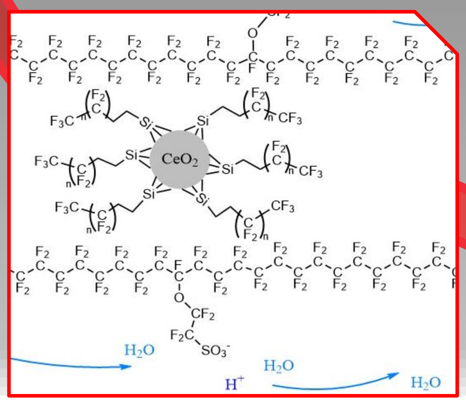
Aquivion®-based nanocomposite proton exchange membranes containing perfluoroalkylic decorated cerium oxide nanoparticles as radical scavengers

Diego Stucchi[I], Antonio Di Tolla[I], Alessandro Ferrari[I], Tommaso Caielli[I], Giulia Stucchi[I], Siro Saronni[I], Mohammad. R. S. Kebria[I], Piercarlo. Mustarelli[I]
d.stucchi7@campus.unimib.it
[I] Department of Material Science, Università degli Studi di Milano Bicocca, Via Cozzi 55, Milano 20125, Italy.

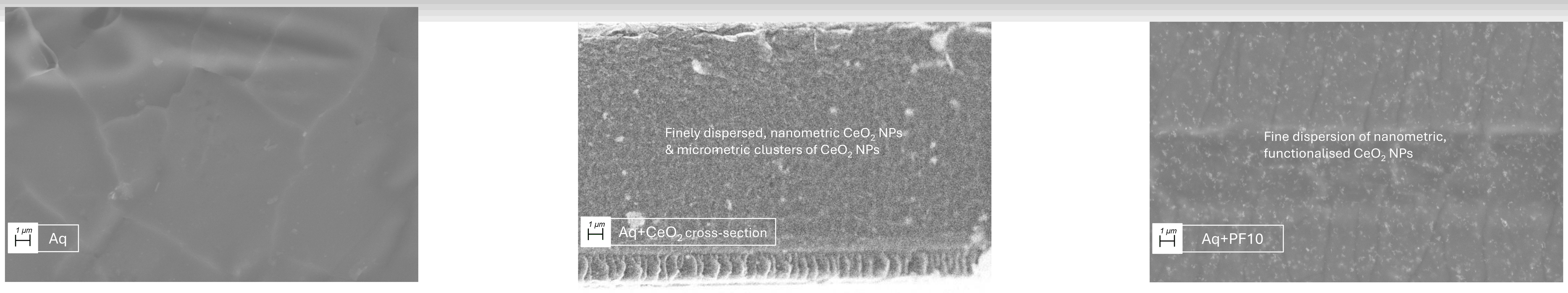
Graphic abstract



Introduction

The main limit of low temperature fuel cells is their relatively low lifetime caused by the degradation of the polymeric chains due to the attack by radical species (•OH, •OOH) generated at the cathode[1]. The best strategy to improve the device's lifetime is the introduction of radical scavenger species in the Membrane Electrode Assembly (MEA)[2]. To enhance the compatibility between the inorganic filler and the organic polymeric matrix, we fabricated, trough a grafting of the nanoparticles surface with organosilanes, CeO_2 NPs decorated with 4 different fluorinated moieties. This is expected to anchor them in the hydrophobic domain of the membrane; causing a lower disturbance on the delicate ionic channel network, while also possibly acting as a physical cross-linker and slowing down the oxide dissolution expected in the strongly acidic environment of the PEM. To do so, we dispersed both pristine and functionalized nanoparticles in an Aquivion® matrix.

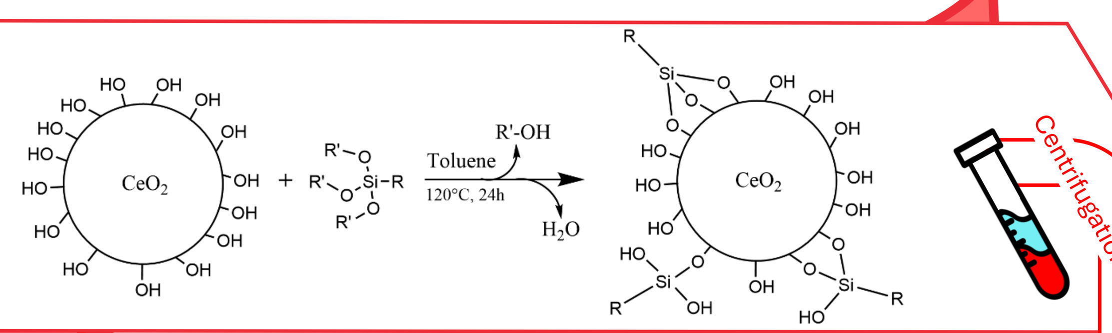
The membranes were characterized as far as the physico-chemical and functional properties are concerned.

