

Decoration of CeO₂ nanoparticles radical scavengers with innovative anchoring groups in Aquivion[®]-based Proton Exchange Membranes

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Perm^{ment}

The climatic crisis



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

New green deal



2030

-55% emission

2050

Carbon neutrality

H₂

Circular economy



PEM Fuel-Cells

What are their limits?



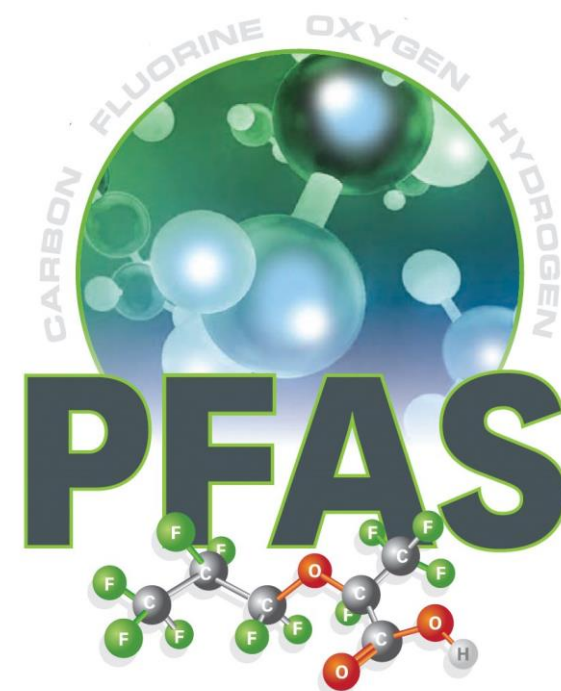
Costly catalysts needed

44 Ruthenium Ru 101.07 2334	45 Rhodium Rh 102.906 1963	46 Palladium Pd 106.42 1555
76 Osmium Os 190.23 3033	77 Iridium Ir 192.22 2446	78 Platinum Pt 195.08 1769

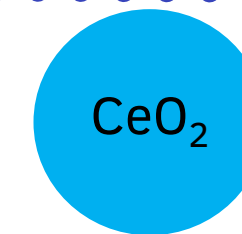
<https://batteryindustry.tech/johnson-matthey-and-sibanye-stillwater-form-a-strategic-partnership-to-secure-critical-metals/>



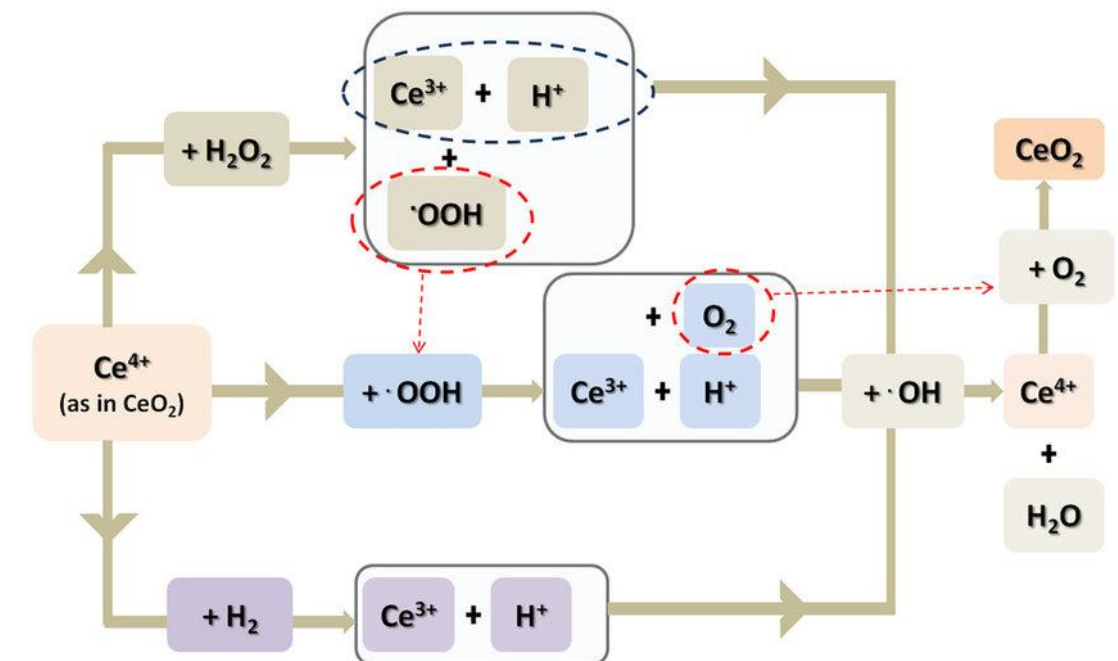
Perfluorinated polymers



<https://www.rubbernews.com/pfas/rubber-division-association-rubber-products-manufacturing-plan-pfas-programming>



Limited lifetime



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



Decorating CeO₂ NPs

Using silanes bearing a perfluorinated alkyl chain

- Higher compatibility
- Improved mechanical properties
- Lower detrimental effect on microstructure
- Anchoring CeO₂ NPs to impede their migration

Maintaining the radical scavenging effect of CeO₂



Nano-powders characterization

01

Thermal characterization: TGA

$$\eta_{-OH} = \frac{2\Delta Wt_{(150-950^{\circ}C)}}{MW_{H_2O} Wt_{CeO_2(950^{\circ}C)}}$$

$$\Delta Wt_{150-950^{\circ}C} = \eta_{silane} \cdot MW_R + \frac{1}{2} \cdot (\eta_{OH} \cdot Wt_{CeO_2(950^{\circ}C)} - 2\eta_{silane}) \cdot MW_{H_2O} + \frac{1}{2} \cdot \eta_{OH-silane} \cdot MW_{H_2O}$$

