Cerium oxide nanoparticles decorated with different perfluoroalkyl silanes as radical scavengers in Aquivion®-based composite PEMFC

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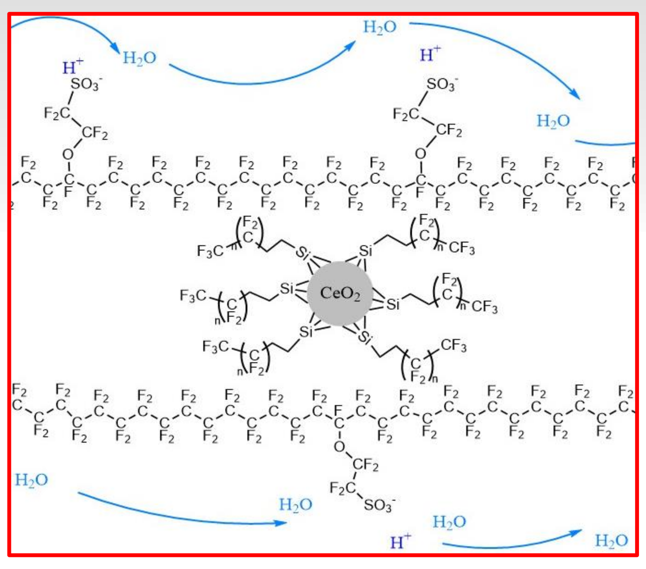
Introduction

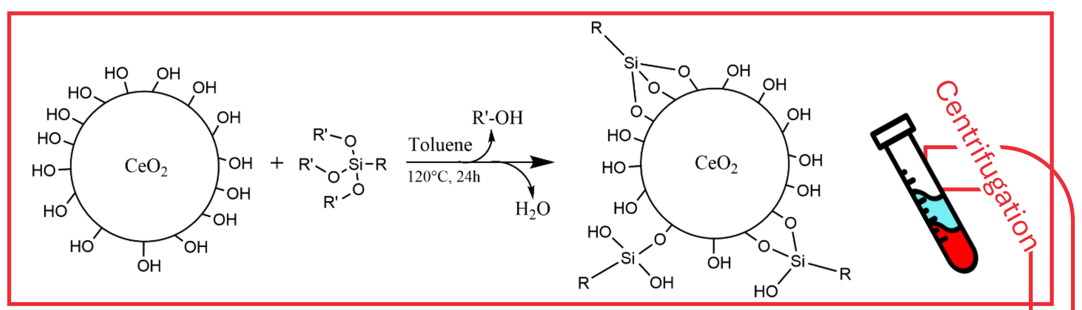
The main limit of polymer fuel cells is their relatively low lifetime caused by the degradation of the polymeric chains[1] due to the attack by radical species (•OH •OOH) generated at the cathode. The best strategy to improve the device's lifetime is the introduction of radical scavenger species in the membrane electrode assembly (MEA)[2]. To improve 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 perfluoroalkyl chains. This is expected to anchor them in the hydrophobic domain of the membrane; causing a lower disturbance on the delicate ionic channel network. We then dispersed both pristine and functionalized NPs in an Aquivion® matrix and characterized the nanocomposite membranes obtained this way physicochemically as well as from a more functional point of view.

