping the mixture oxygen/hydrogen within the safety limits.

Radical Scavenger Introduction: Aquivion RSP



- The key of the mitigation mechanism is based on the redox potential of the metal matching the potential of peroxy radicals
- The scavenging reaction must be fast enough to compete with the rate of reaction between ionomer and radicals.



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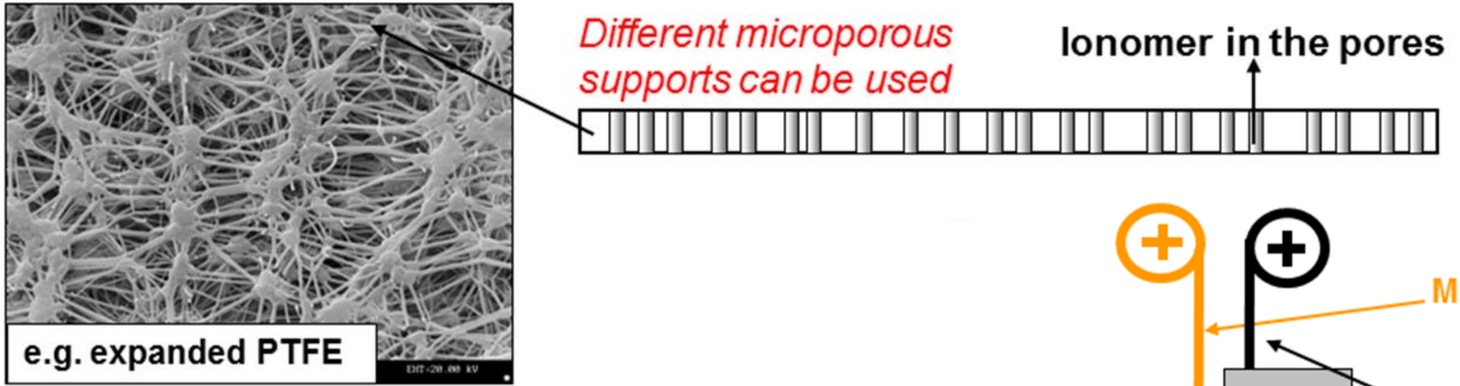
D'Urso, C.; Oldani, C.; Baglio, V.; Merlo, L.; Aricò, A.S. *J. Power Sources* **2014**, *272*, 753-758.
D'Urso, C.; Oldani, C.; Baglio, V.; Merlo, L.; Aricò, A.S. *J. Power Sources* **2016**, *301*, 317-325.

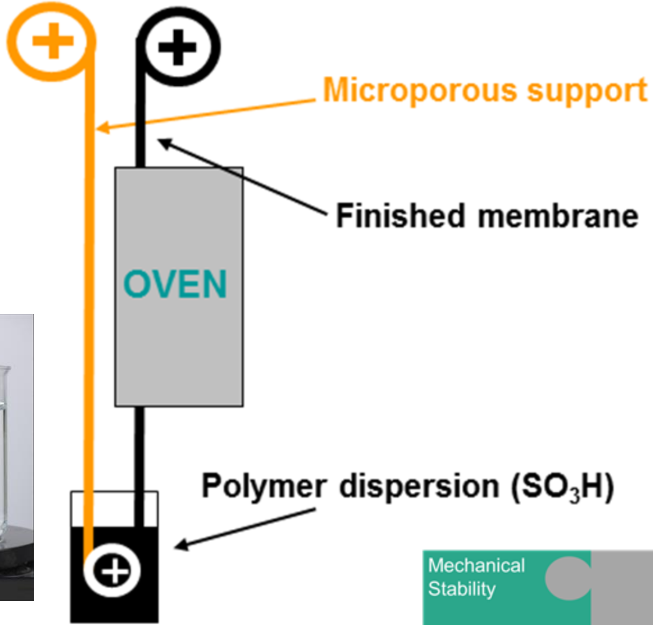
Mechanical Stability | Chemical Stability | Electrochemical Performance | Cost

