

Supporting information:

Effect of Nafion content and hydration level on the electrochemical area of Pt nanocatalyst in the triple-phase boundary

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1. Computational analysis

1.1 Model Preparation of Nafion

A model of hydrated Nafion membrane (composed of Nafion, water, and hydronium) was prepared before its deposition on a Pt/C surface. The monomeric unit (n) of Nafion (Fig. S1) was repeated 10 times to form an oligomer; 10 hydronium ions were added to a single chain to maintain charge neutrality. In the initial configurations, the hydration level $\lambda = n \text{ H}_2\text{O} / \text{SO}_3^-$ (number of water molecules per sulfonic acid groups) was set to 43. Nafion oligomers were equilibrated to blend all components and to obtain random initial configurations for the MD simulation (Table S1).

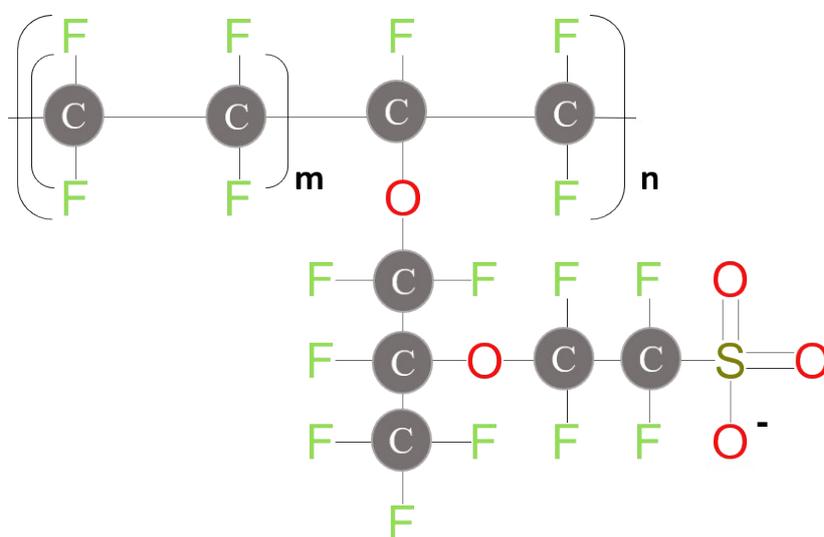


Fig. S1 Chemical structure of Nafion.

Table S1 Characteristics of the model systems

λ ($\text{H}_2\text{O} / \text{SO}_3^-$)	7% Nafion	14% Nafion	20% Nafion	32% Nafion	42% Nafion
43	4 Oligomer 40 H ⁺ 1720 H ₂ O	8 Oligomer 80 H ⁺ 3440 H ₂ O	12 Oligomer 120 H ⁺ 5160 H ₂ O	24 Oligomer 240 H ⁺ 10320 H ₂ O	36 Oligomer 360 H ⁺ 15480 H ₂ O
15	4 Oligomer 40 H ⁺ 600 H ₂ O	8 Oligomer 80 H ⁺ 1200 H ₂ O	12 Oligomer 120 H ⁺ 1800 H ₂ O	24 Oligomer 240 H ⁺ 3600 H ₂ O	36 Oligomer 360 H ⁺ 5400 H ₂ O
0	4 Oligomer 40 H ⁺	8 Oligomer 80 H ⁺	12 Oligomer 120 H ⁺	24 Oligomer 240 H ⁺	36 Oligomer 360 H ⁺

1.2 Atomic Strain on electrochemical surface area (ECSA)

Catalytic activity could be affected due to modifications of the electroactive exposed area. Therefore it can be useful to observe the atomic strain distribution in the exposed surface area. In Fig. S2 we show that the effect of the strong interactions between the sulfonic groups of Nafion and the surface of the Pt NPs is observed in the atomic strain analysis for the cases with high content of Nafion. From this analysis, it is clear the existence of a higher strain over metallic atoms exposed on the surface. However, the ECSA is almost unaltered by this surface reconstruction, and we do not expect important changes in the catalysts' activity.

