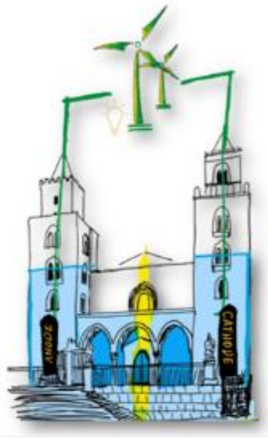


GIORNATE dell' ELETTROCHIMICA ITALIANA

17-21 September 2023, Cefalù, Italy

Innovative ceria nanoparticles decoration for composite Aquivion® proton exchange membranes with improved lifetime

Stucchi, D.*; Ferrari, A. R.*; Caielli, T. *; Stucchi, G. *; Bonizzoni S. *; Mustarelli, P. *

*Università degli Studi di Milano-Bicocca

UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

PERMANENT

The climatic crisis

New green deal

- 2030 — -55% emission
- 2050 — Carbon neutrality
- H_2 — Circular economy

https://youtu.be/JDcro7dPqpA?t=1112

Good news

Hyundai Nexo breaks world record for longest distance travelled in a FCEV

New FCEV in Australia

H_2 Fuel Cell Electric Vehicle

887.5 Km range

3-5 Minutes to refill

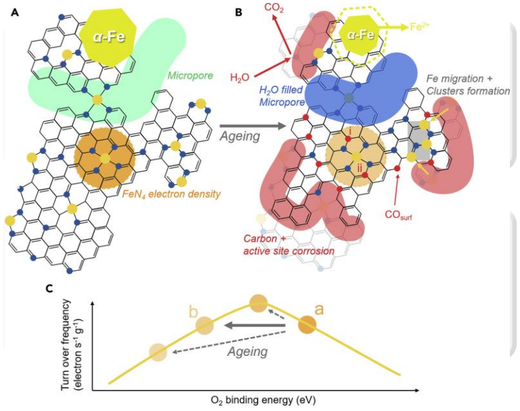
PEM Fuel-Cells

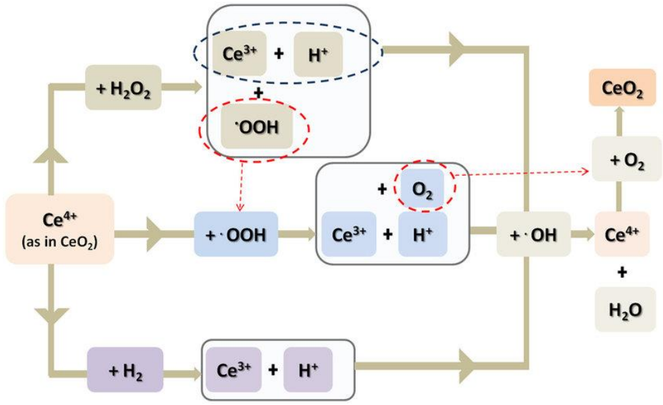
What are their limits?

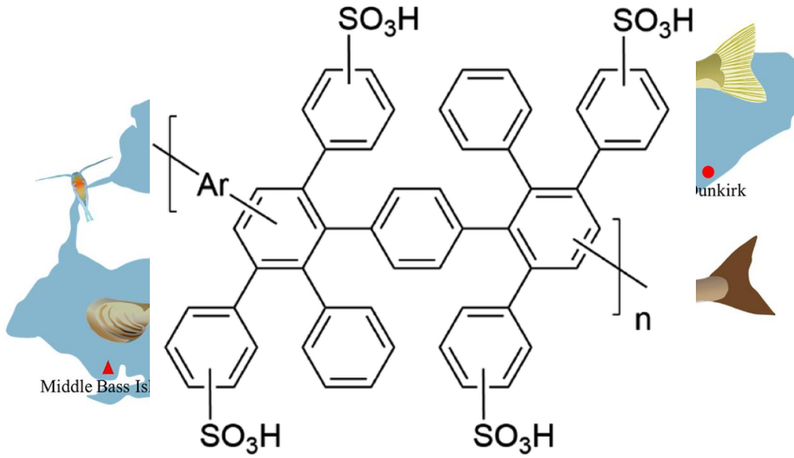
Costly catalysts needed

CeO_2 Limited lifetime

Perfluorinated polymers







https://betterindustrytech/johnson-matthey-and-sibanye-stillwater-form-a-strategic-partnership-to-secure-critical-metals