Reinforced Membranes

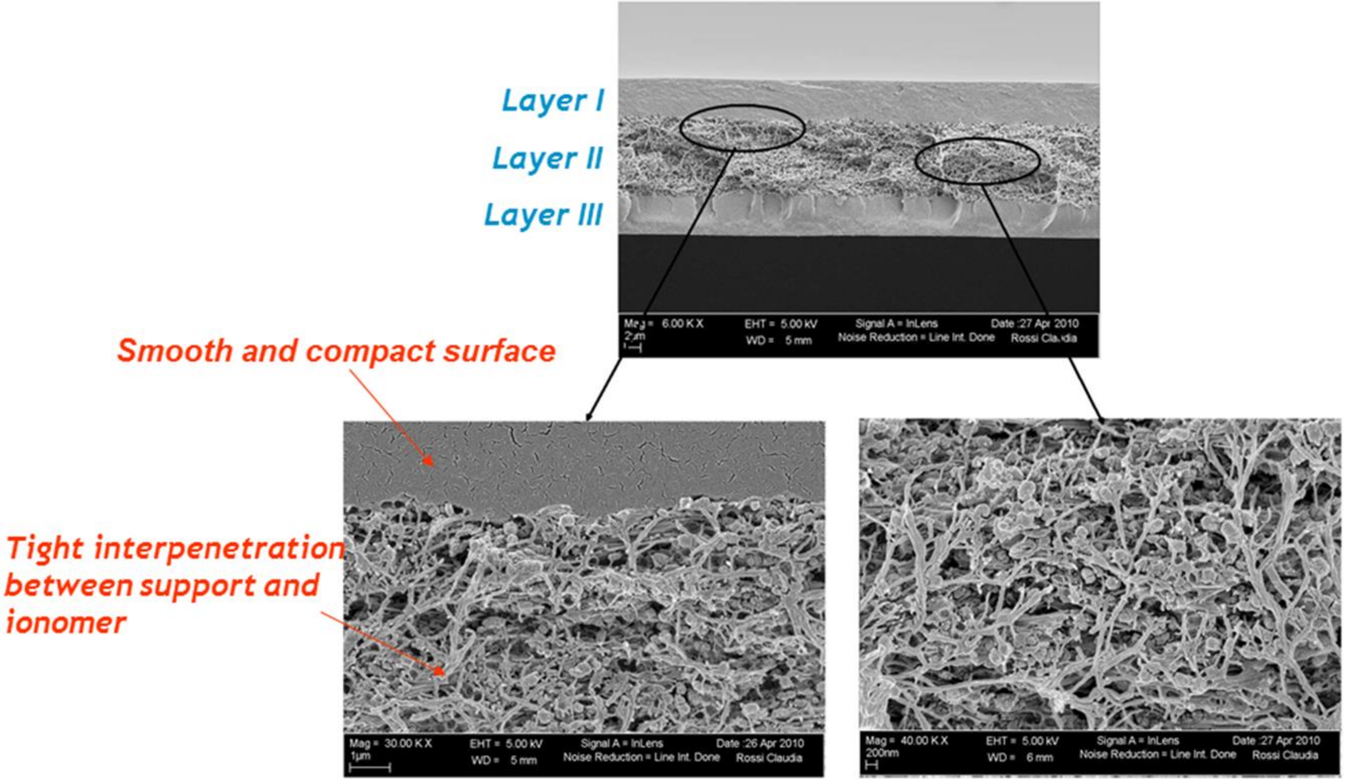


Pristine ePTFE

Reinforced Membrane

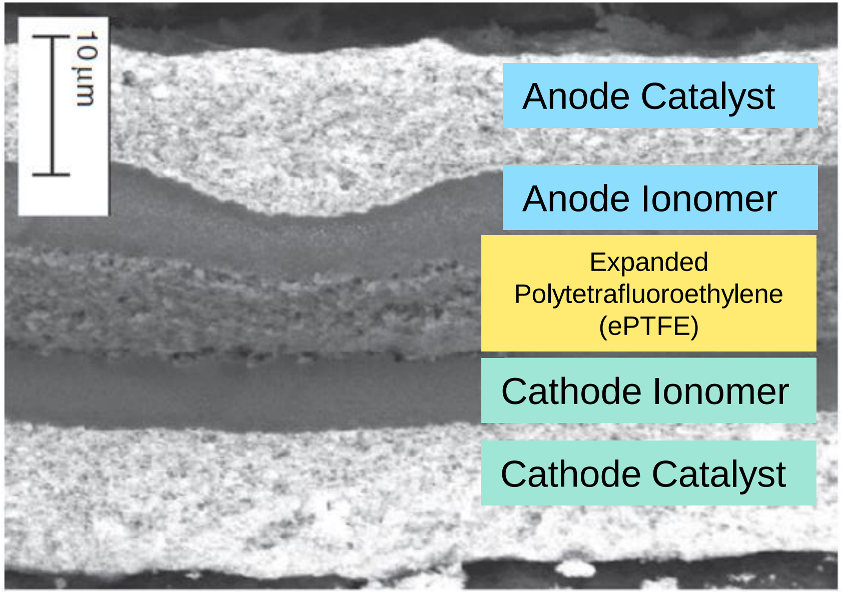


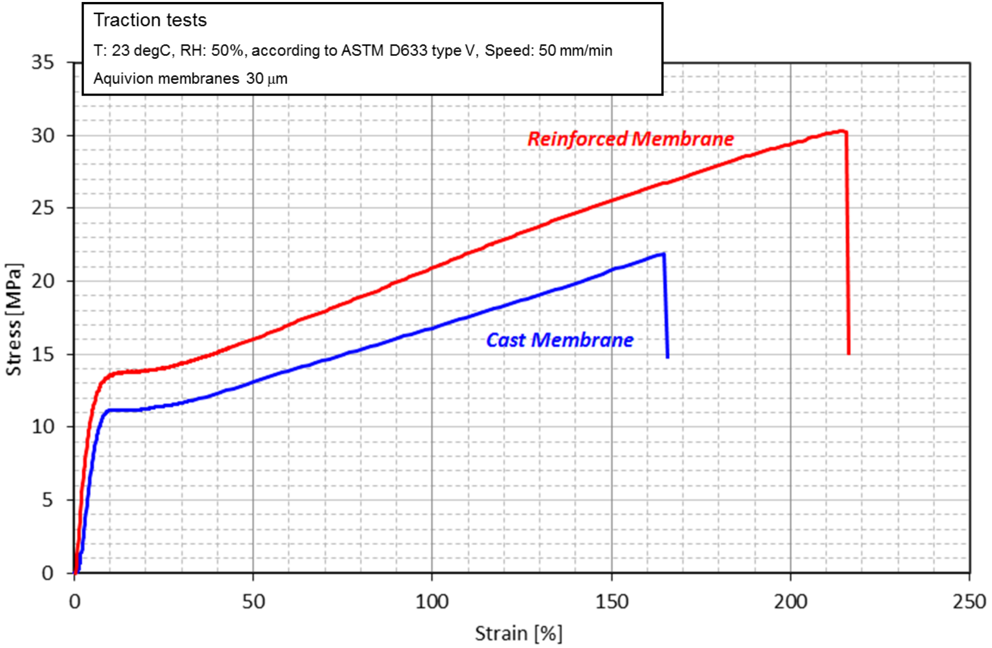
Reinforced Membranes: Morphology



Gatto, I.; Saccà, A.; Baglio, V.; Aricò, A.S.; Oldani, C.; Merlo, L.; Carbone, A. *J. Energy Chem.* **2019**, *35*, 168-173