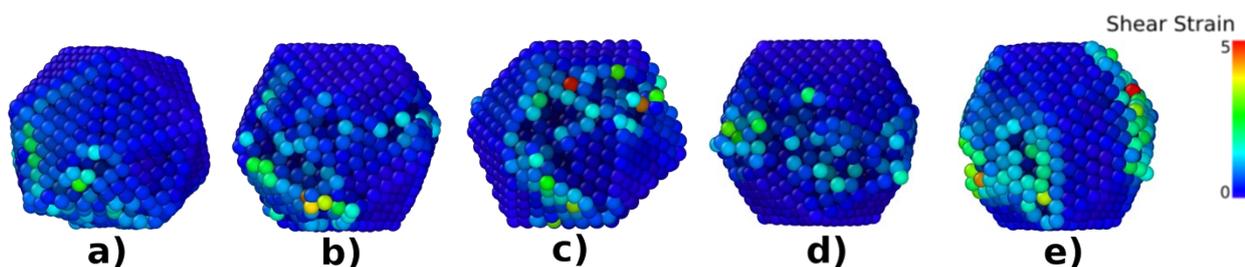


Fig. S2 Atomic strain in Pt nanoparticles with different Nafion contents. a) 4, b) 8, c) 12, d) 24, e) 36 Oligomers.

In Fig. S3 we observed that the surface geometries are more affected by ionomer content for ICO NPs. In NPs with a higher size (around 8 nm), the same trend is observed, the modification in the metallic surface area is lower in OT NPs compared with ICO NPs. This could be related to the FCC structure of OT, with presents higher cohesive energy.

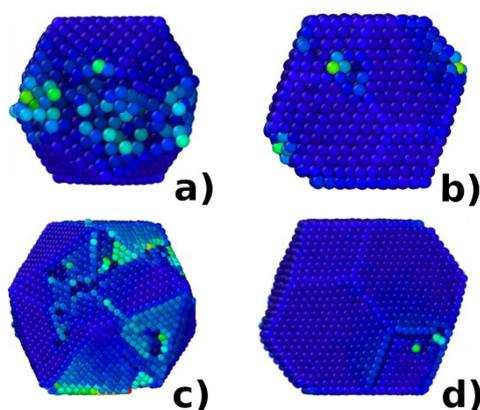


Fig. S3 Atomic strain in Pt nanoparticles with different structure geometries around 4 nm a) ICO NPs, b) OT NPs and 8 nm c) ICO NPs, d) OT NPs.

1.3 Catalyst utilization

We calculate the ECSA and percentages of the catalyst utilization for different contents of Nafion and hydration levels. Percentages of sulfonic groups, hydrophobic chain, water and hydronium in contact with Pt atoms are shown in Fig. S4. We observe a decrease in the active area as the oligomer content increases.