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

Pristine and functionalized nanoparticles were compared

02

Infrared spectroscopy

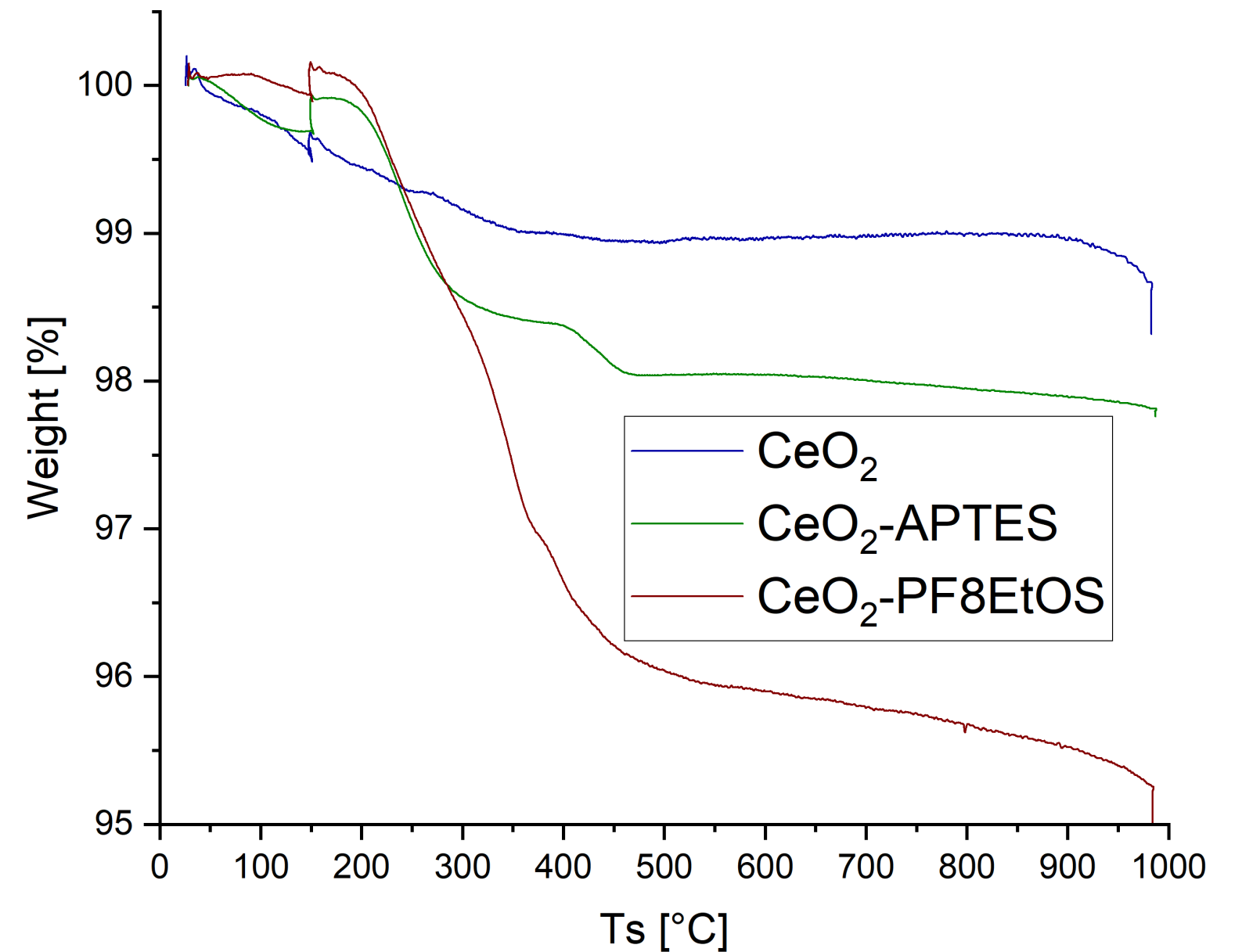


TGA

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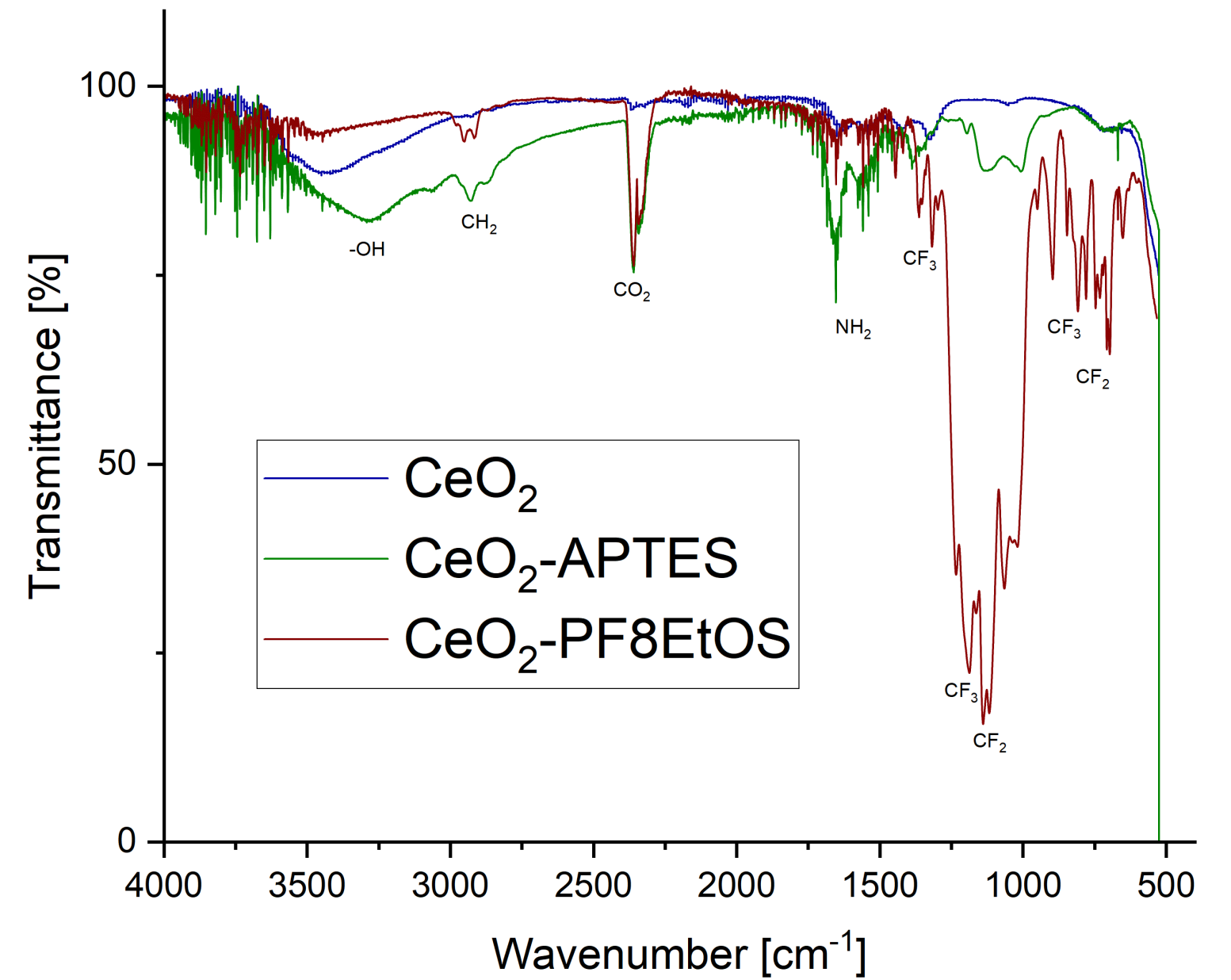
	η_{-OH} [mol/g]	η_{silane} [mol/g]
CeO ₂	0.00084	
CeO ₂ -APTES		0.00027
CeO ₂ -PF8EtOS		0.00012