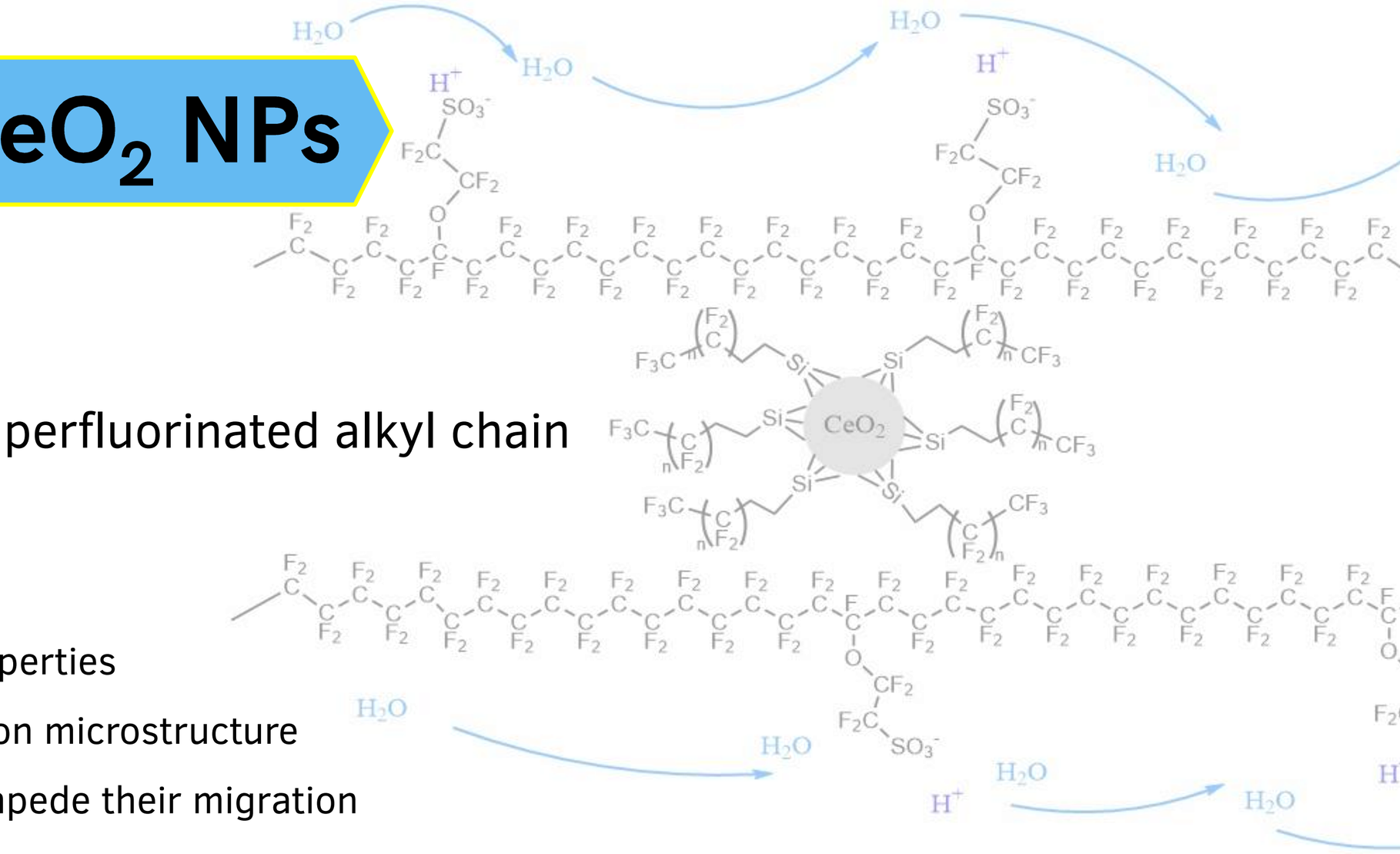
Asset, T., & Atanassov, P. (2020). Joule, 4(1), 33–44.

Rui, Z., & Liu, J. (2020) *Progress in Natural Science: Materials International*, *30*(6), 732–742.

Nguyen, T., Abdin, Z., Holm, T., & Mérida, W. (2021). *Sustainable Energy and Fuels*, *5*(14), 3687–3699.

Britton, B., Holdcroft, S., Vierrath, S., & Breitwieser, M. (2017). *Scientific Reports*, *7*(1), 1–7.

Decorating CeO_2 NPs



Using silanes bearing a perfluorinated alkyl chain

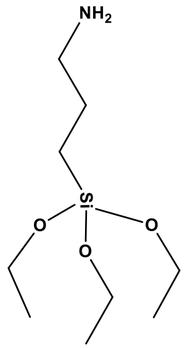
- Higer compatibility
- Improved mechanical properties
- Lower detrimental effect on microstructure
- Anchoring CeO_2 NPs to impede their migration

Maintaining the radical scavenging effect of CeO_2

Silane functionalization

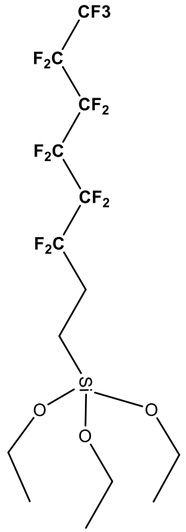
Two silanes were investigated

APTES



(3-AminoPropyl)TriEthoxySilane

PF8EtOS



1H,1H,2H,2H-PerFluoroOctyltriEthoxySilane

Solvent

DMF

Toluene

Ethanol

Conditions

24h

120°C

3:1

Anhydrous

Nano-powders characterization

Pristine and functionalized nanoparticles were compared

01 Thermal characterization: TGA

$$\eta_{-OH} = \frac{2\Delta Wt_{(150-950°C)}}{MW_{H_2O}\, Wt_{CeO_{2(950°C)}}}$$

$$\Delta \mathrm{Wt}_{150-950°\mathrm{C}} = \eta_{silane} \cdot \mathrm{MW_R} + \frac{1}{2} \cdot \left(\eta_{\mathrm{OH}} \cdot \mathrm{Wt}_{\mathrm{CeO_2}(950°\mathrm{C})} - 2\eta_{silane}\right) \cdot \mathrm{MW_{H_2O}} + \frac{1}{2} \cdot \eta_{\mathrm{OH}-silane} \cdot \mathrm{MW_{H_2O}}$$

Mezzomo, L., Bonato, S., Mostoni, S., Di Credico, B., Scotti, R., D'Arienzo, M., Mustarelli, P., & Ruffo, R. (2022). *Electrochimica Acta*, *411*, 140060.