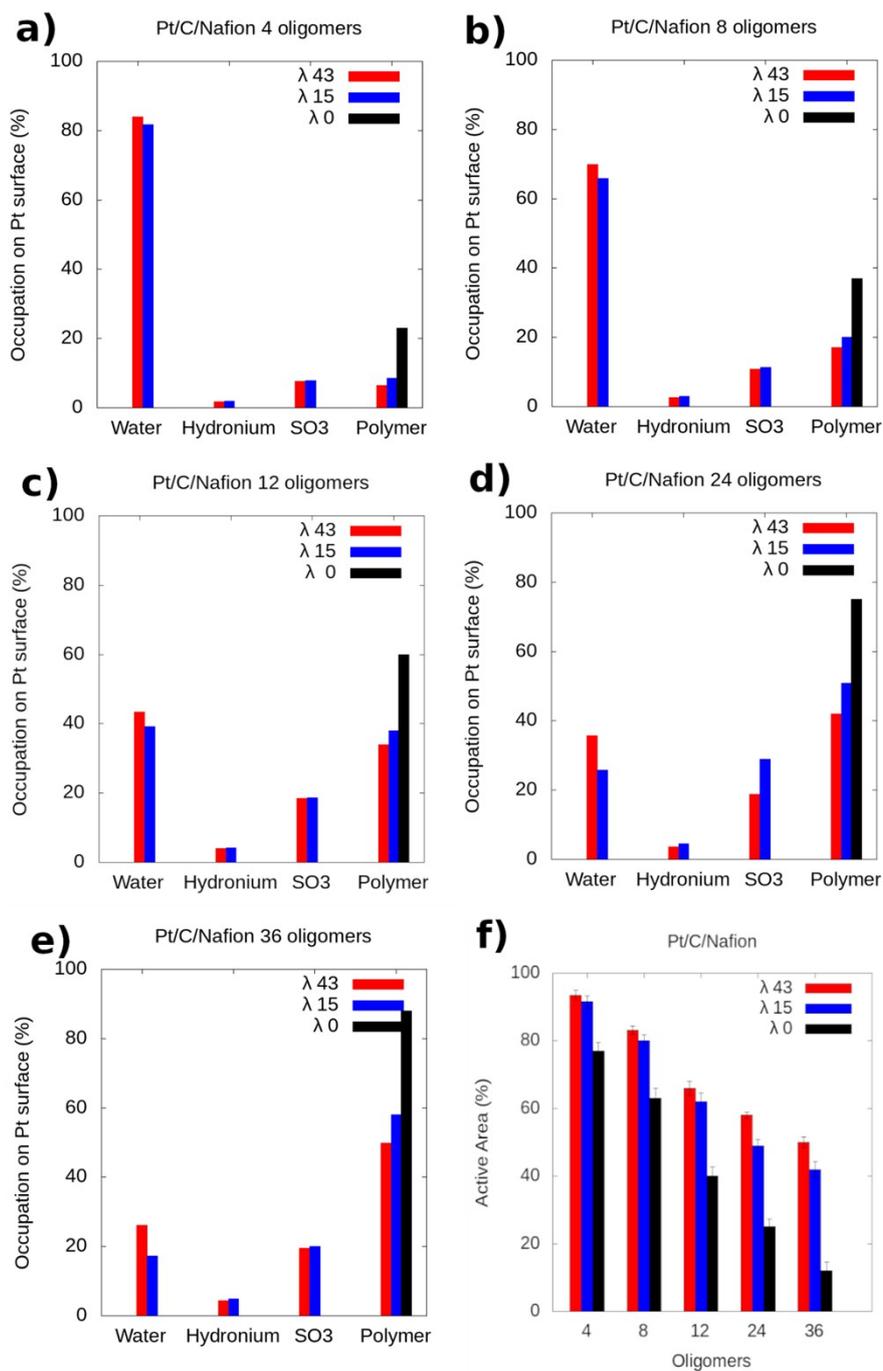


Fig. S4 Percentages of the catalyst utilization for different contents of Nafion and hydration levels. a) 4, b) 8, c) 12, d) 24, e) 36 oligomers and f) active area for systems with different quantities of oligomers.

1.4 Nafion Content, hydration and temperature

We observe that higher contents of hydrated Nafion increase the hydrophilicity in the system, the solvation of the sulfur atoms avoids the constraint in sulfonic groups and the water molecules push the Nafion backbone chains away from the interfacial region of the Pt surface decreasing the poisoning of the metallic surface area. We observe in our results that the covering of NPs Surface increases at low hydration level, which decreases the active area (Fig. S5). It is in agreement with experimental studies.¹