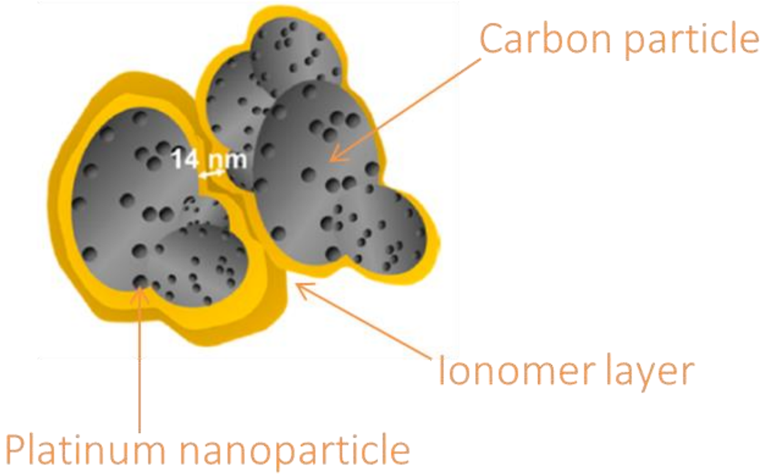
Reinforced Membranes: Morphology

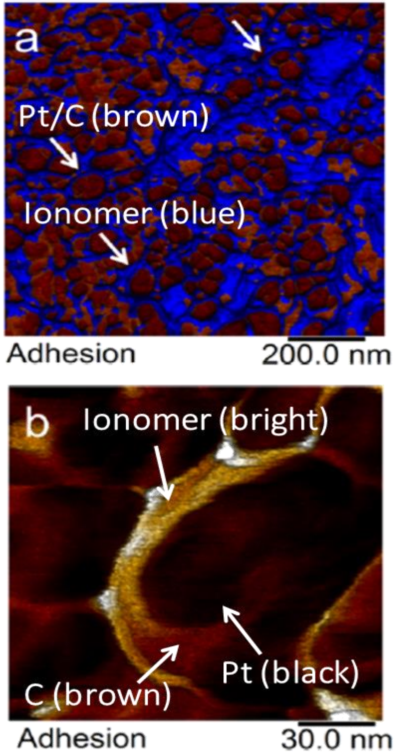




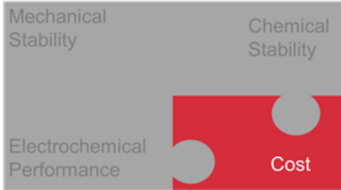
Yandrasits, M.; Hamrock, S. Poly(Perfluorosulfonic Acid) Membranes in: *Polymer Science: A Comprehensive Reference, Vol. 10* pag. 601-619.

Fuel Cell Cathode Microstructure



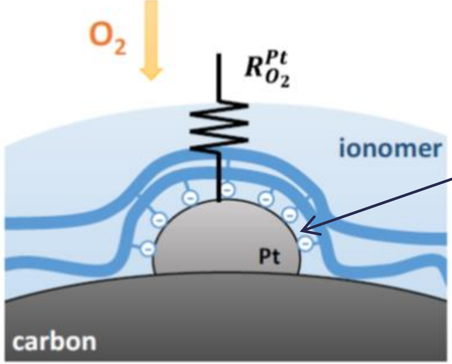


Fuel cell cathode is a complex three-phase system comprising Pt nanoparticles (acting as catalysts for the reaction) dispersing on C (used to increase available surface) and consolidated by an ionomer which guarantees protonic conductivity.

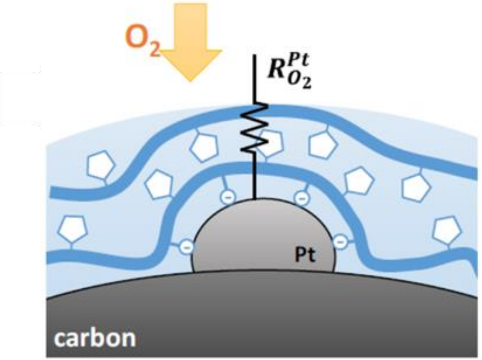


Morawietz, T.; Handl, M.; Oldani, C.; Friedrich, K.A.; Hiesgen, R. *ACS Appl. Mater. Interfaces* 2016, *8*, 27044-27054.

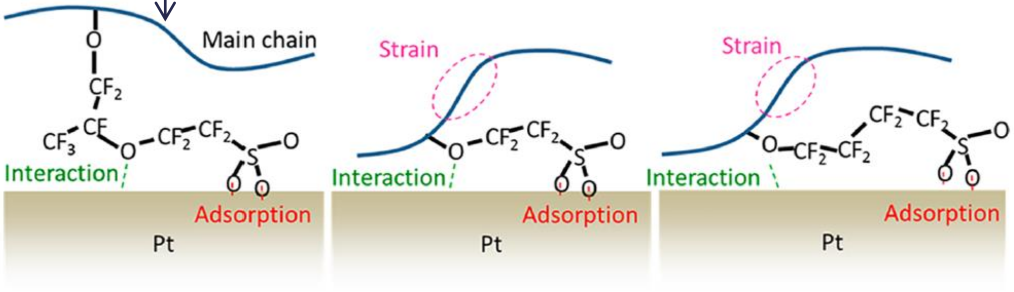
Solutions to Improve the O_2 Permeability



The thin ionomer film (1-10 nm thick) loses its ability to phase segregate and form polymer and water domains due to a confinement effect as well as adsorption on the Pt surface (HSAB), leading to stiffer backbone and increases in O_2 and H_2O transport resistance.