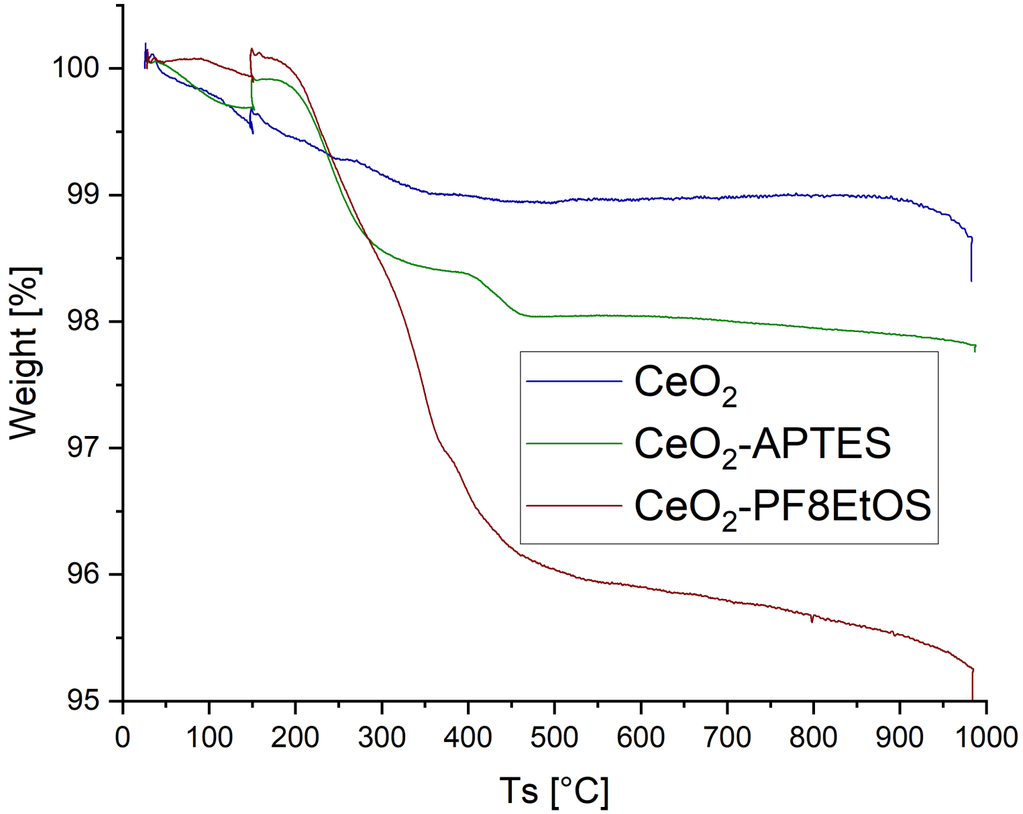
02 Infrared spectroscopy

TGA

$$\eta_{-OH} = \frac{2\Delta Wt_{(150-950°C)}}{MW_{H_2O}\, Wt_{CeO_{2(950°C)}}}$$

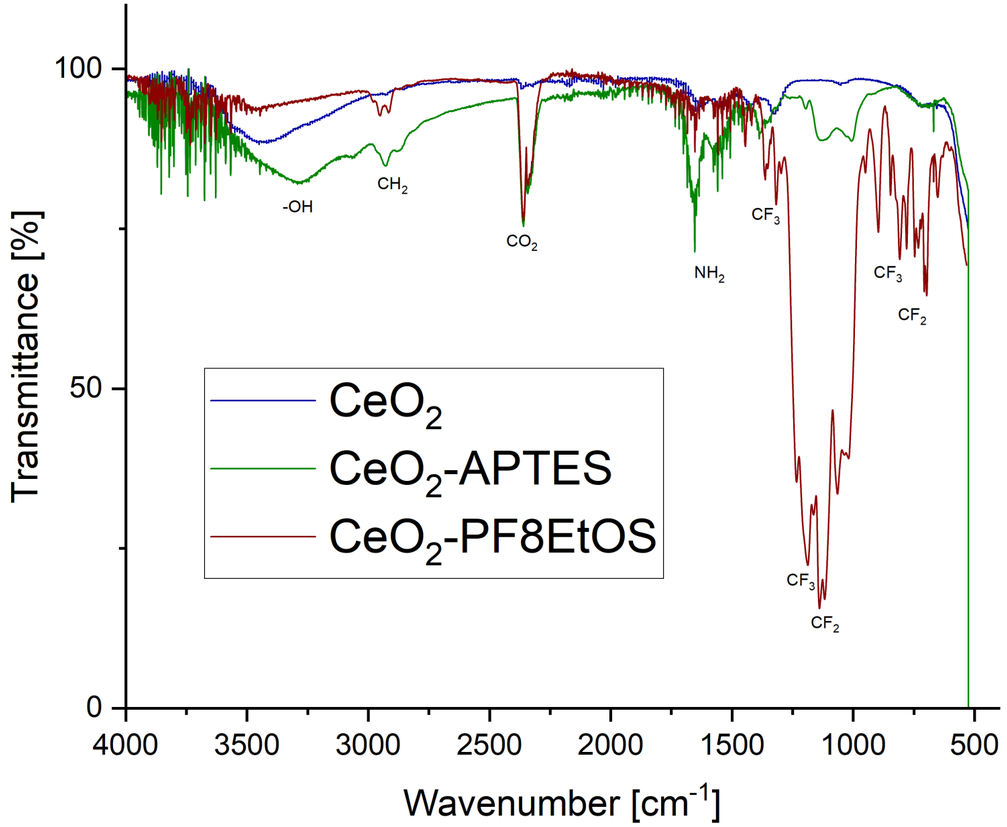
$$\Delta \mathrm{Wt}_{150-950°\mathrm{C}} = \eta_{silane} \cdot \mathrm{MW_R} + \frac{1}{2} \cdot \left(\eta_{\mathrm{OH}} \cdot \mathrm{Wt}_{\mathrm{CeO_2(950°C)}} - 2\eta_{silane}\right) \cdot \mathrm{MW}_{\mathrm{H_2O}} + \frac{1}{2} \cdot \eta_{\mathrm{OH}-silane} \cdot \mathrm{MW}_{\mathrm{H_2O}}$$

	η -OH [mol/g]	η silane [mol/g]
CeO_2	**0.00084**	
CeO_2-APTES		**0.00027**
CeO_2-PF8EtOS		**0.00012**



From 30°C to 1000°C at a speed of 10°C/min with an isotherm of 10 min at 150°C; under 50mL/min air flux

Infrared spectroscopy



Preparation of the nanocomposite membranes

Slight modification of Solvay's casting procedure

Commercial Aquivion®

Commercia D72 dispersion was provided by Solvay.