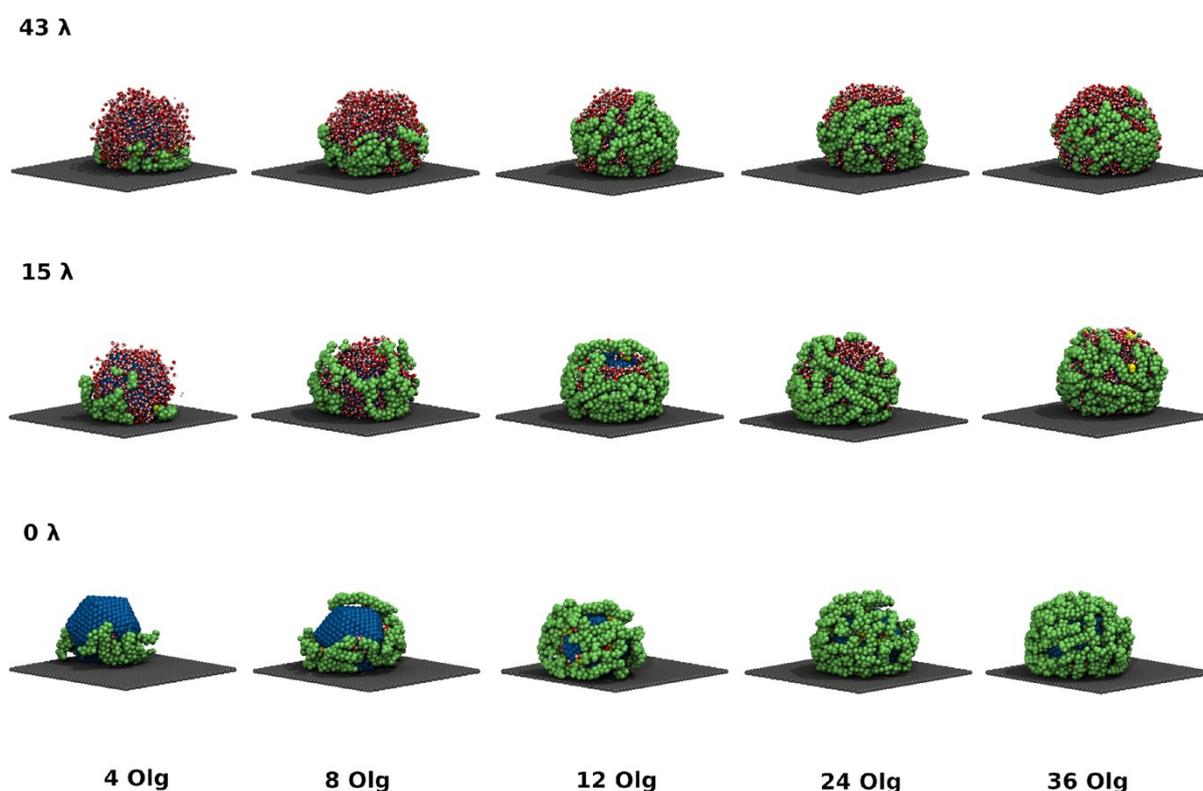
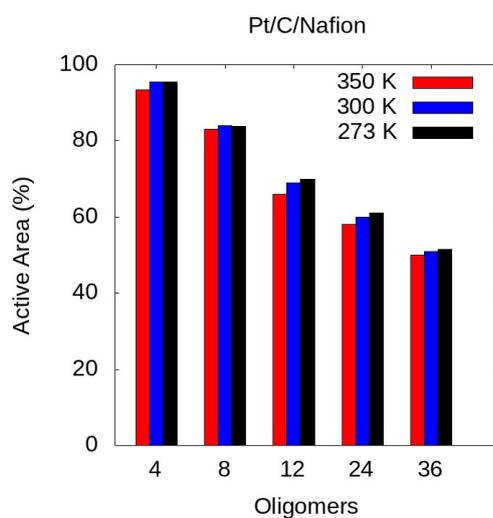


Fig. S5 Hydrated-Nafion/Pt/C structures (interfacial region around 10 Å of Pt NPs). Color code: blue: Pt, gray: carbon, green: hydrophobic chain (Nafion), yellow: sulfonic group (Nafion), red: oxygen and white: hydrogen.

1.5 Effect of the temperature

The impact of temperature on the catalyst utilization seems to be negligible. Also, the active surface area



tends to decrease as the Nafion content increases (Fig. S6).

Fig. S6 Catalyst utilization (in percentages) for different contents of Nafion and three temperatures.

1.6 Size and geometries of Pt NPs

Values in the Fig. S7 is also similar to the maximum theoretical surface area measured in our previous work ($36.1 \text{ m}^2\cdot\text{g}^{-1}$), with the nanoparticles supported on graphene in absence of Nafion. Therefore, for nanoparticles with a diameter of 4 nm, we do not expect important changes in the maximum theoretical surface area due to particle deformation.

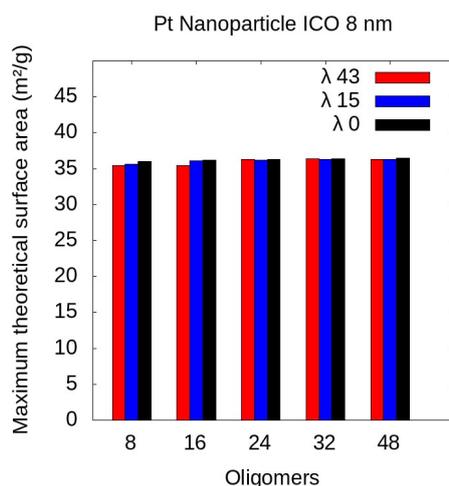


Fig. S7 Maximum theoretical surface area in ICO NP (8 nm) for different contents of Nafion (number of oligomers) at three hydration levels ($\lambda = 0, 15$ and 43), at 350 K.