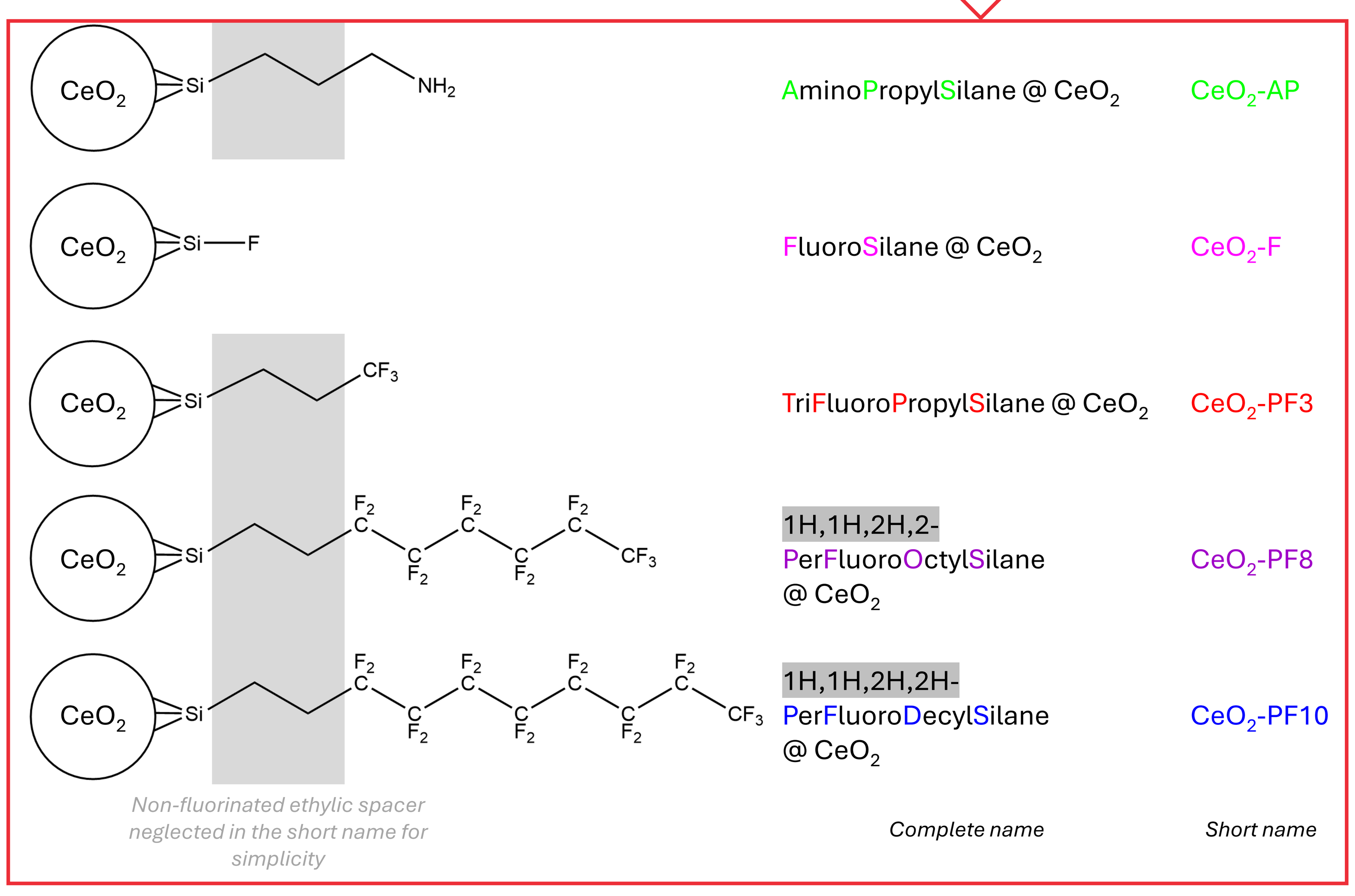
Graphical abstract



Nanoparticles functionalization

The surface of commercial CeO_2 NPs was decorated with different organosilanes. The simplified reaction scheme is reported below