Adding the NPs

All NPs are dispersed in 7:3 THF:DMF dispersion.

That is also added to Aquivion®_reference

Cast in Petri dishes

Casting were performed both with Dr. Blade and petri dish solvent evaporation.

Drying procedure

I. Overnight at 60°C

II. 5h at 90°C

III. 1h at 190°C

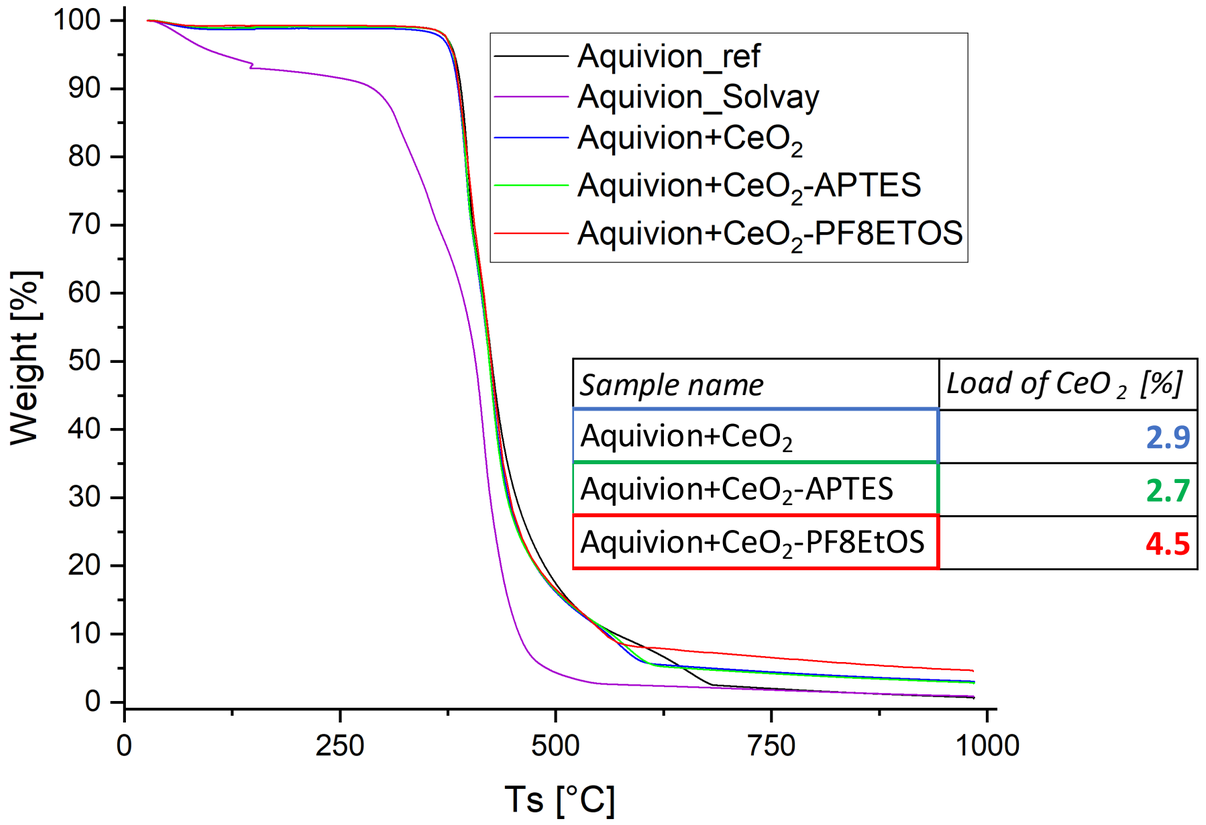
Nanocomposite membrane characterization

Thorough physicochemical characterization

- TGA
- DSC
- XRD
- IR
- Water uptake
- Swelling ratio
- Traction test
- Fenton test
- Conductivity