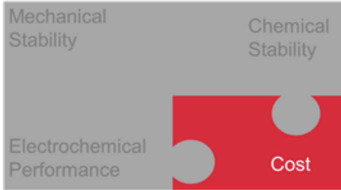


The sulfonate adsorption onto the Pt surface and the ORR suppression is related to the different flexibility of LSC and SSC structure.

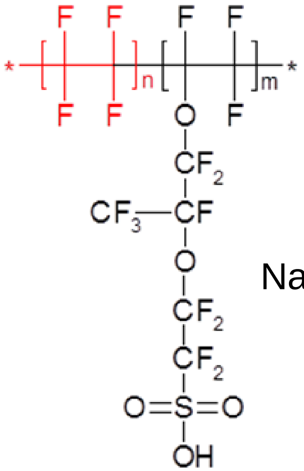


Kodama, K. *Et al. ACS Catal.* **2018**, *8*, 694-700.

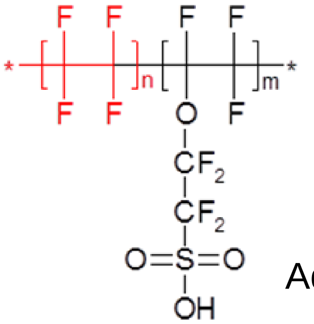
Kongkanand, A.; Mathias, M.F. J. *Phys. Chem. Lett.* **2016**, *7*, 1127-1137.



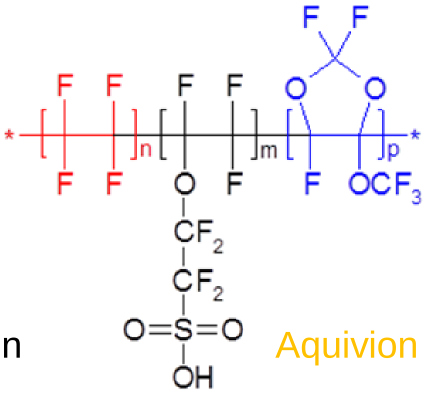
Solutions to Improve the O_2 Permeability



Nafion



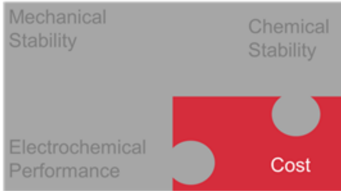
Aquivion



Aquivion FCC

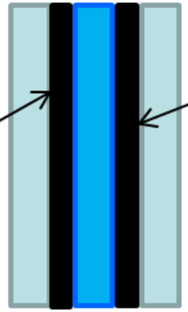
Improving local O_2 transport by:

- reducing the concentration of sulfonic acid groups.
- restricting the mobility of sulfonic acid groups by using shorter side chain ionomer.
- modifying the ionomer main chain to avoid dense aggregation using steric hindered monomers.