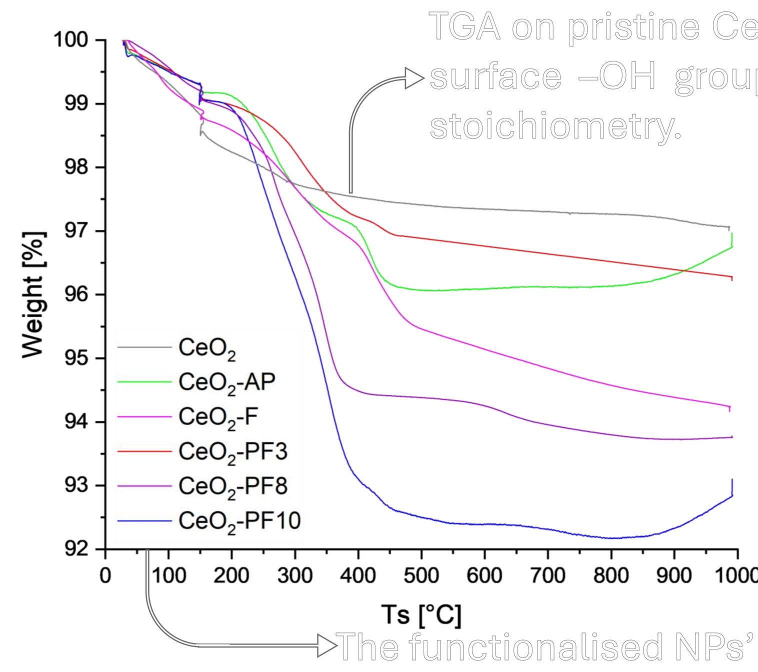
Membrane preparation

- Aquivion® for reference→ **Aq**
- Aquivion®+CeO_2 NPs → **Aq+CeO_2**
- Aquivion®+CeO2-AP → **Aq+APS**
- Aquivion®+CeO2-F → **Aq+FS**
- Aquivion®+CeO2-PF3 → **Aq+PF3**
- Aquivion®+CeO2-PF8 → **Aq+PF8**
- Aquivion®+CeO2-PF10 → **Aq+PF10**

Substance	Amount [%]
Aquivion®	19.8
Water	50
1-propanol	24.8
DMSO2	4.5
NPs	1

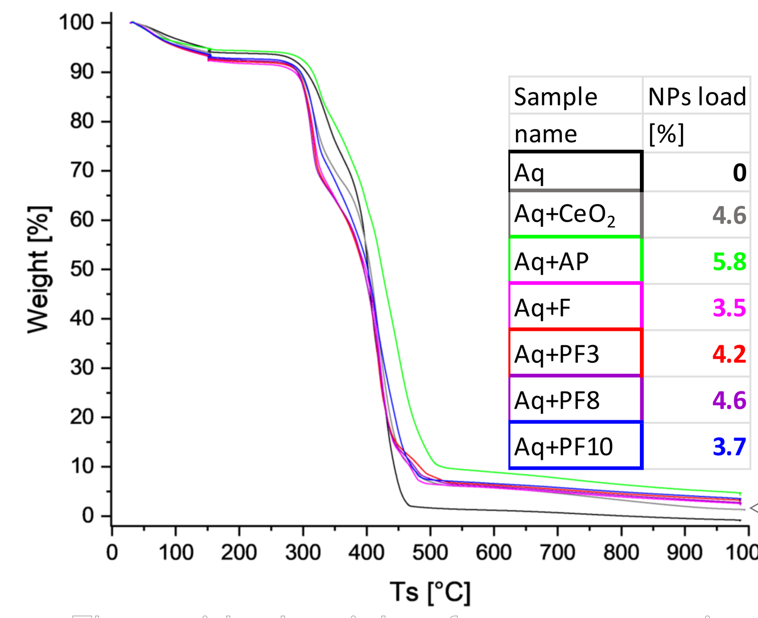
Physicochemical characterization

TGA on pristine CeO2 NPs gives the amount of surface –OH groups, used for the decoration stoichiometry.