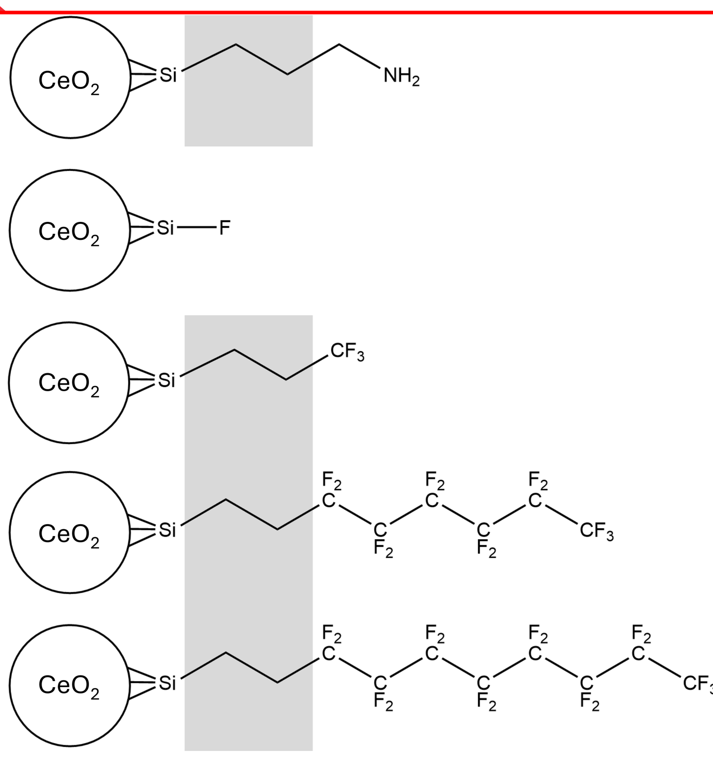


SEM images show a uniform distribution of CeO_2 NPs both in- and trough-plane, clusters can also be seen; however, sub-micrometric particles are also visible.

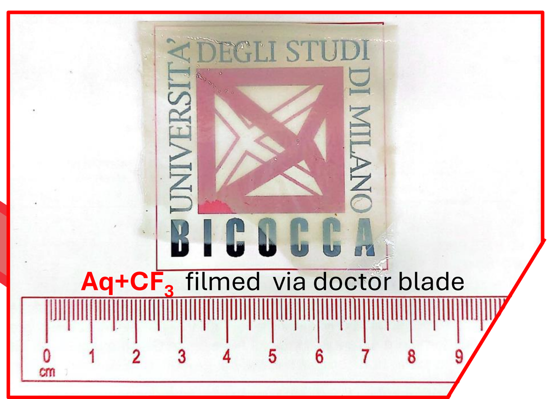
Nanoparticles functionalisation

Commercial CeO_2 NPs (25nm diameter) were decorated with different organosilanes. Here below are reported the reaction conditions.





Complete name	Short name
AminopropylSilane @ CeO_2	CeO_2+Si-NH_2
FluoroSilane @ CeO_2	CeO_2+SiF
TriFluoropropylSilane @ CeO_2	CeO_2+Si-CF_3
1H,1H,2H,2H-PerFluoroOctylSilane @ CeO_2	CeO_2+Si-PF8
1H,1H,2H,2H-PerFluoroDecylSilane @ CeO_2	CeO_2+Si-PF10