From 30°C to 1000°C at a speed of 10°C/min with an isotherm of 10 min at 130°C; under 50mL/min air flux



Infrared spectroscopy



Preparation of the nanocomposite membranes



Slight modification of Solvay's casting procedure



Commercial Aquivion®

Commercial D72 dispersion was provided by Solvay



Cast in Petri dishes

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



Adding the NPs

Functionalized and un-functionalized NPs are dispersed in 7:3 THF:DMF dispersion.

This is also added to pristine Aquivion® dispersion for control



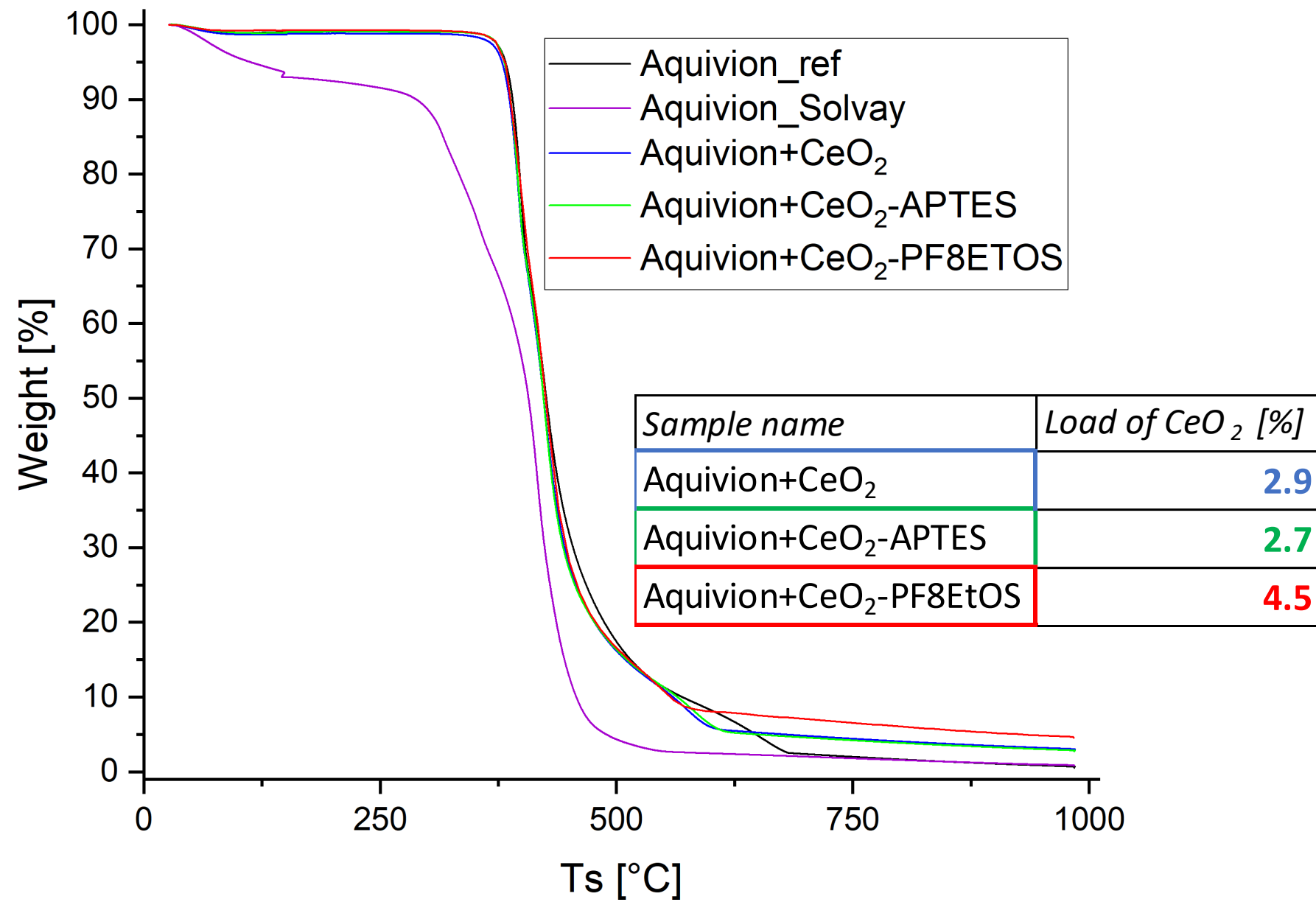
Drying procedure

- I. Overnight at 60°C
- II. 5h at 90°C