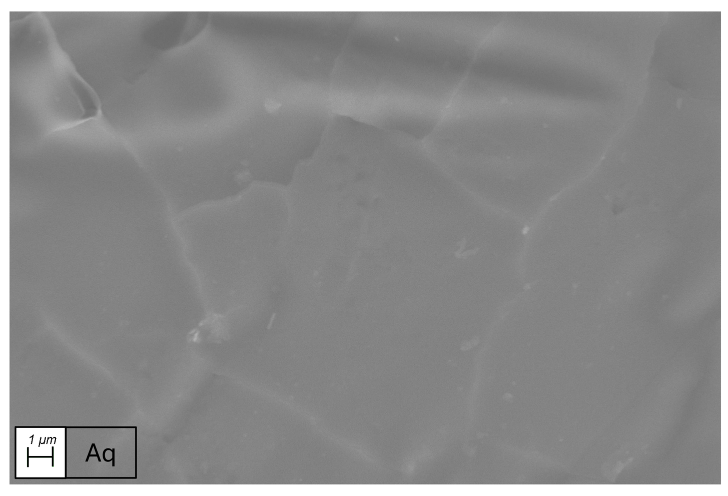
Sample name	η -OH [mol/g]	η -OH [mol]	η Silane [mol/g]	Grafting [%]
CeO_2	9.4E-04	/	/	/
CeO_2-AP	9.4E-04	2.7E-06	4.7E-04	49.9
CeO_2-F	9.4E-04	6.1E-06	7.4E-04	78.5
CeO_2-PF3	9.4E-04	2.2E-06	1.5E-04	15.7
CeO_2-PF8	9.4E-04	1.8E-06	1.1E-04	12.0
CeO_2-PF10	9.4E-04	6.7E-07	1.4E-04	14.9

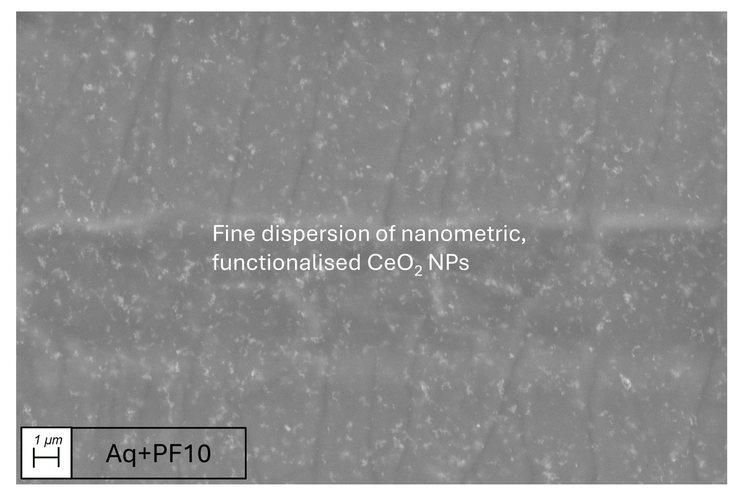
The functionalised NPs' TGA gives the grafting %.



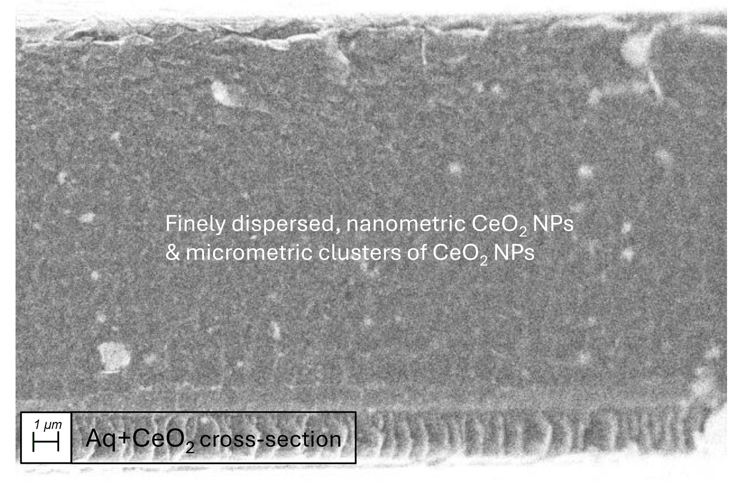
Sample name	NPs load [%]
Aq	0
Aq+CeO_2	4.6
Aq+AP	5.8
Aq+F	3.5
Aq+PF3	4.2
Aq+PF8	4.6
Aq+PF10	3.7