Ex-Situ Oxygen Permeability Measurement

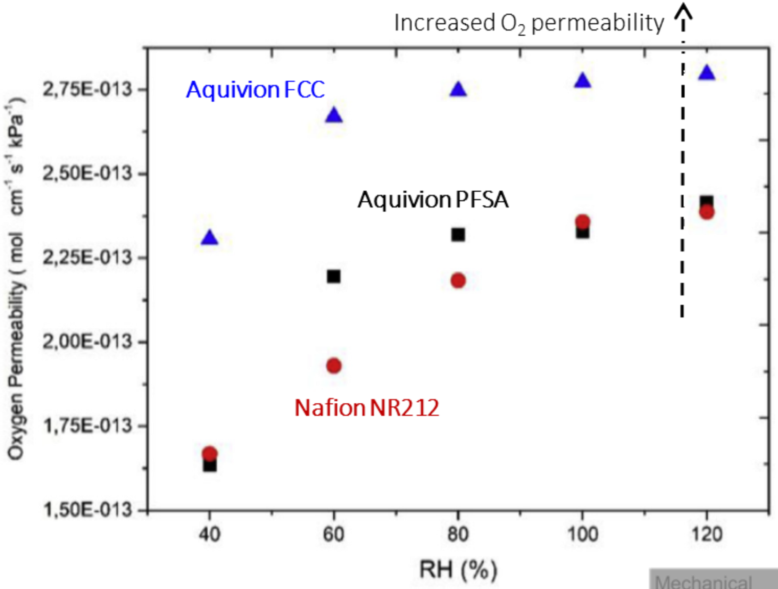
Sigracet 25BC GDL



Cathode
Catalyst: Pt/C
Binder: Aquivion commercial dispersion

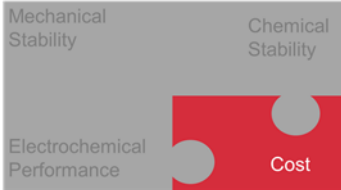
Anode
Catalyst: IrO_x/C
Binder: Aquivion commercial dispersion

Aquivion commercial or
Aquivion FCC cast membrane

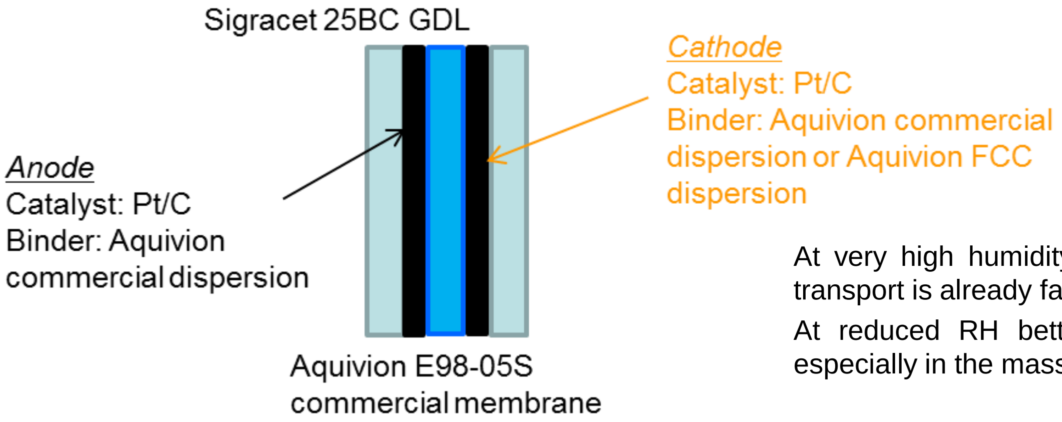


T: 60 degC; RH: from 40% to 120%
P: 1.2 barA (either side);
Voltage: 1 V
Cathode: N_2; Flow: 500 sccm
Anode: O_2; Flow: 1000 sccm

Zhang, J.; Gasteiger, H.A.; Gu, W. *J. Electrochem. Soc.* **2013**, *160*, F616-F622