- III. 1h at 190°C

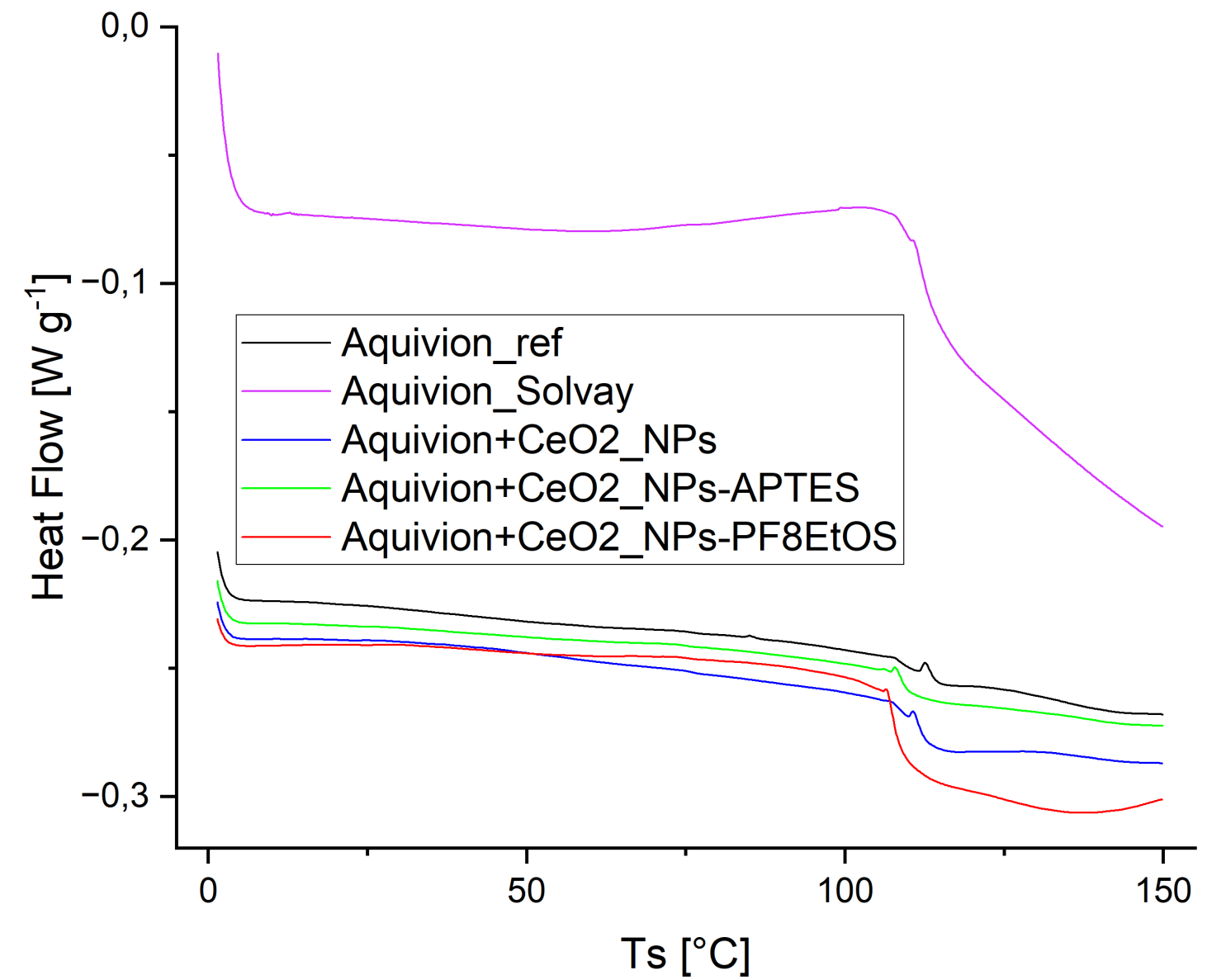


Thermal characterization

TGA

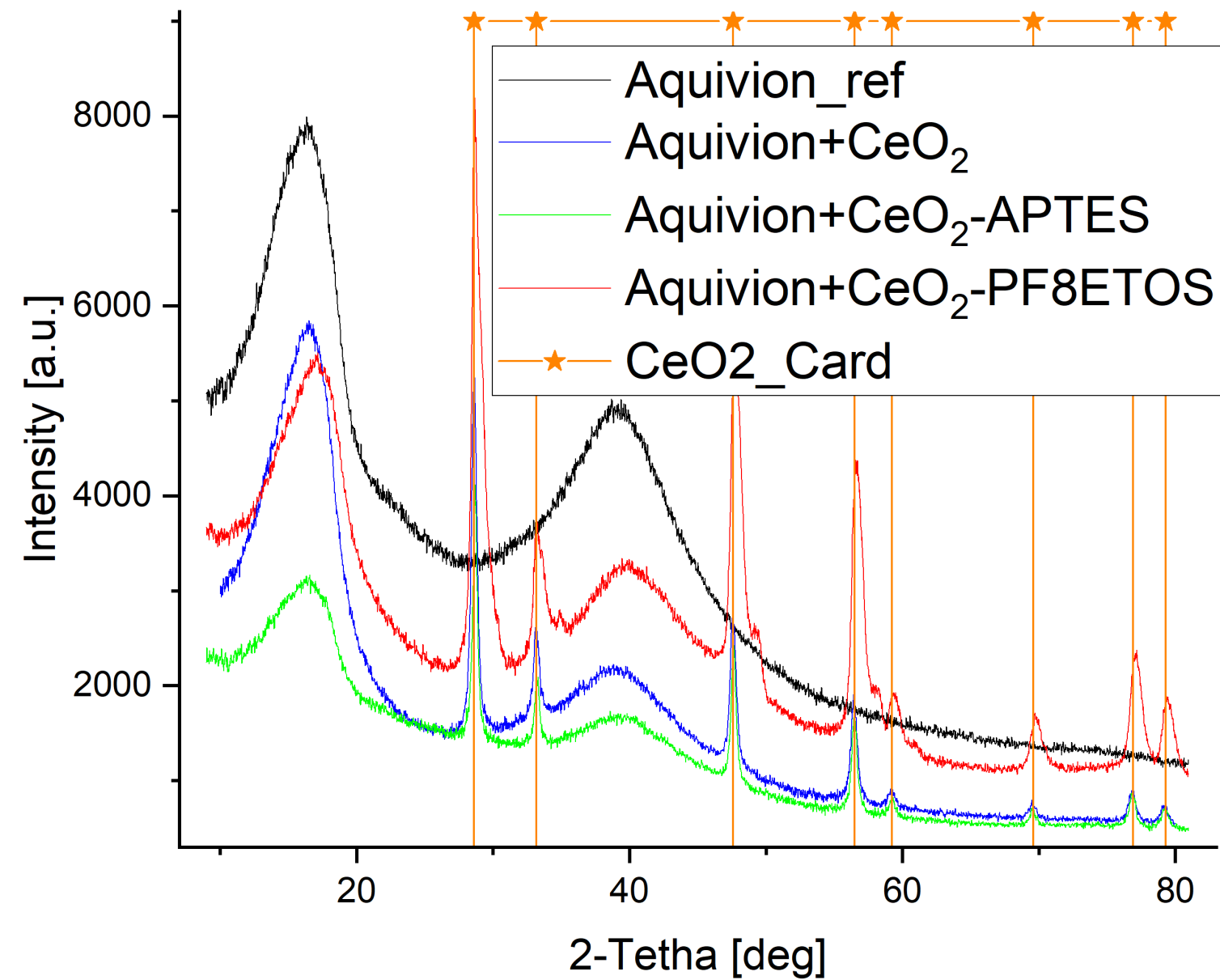


DSC

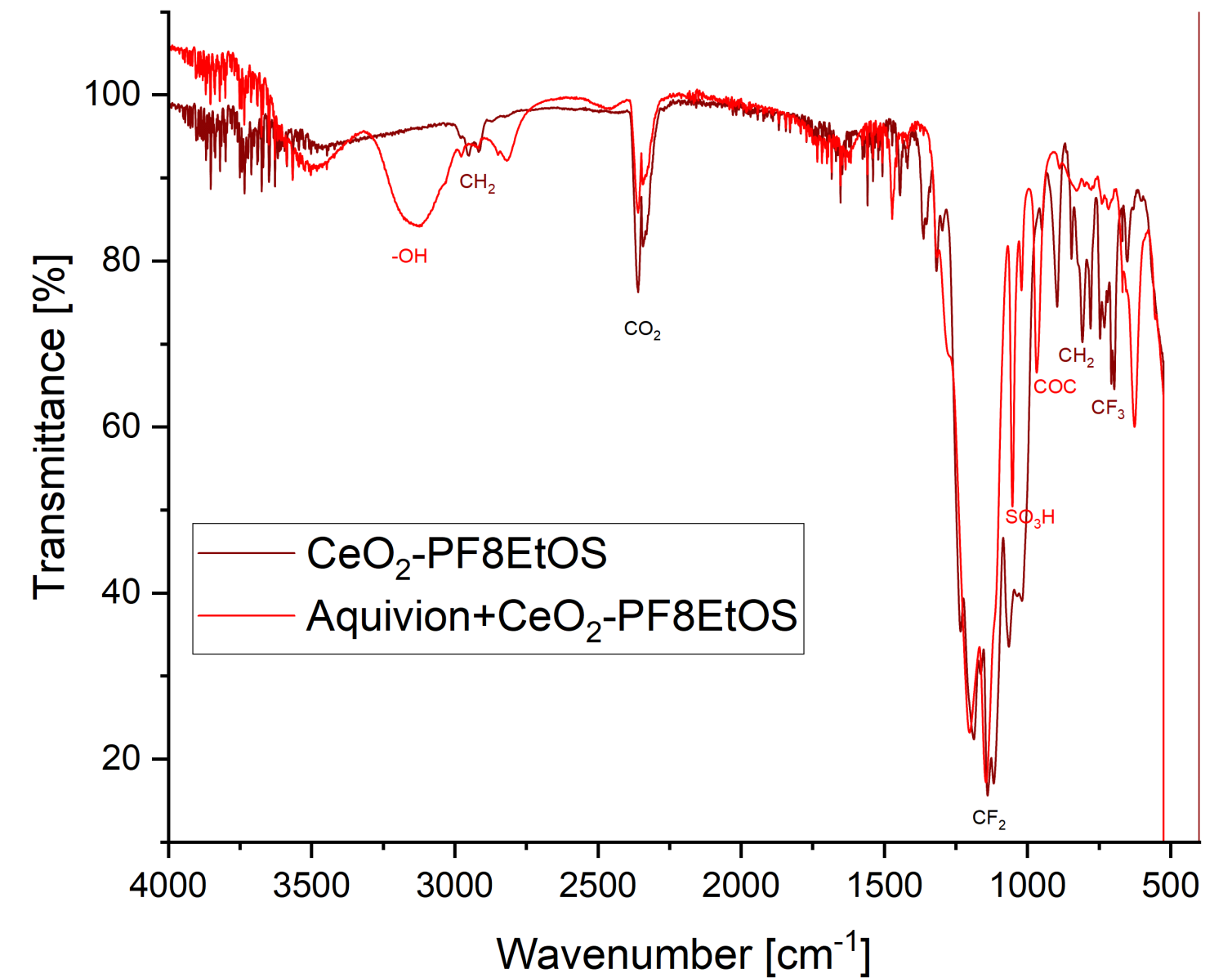


Compositional characterization

XRD

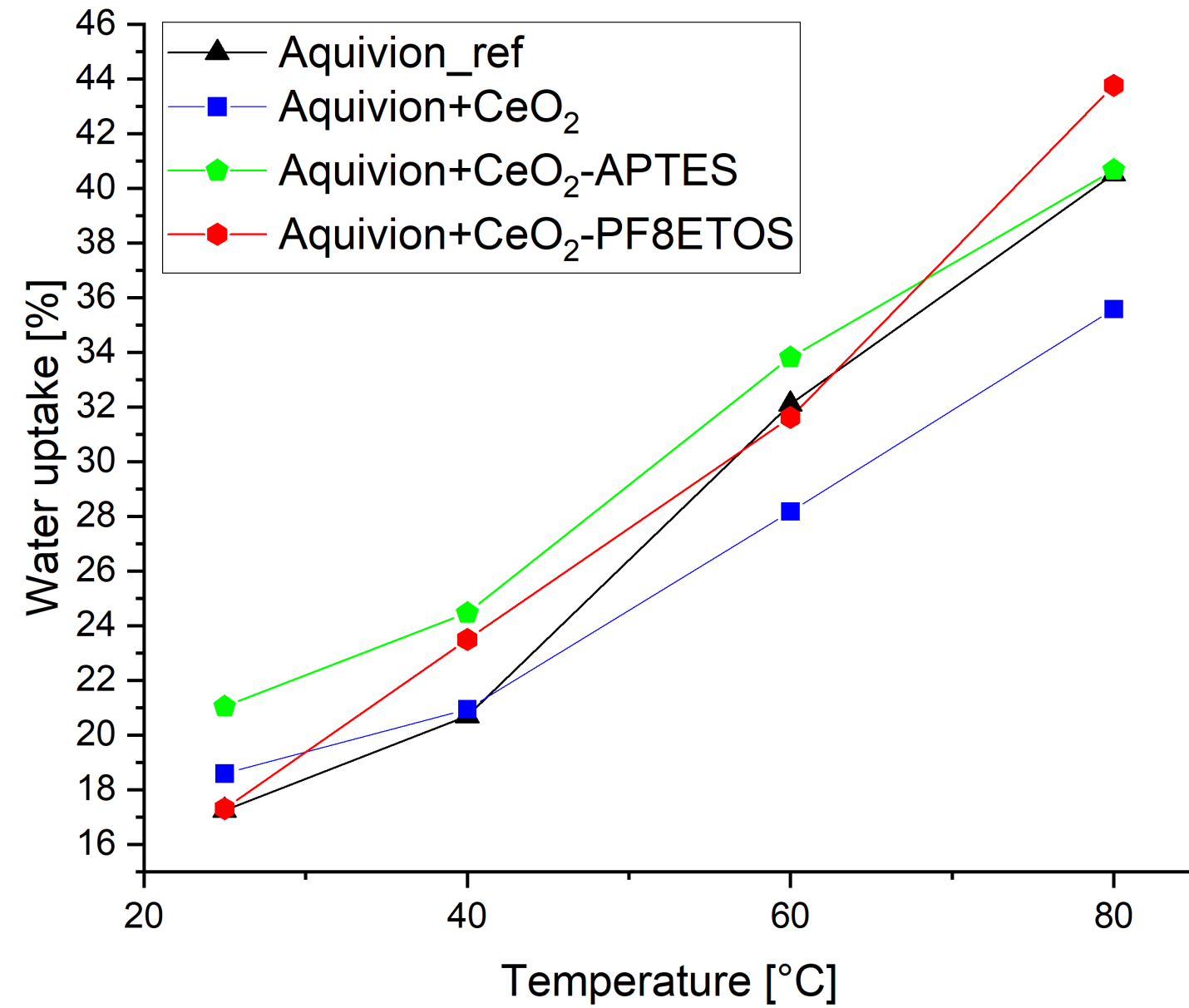


IR

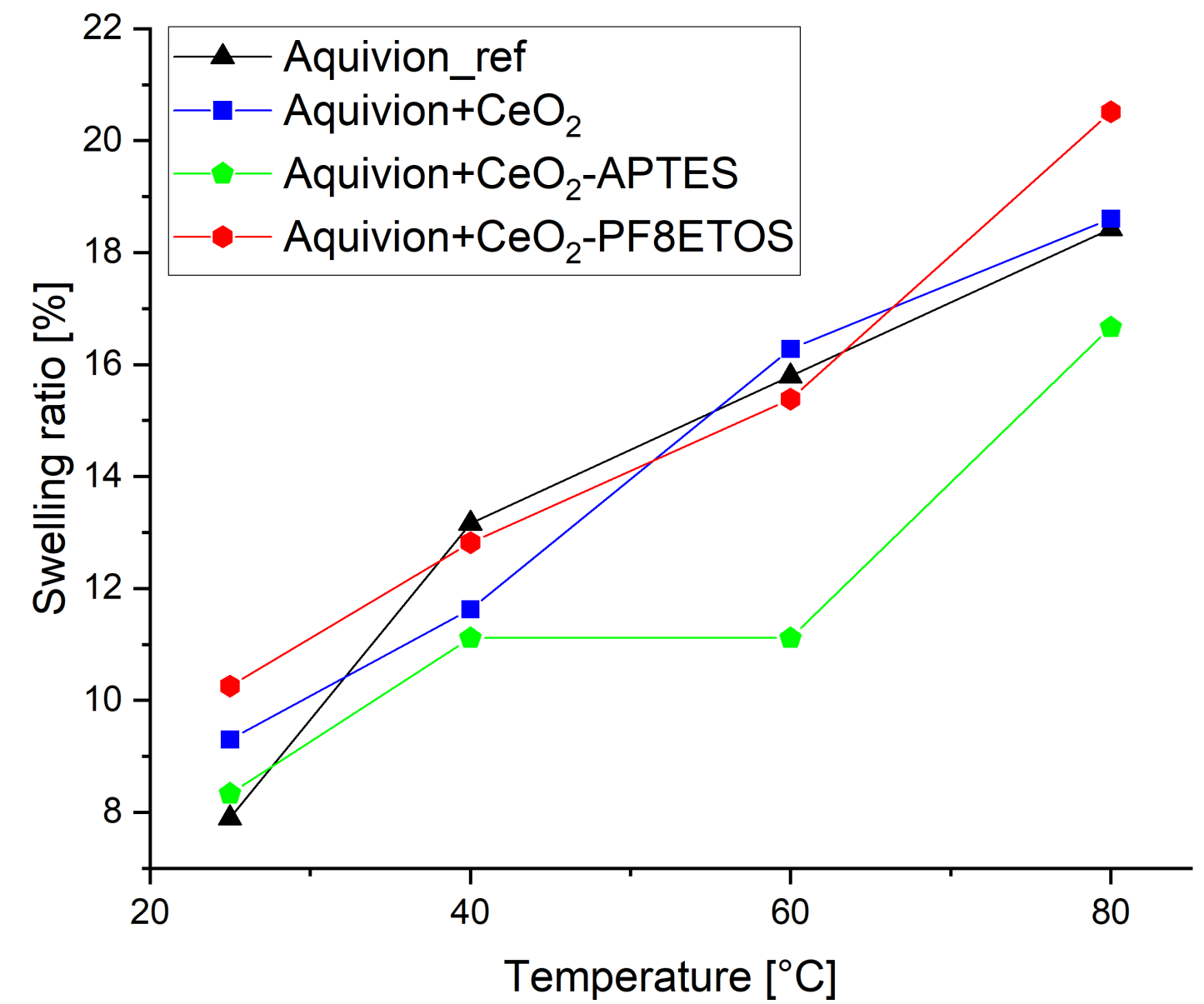