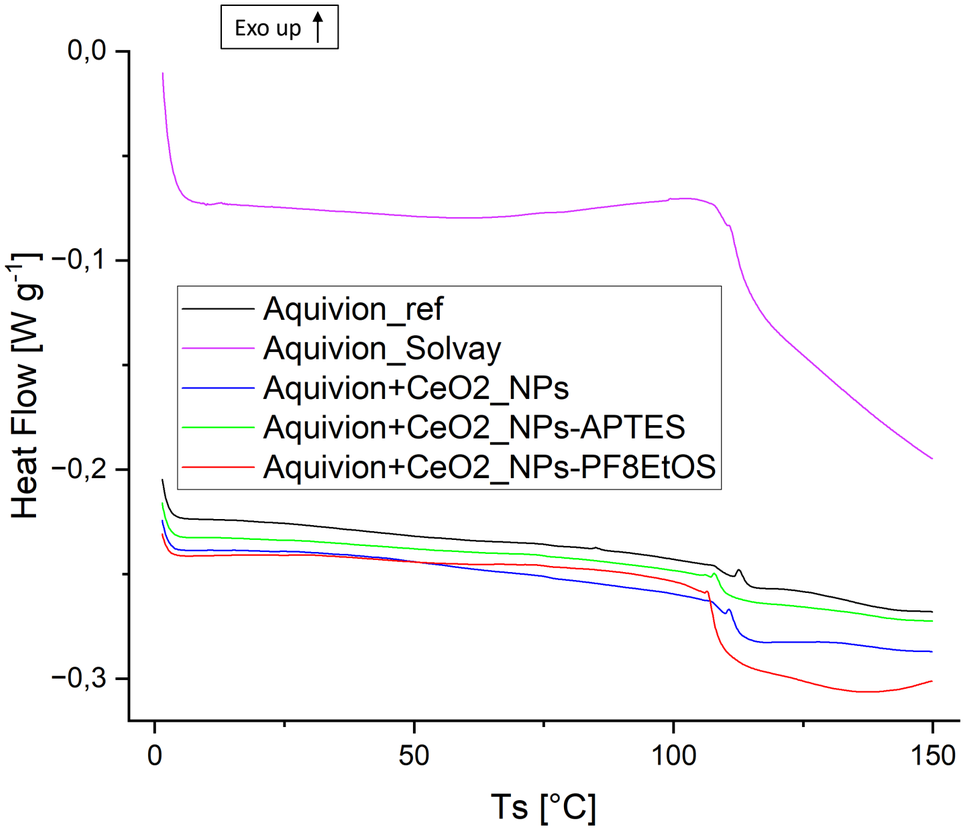
Thermal characterization

TGA



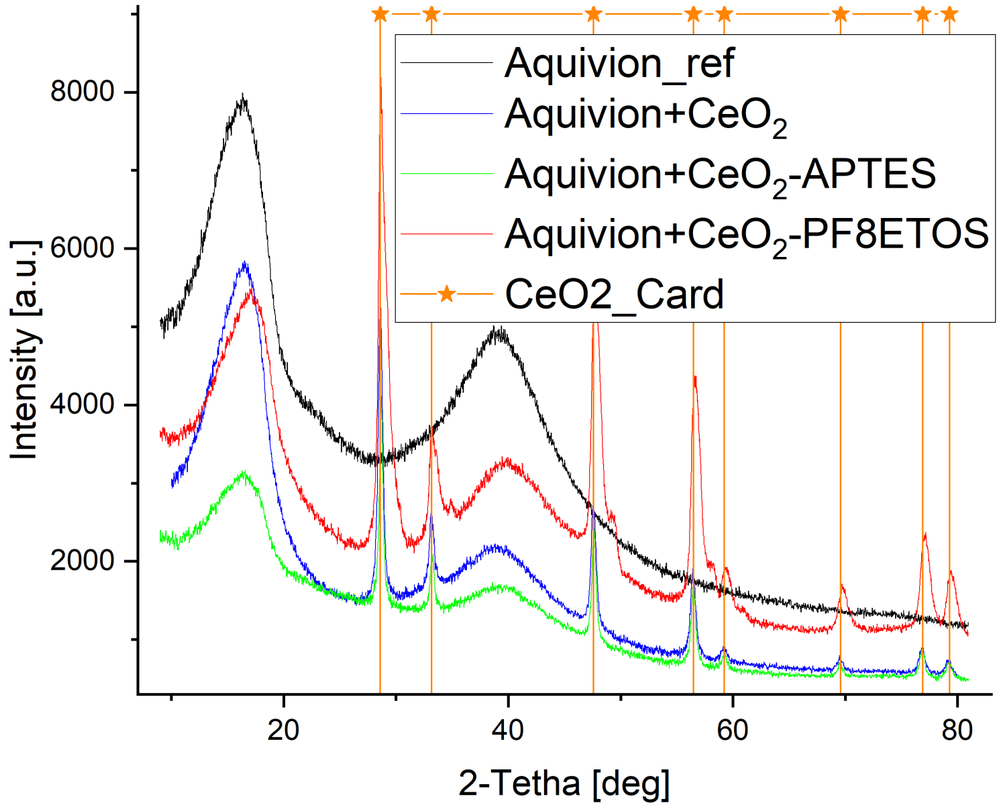
Sample name	*Load of CeO_2 [%]*
Aquivion+CeO_2	2.9
Aquivion+CeO_2-APTES	2.7
Aquivion+CeO_2-PF8EtOS	4.5