Membrane preparation

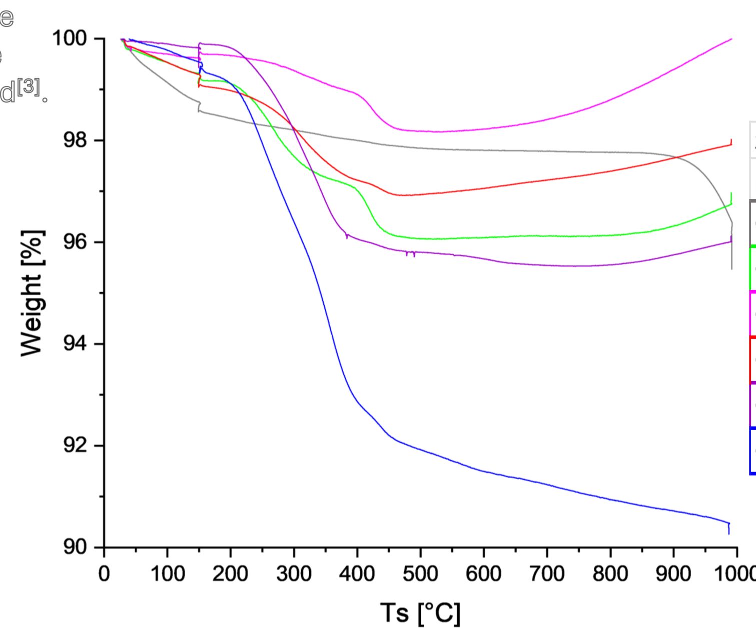
- Aquivion® → Aq
- Aquivion®+CeO_2 → Aq+CeO_2
- Aquivion®+CeO_2+Si-NH_2 → Aq+NH_2
- Aquivion®+ CeO_2+SiF → Aq+F
- Aquivion®+ CeO_2+Si-CF_3 → Aq+CF_3
- Aquivion®+CeO_2+Si-PF8 → Aq+PF8
- Aquivion®+CeO_2+Si-PF10 → Aq+PF10

Substance	Amount [%]
Aquivion®	19.8
Water	50
1-propanol	24.8
$DMSO_2$	4.5
NPs	1.0

Physicochemical characterization

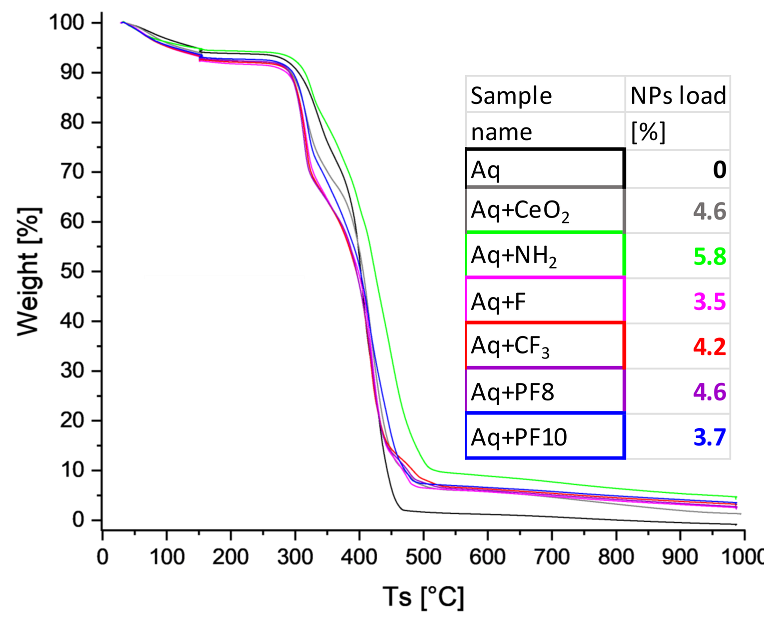
-OH groups on the surface of CeO_2 NPs, needed for the 1:3 stoichiometry in the decoration, are derived[3].

Surface coverage S.C is calculated from BET surface area.



Sample name	Grafting [%]	S.C. [$mmol/cm^2$]
CeO_2	/	5.31
CeO_2+Si-NH_2	50.9	2.70
CeO_2+SiF	73.7	3.92
CeO_2+Si-CF_3	16.5	0.88
CeO_2+Si-PF8	11.4	0.61
CeO_2+Si-PF10	19.0	1.01

The weight loss of functionalised NPs is correlated to the quantity of silanes grafted on them[3]. Normalisation on the quantity of –OH groups gives the grafting %.