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





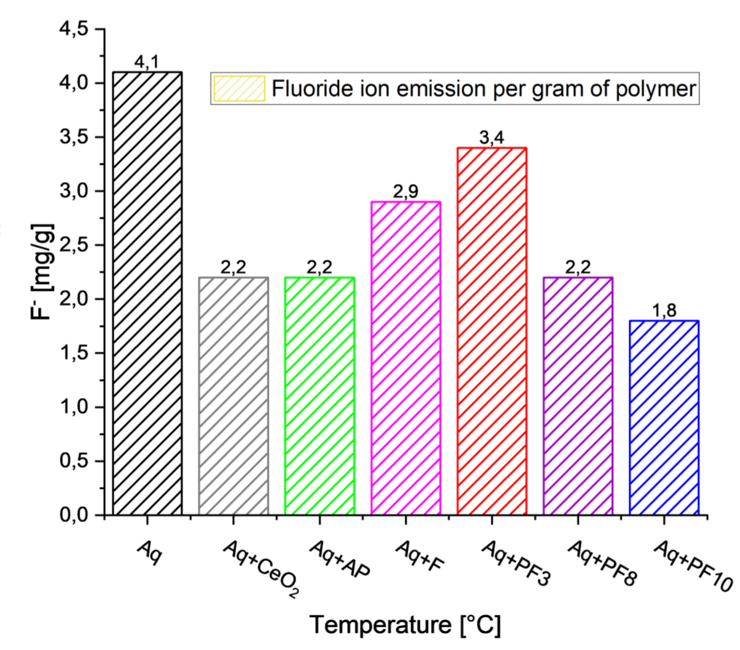
SEM images show the uniform distribution of CeO_2 NPs (as proven by EDX analysis), both in- and trough-plane, within the polymeric matrix.