Water management

Water uptake

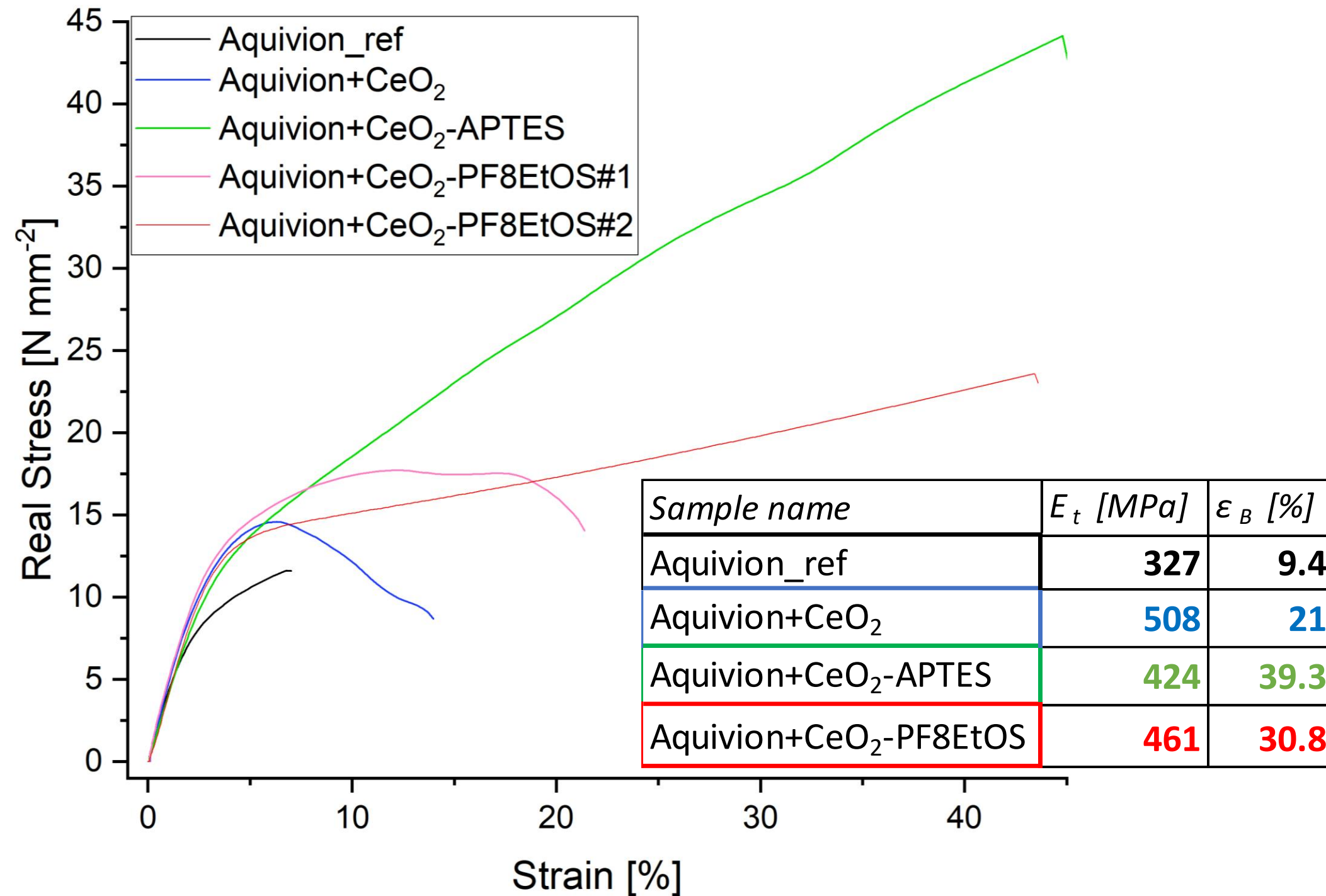


Swelling ratio



Durability tests

Stress-strain curves



Preliminary Fenton test

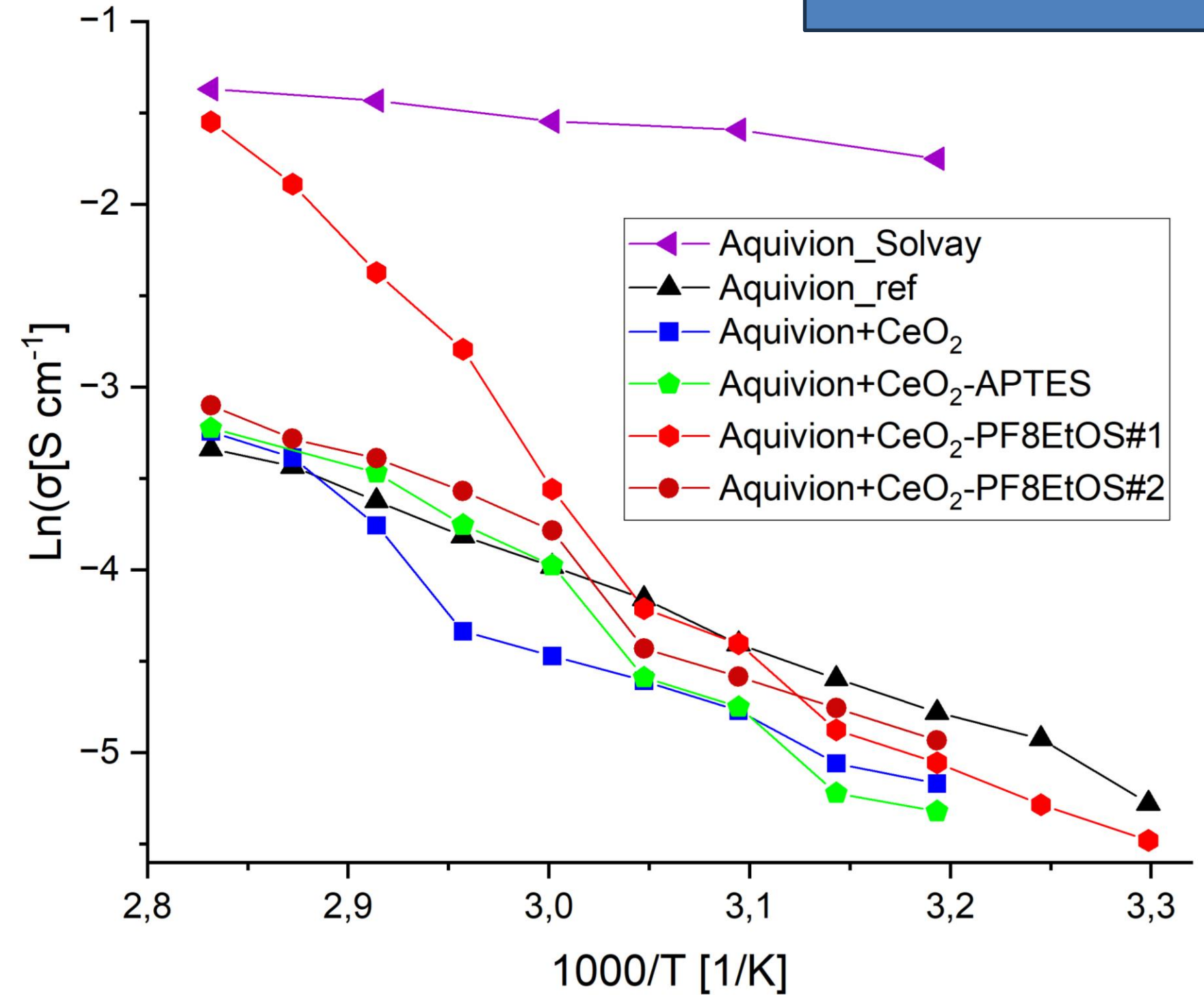
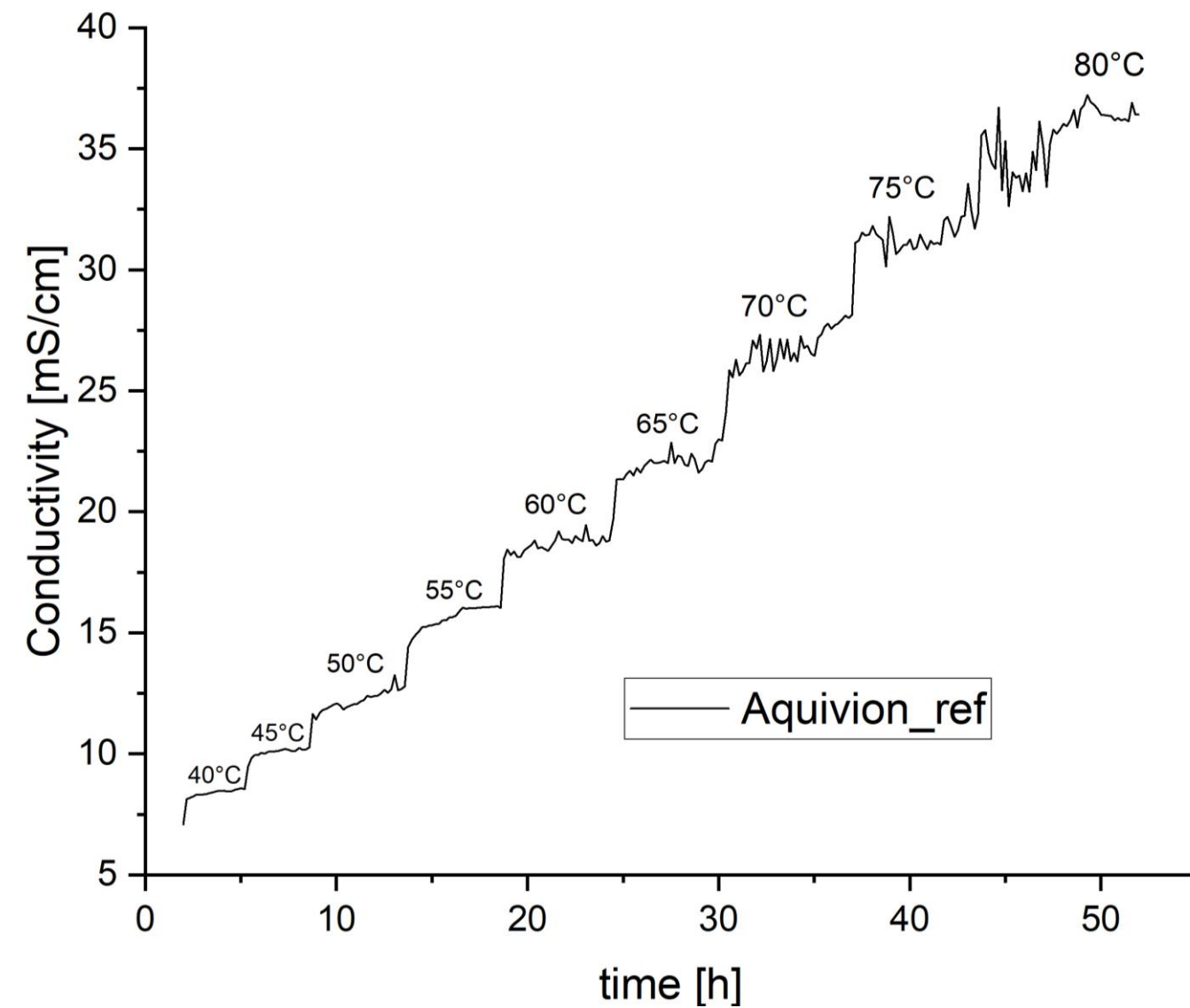
*1 week at room temperature
5mL of 4ppm Fe^{II} solution +
15 mL of 30% H₂O₂ wt/wt*

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 hope was to produce nanocomposite membranes with longer lifetimes and improved properties

- To assess 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, ²⁹Si NMR, and EDX-SEM imaging
- Further characterization includes BET on the NPs, as well as IEC measurements and DMA tests on the composite membranes



Future works

The results are only partial;
thus, 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.
- Newer 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.





That would be all!

Thanks for participating.

I'm here for questions.

Frankfurt am Main,
September 5th 2023