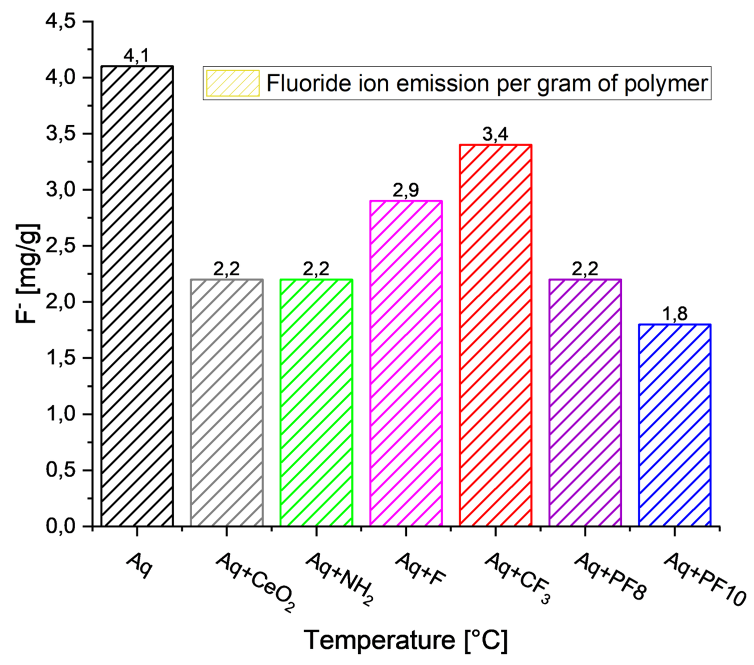


Sample name	NPs load [%]
Aq	0
Aq+CeO_2	4.6
Aq+NH_2	5.8
Aq+F	3.5
Aq+CF_3	4.2
Aq+PF8	4.6
Aq+PF10	3.7

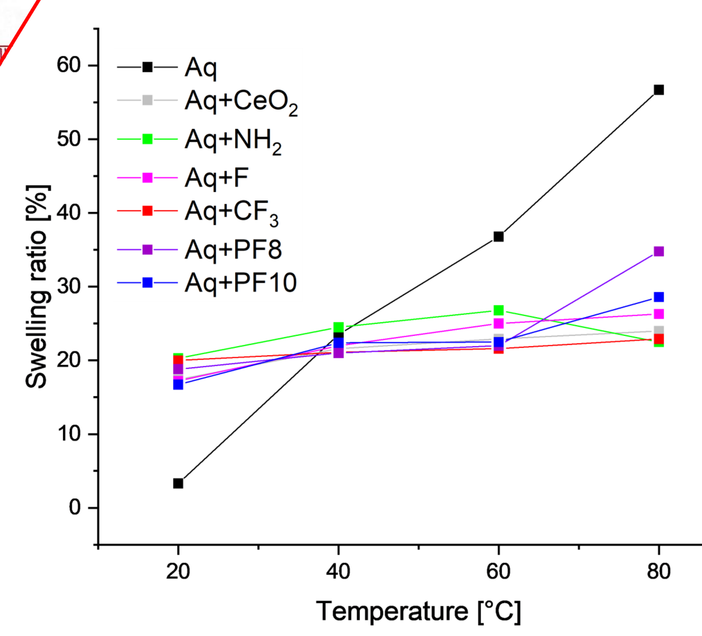
The residual weight of nanocomposite membranes at 1000 °C indicates the NPs loading; it was aimed at 5 % wt/wt.

Fenton test was carried out by immersing the membranes in 20 mL of 1:1 Vol/Vol mixture of 30% wt/wt H_2O_2 and 400 ppm Fe^{II} in pH 4 $H_2SO_{4(aq)}$ solution for 4 h at 80 °C.