DSC

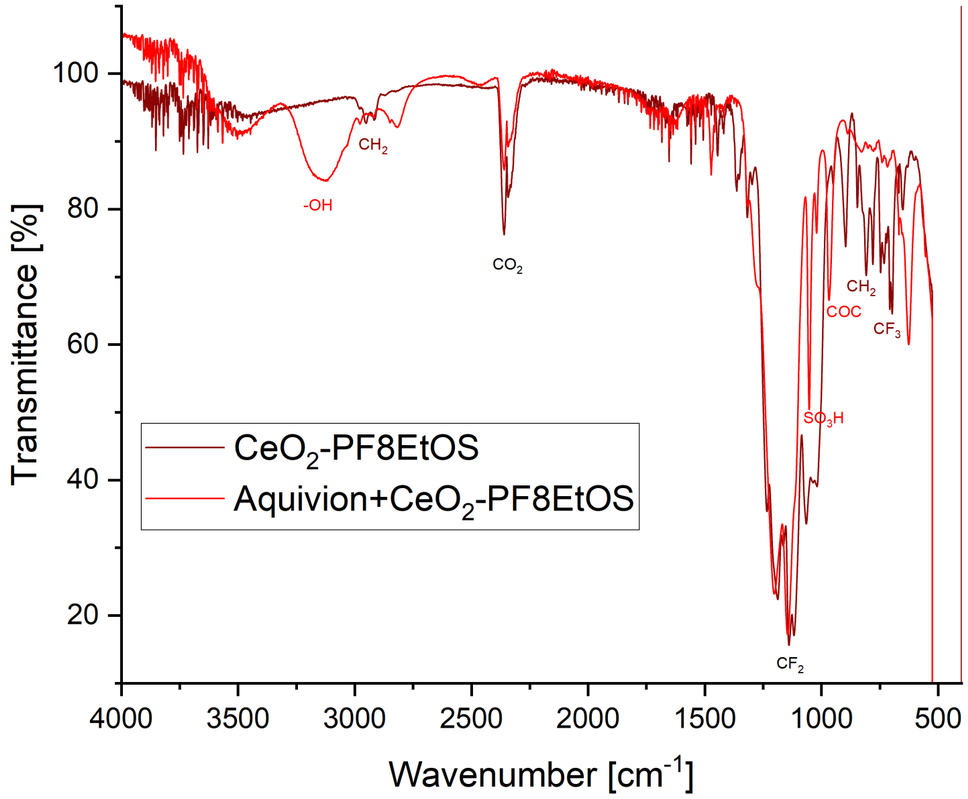


Compositional characterization

XRD

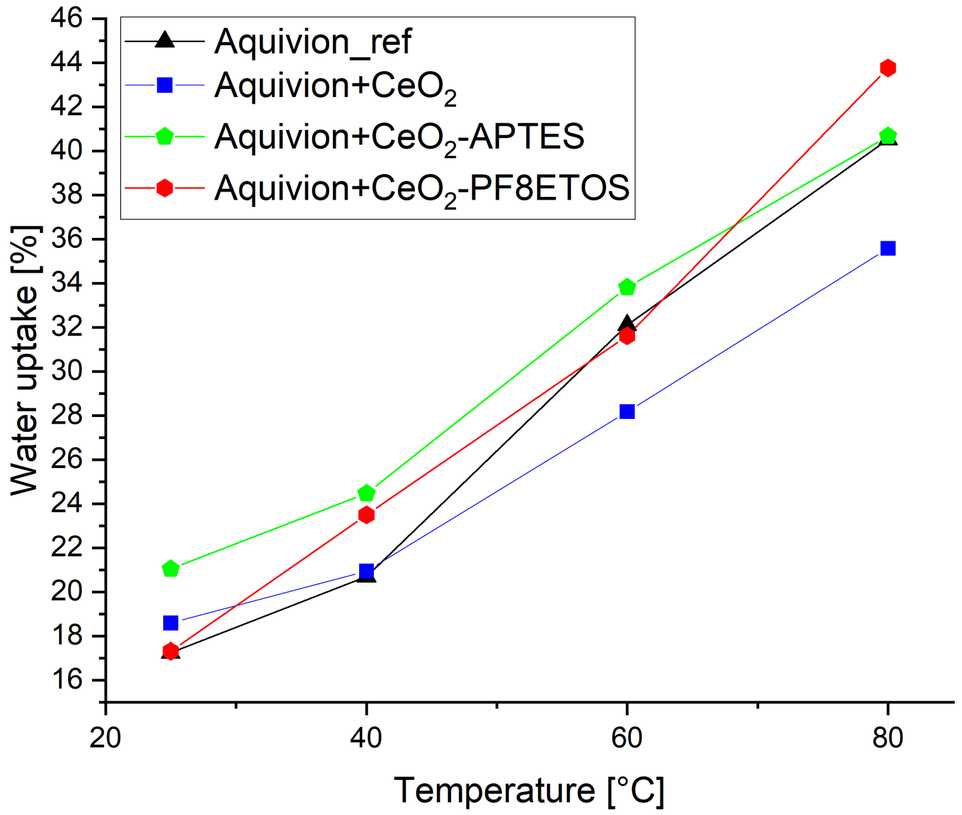


IR

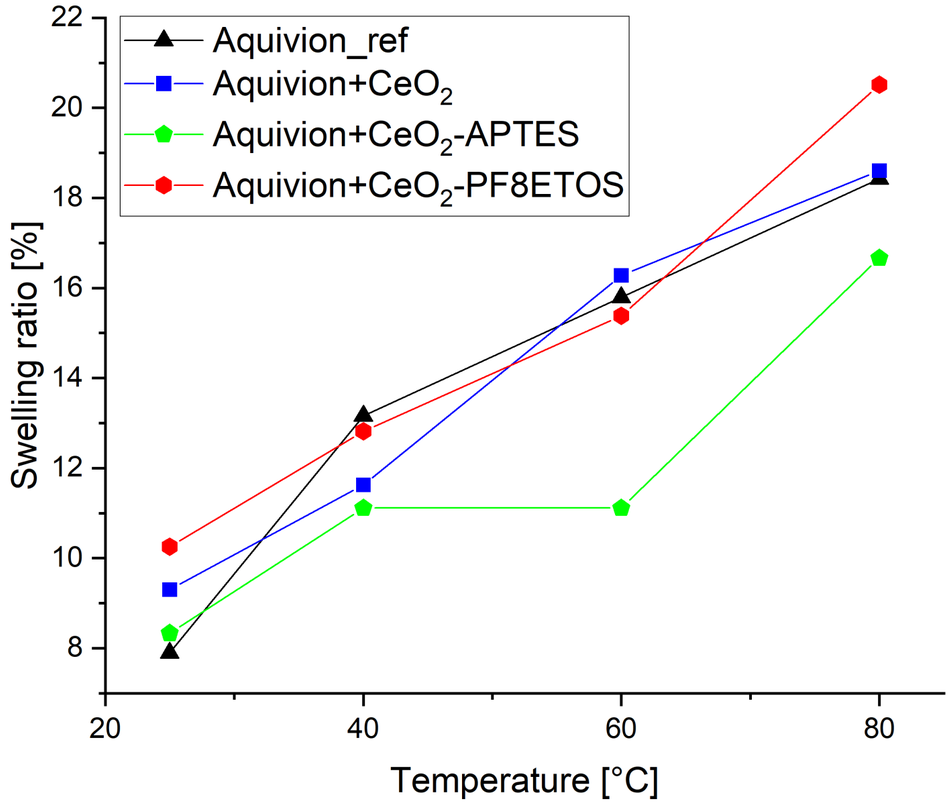


Water management

Water uptake

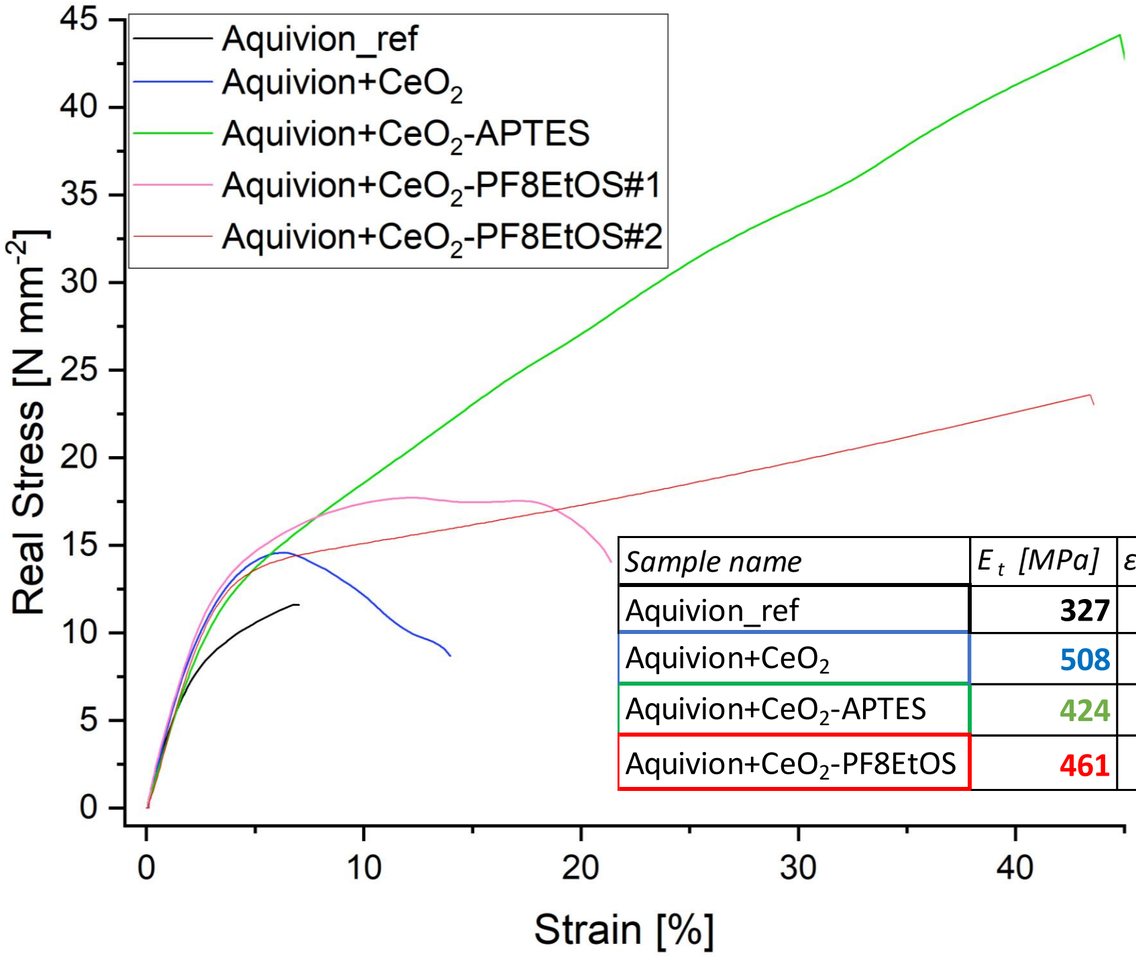


Swelling ratio



Durability tests

Stress-strain curves



Sample name	E_t *[MPa]*	ε_B *[%]*
Aquivion_ref	**327**	**9.4**
Aquivion+CeO_2	**508**	**21**
Aquivion+CeO_2-APTES	**424**	**39.3**
Aquivion+CeO_2-PF8EtOS	**461**	**30.8**