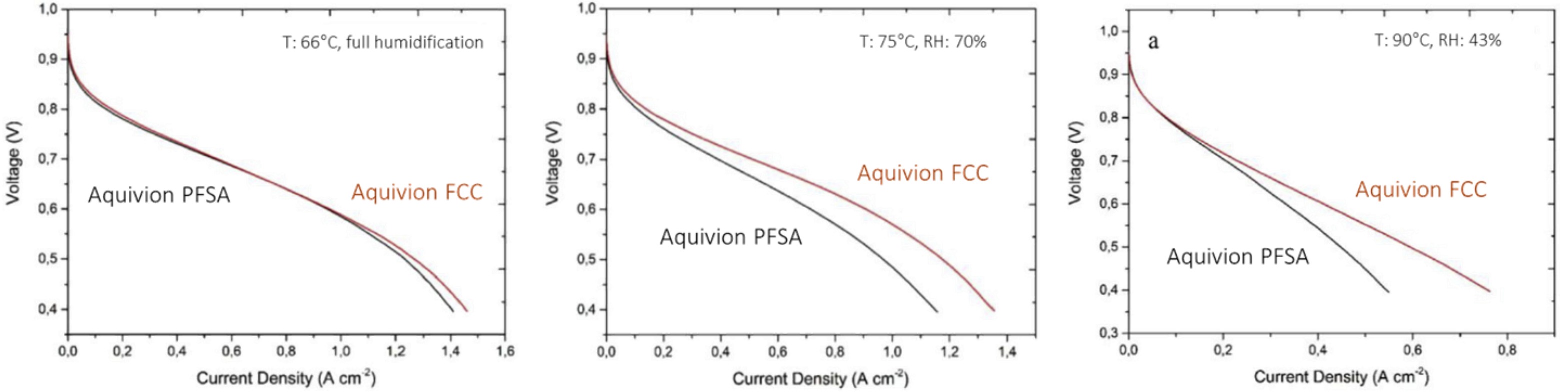


In-Situ Oxygen Permeability Measurement

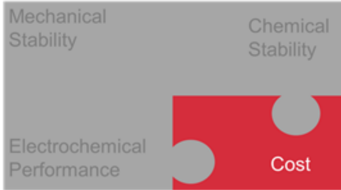


At very high humidity both materials are completely soaked of water thus oxygen transport is already favoured.

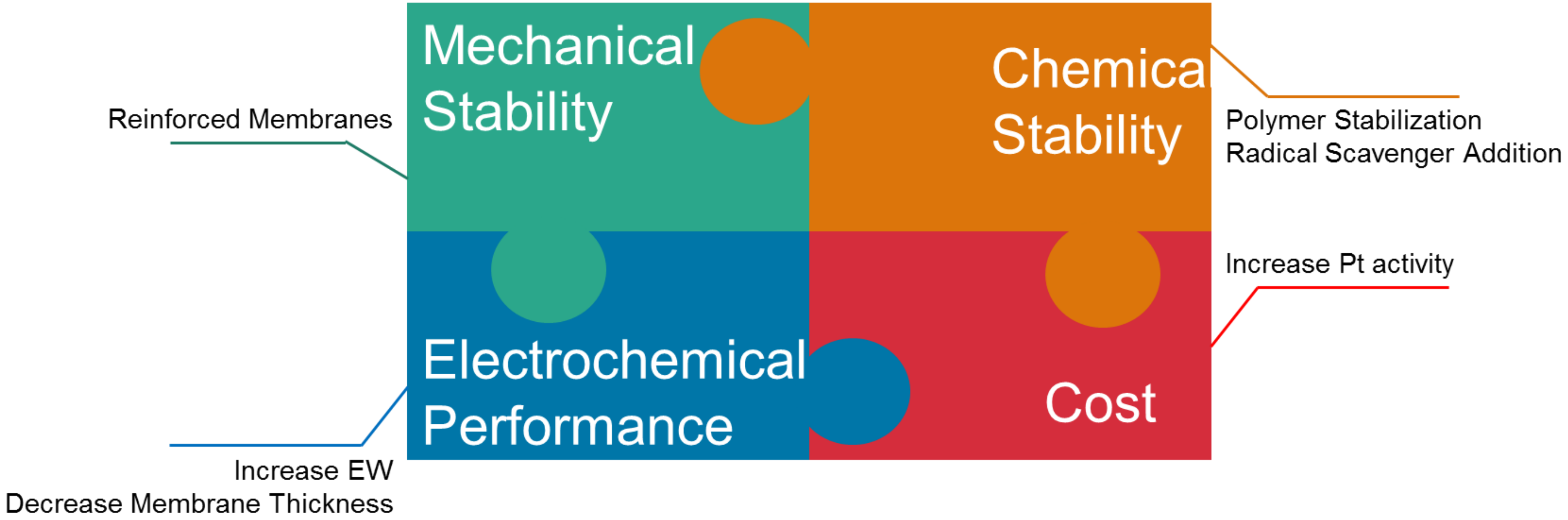
At reduced RH better performance of Aquivion FCC-based system are evident especially in the mass transport region.



Rolfi, A.; Oldani, C.; Merlo, L.; Facchi, A.; Ruffo, R. *J. Power Sources* **2018**, *396*, 95-101.



The Blueprint for Material Development



Thank you.

For further information: claudio.oldani@solvay.com
daniele.facchi@solvay.com

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