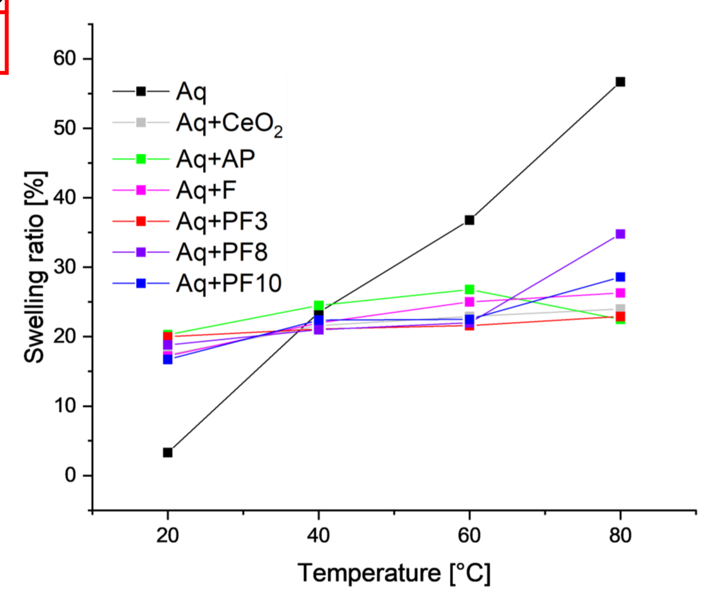


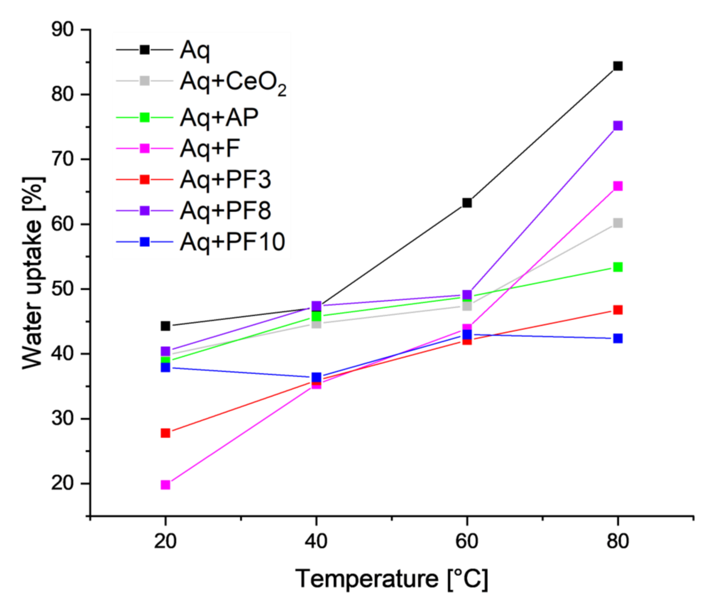
Functional characterization

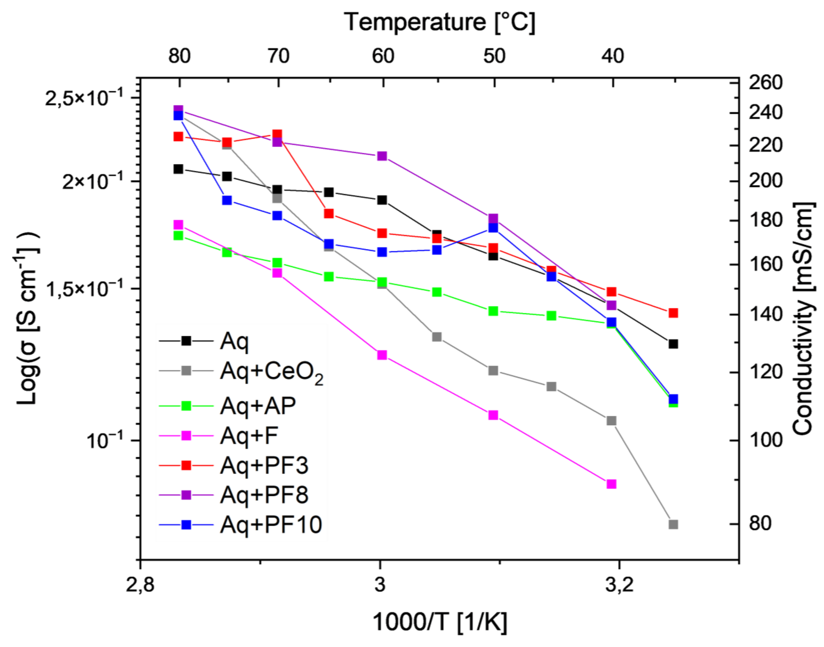
Fenton test was carried out by immersing the membranes in 20 mL of 1:1 vol/vol solution of 30% wt/wt H_2O_2 and 400ppm Fe^{III} in pH 4 $H_2SO_{4\,(aq)}$ solution for 24h at 80°C.

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









Water management measurements show a lower S.R., as temperature increases, in nanocomposite membranes when compared to pure Aquivion®, despite comparable values of W.U. Conductivity values are always above 170 mS cm-1 at 80°C.

Conclusion & further prospects

In summary, 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 filler. These proved to be homogeneous and more resilient to the attack of oxygen radical species , especially the ones decorated with the longer perfluorinated chain. All nanocomposite samples also suffer a lower amount of geometrical deformation, especially at higher temperature, when compared to pure Aquivion® membranes, while absorbing a similar amount of water and thus achieving values of conductivity comparable to pure Aquivion® membrane ranging from roughly 80 mS cm^{-1} at 40°C, in worst cases, to over 200 mS cm^{-1} at 80°C in the best samples.

References

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

Acknowledgements

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RICERCA E SVILUPPO SULL'IDROGENO lettera A.