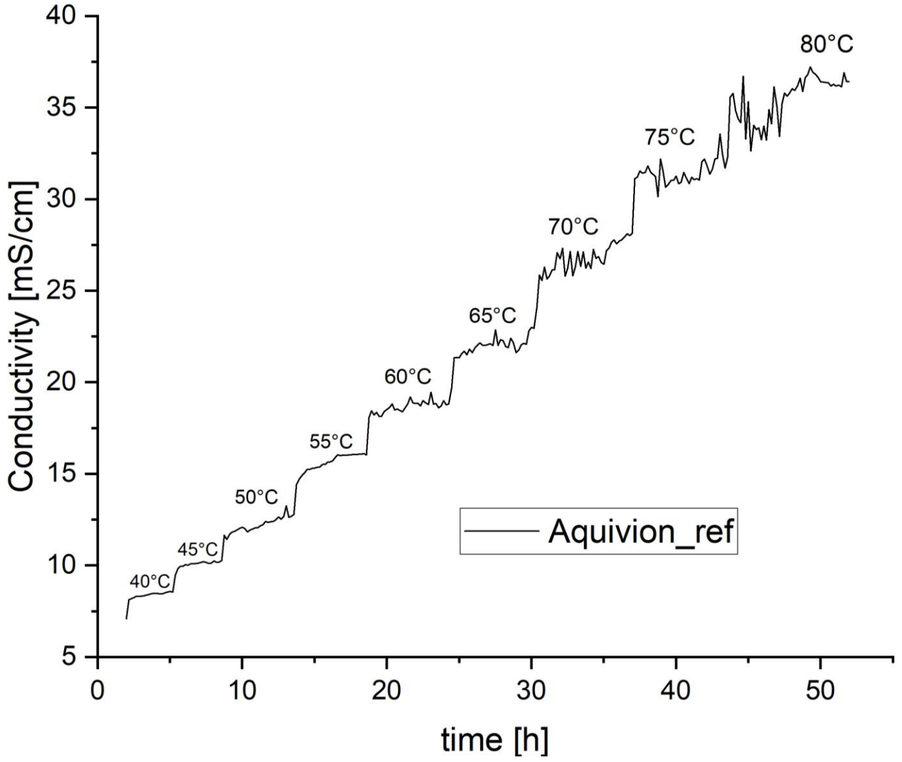
Preliminary Fenton test

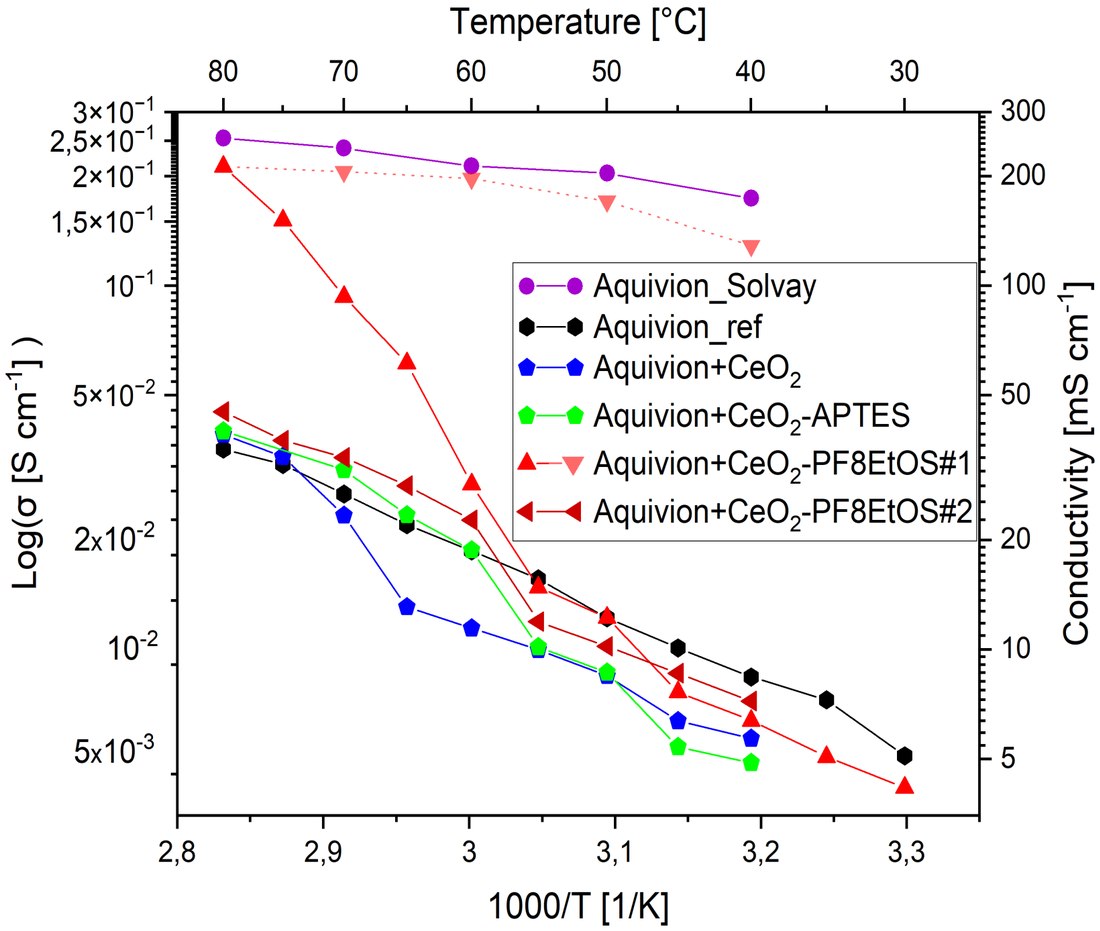
1 week at room temperature in
5mL of 4ppm FeII solution +
15 mL of 30% H_2O_2 wt/wt

Sample name	*Weight loss [%]*
Aquivion ref	**0.61**
Aquivion+CeO_2	**0.52**
Aquivion+CeO_2-APTES	**0.92**
Aquivion+CeO_2-PF8EtOS	**0.28**

Conductivity

4 electrodes DC measurements at 100% RH





Conclusion

The goal was to produce nanocomposite membranes with longer lifetimes and improved properties

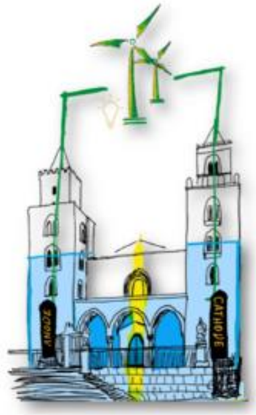
- To asses the radical scavenging effect, a proper Fenton test and accelerated stress test will be conducted.
- Nanocomposite membranes show better mechanical properties than reference; the grafting helps achieve higher elongation before breaking.
- Conductivity proved to be far lower than expected even in the reference membrane.
- This could be ascribed to a detrimental effect the THF:DMF mixture has had on the microstructure of the film.
- To investigate this further analysis will be conducted in the form of time-domain NMR, ^{29}Si NMR, and EDX-SEM imaging.
- Further characterization includes BET on the NPs, as well as IEC measurements and DMA tests on the composite membranes.

Besghini, D., Mauri, M., & Simonutti, R. (2019). T *Applied Sciences*, *9*(9).

Future works

The results are only partial additional research will be conducted on the matter

- Firstly, different treatment on the pristine NPs will be explored in order to obtain a higher decoration.
- New silanes bearing different perfluorinated lateral chains will be investigated to evaluate the effect of chain length.
- The use of surfactants, in place of the THF:DMF mixture, will be explored to disperse the functionalized NPs in the commercial D72 Aquivion®.
- Finally, MEAs will be prepared and tested with the most promising nanocomposite membranes.



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That would be all

Thank you for your attention

I am here for questions