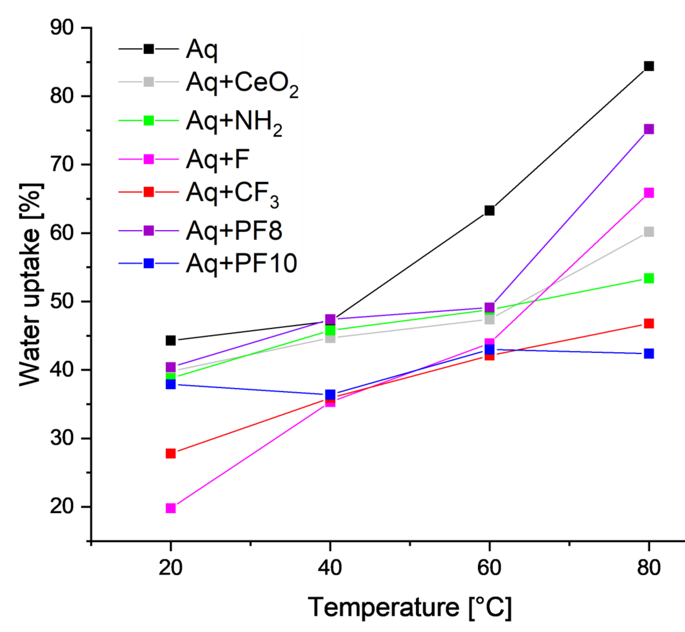
A reduction of roughly 50 % in the amount of F^-, generated as a result of the attack on the polymeric matrix of radical species, happened in most nanocomposite membranes.



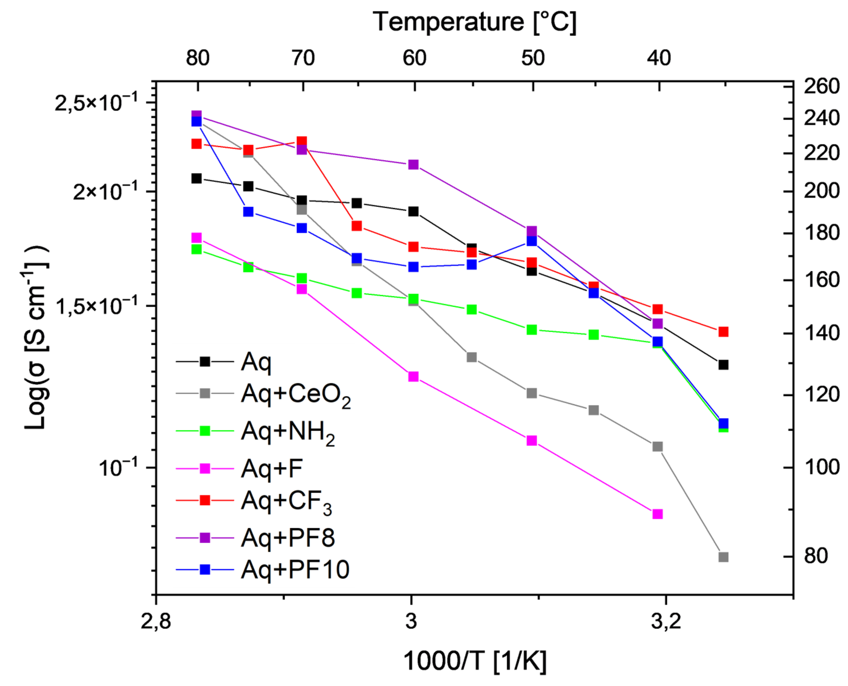
Functional characterization



Water management measurements show a lower S.R. in nanocomposite membranes when compared to pure Aquivion®, as temperature increases.



Meanwhile W.U. values are comparable, albeit lower.



In plane protonic conductivity is comparable to **Aq**, especially in samples with fluorinated NPs.

Conclusion & further prospects

We have successfully decorated the surface of commercial nanoparticles of cerium oxide with different organosilanes, as proved by TGA analysis, four of which carry fluorinated moieties to improve the compatibility with the polymer. With those, we fabricated 7 Aquivion®-based membranes, six of which are nanocomposite, loaded with 4-5% radical scavenger. The dispersion of filler proved to be homogeneous, and the PEMs are more resilient to the attack of radical species, particularly the ones decorated with the longer perfluorinated chains. All nanocomposite samples also suffer from a lower S.R., especially at higher temperature, when compared to pure Aquivion® membranes, while absorbing a similar amount of water and achieving values of conductivity comparable to pure Aquivion®. Once again, this is particularly true in the case of membranes with particles decorated with fluorinated NPs, thus proving our hypothesis of causing a lower disturbance on the ionic channels network correct. The preparation of a CCM and performing some tests in an actual Fuel cell setup are the next step or our research, paired with a more in depth-study on the fluoride emission in Fenton reagent overtime.

References

[1] Ren et al. Prog. Energy Combust. Sci. 2020, 80, 100859
[2] Akrout et al. Membranes. 2020, 10, 208
[3] Mezzomo et al. Electrochim. Acta. 2022, 411, 140060

Acknowledgments

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