In Fig. S8, the occupation of sulfonic groups on the Pt surface reveals that it is higher in ICO nanoparticles. This can be due to the strong interactions between sulfonic groups that are adsorbed on ICO NPs through the crystalline planes (111), which has already been reported in previous works.²

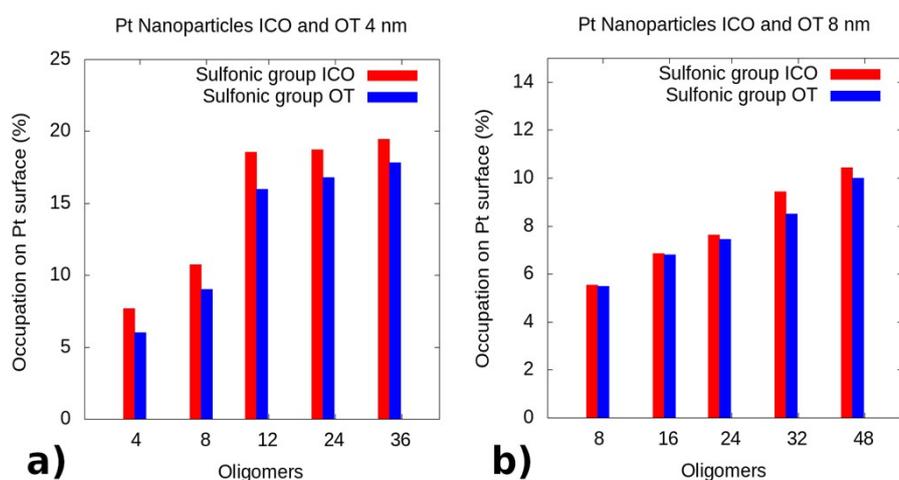


Fig. S8 Percentages of the catalyst utilization of sulfonic groups (Nafion) for different content of Nafion with different geometries and diameters around a) 4 nm and b) 8 nm.

1.7 Comparison with experimental data

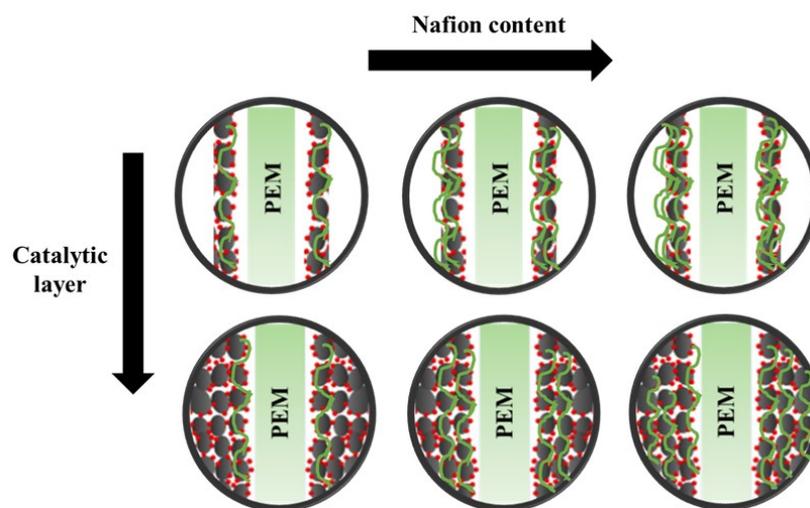


Fig. S9 Scheme of thickness of catalytic layer and Nafion content in triple phase boundary.

In Fig. S9, we schematize the results obtained. In our study we used a lower catalyst loading, therefore, as the proportion of Nafion increases the catalyst utilization is affected. In the literature some studies^{3,4} found a maximum of catalytic activity when increasing the mass of Nafion. These discrepancies could be due to the high catalyst masses used. This high catalyst concentration could make not all of the catalytic layer electrochemically accessible and, therefore, as the proportion of Nafion increases, a greater amount of Pt NPs participates in the triple-phase boundary.

References.

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