

## Atomistic simulation of interface between Nafion electrolyte and Pt catalysts in PEFC

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The availability of Nafion electrolyte and Pt based catalysts and addition of ionomer into the catalyst layer [3-5] are the milestones of the early advancements of the PEFC but yet have not enabled commercialization of PEFCs due to the inherent disadvantages including the high costs of Pt and Nafion and insufficient performance of Pt catalysts in conjunction with Nafion electrolyte. One of the major technical barriers is the very low exchange current density for the oxygen reduction ( $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ ) at the cathode. In the present work we use classical molecular dynamics (MD) and ab initio molecular dynamics (AIMD) methods to probe the interface structure and its role in the charge transfer reactions in PEFCs.

Fig. 1 illustrates the first layer of water on top of Pt crystal. It is clear that the oxygen atoms in water preserve the structure of the (111) face of Pt crystal. Although generally speaking, the water molecules are arranged in a good spatial periodicity or ordering, there are imperfections. As shown in Fig. 2, the unoccupied locations are actually occupied by F atoms. Thus, the ordering of water molecules is partially destructed. The areas with adsorbed F atoms block the transport of water and hydroniums at the interface.

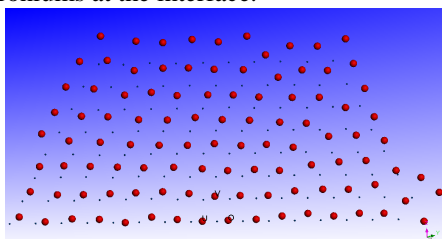


Fig. 1. Configuration of oxygen atoms of water on top of Pt crystal with a (111) face. Red: oxygen; Blue: Pt atom.

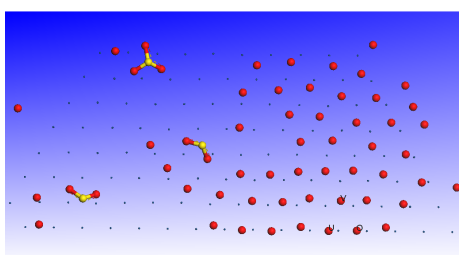


Fig. 2. Configuration of oxygen atoms of water and sulfonated groups on top of Pt crystal with a (111) face. Red: oxygen; Blue: Pt atom; Yellow: S atom in sulfonated groups.

In order to further verify the MD results, an AIMD model containing a  $18 \text{ \AA} \times 18 \text{ \AA} \times 6 \text{ \AA}$  Pt slab was established. Fig. 3 shows the molecules are periodically distributed on the Pt slab. Because AIMD simulations are considered more precise than the MD simulations, the AIMD results convinces the conclusion that there are three ordered layers at the interface between aqueous electrolyte and Pt slab. As to Nafion and Pt interface, there are water-containing areas with ordered layers and areas occupied by hydrophilic CF groups. Water molecules in the first layer on top of the Pt slab form O-Pt bonds.

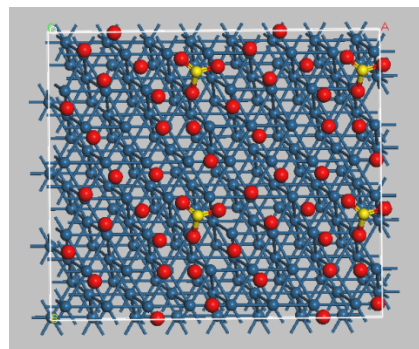
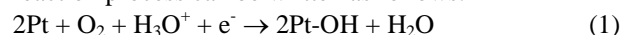


Fig. 3. AIMD simulation results: First layer of water and sulfuric acid on top of Pt slab (bird's eye view).

Fig. 4 is a cartoon of the AIMD trajectory. The adsorbed oxygen molecule (in green) at the right side eventually form two OH groups and no charge transfer between the oxygen molecule and Pt slab can be observed in the entire trajectory with total 501 steps. However, another oxygen molecule on the left side is adsorbed on Pt forming two bonds in a triangular configuration in the first step. In the second step, the O-H bond of top O atom breaks. In the third step, the top O atom forms a bond with a hydrogen atom in a hydronium. Then O-O bond breaks. At the fifth step, the hydronium passes another hydrogen atom to the adsorbed oxygen atom. At the last step, the top oxygen atom breaks away from the hydronium to form a water molecule while the adsorbed oxygen and hydronium form OH groups.

This process enables a charge transfer of 0.6 e. The reaction process can be written as follows:



It seems that there is no involvement of water in this reaction. However, it is not true. A dense water distribution around the reaction center provides a high possibility of bond relay and charge transport during the process. However, how can water get concentrated at the interface area? One of the answers is formation of ordered layers at the interface which we observed in previous simulations.

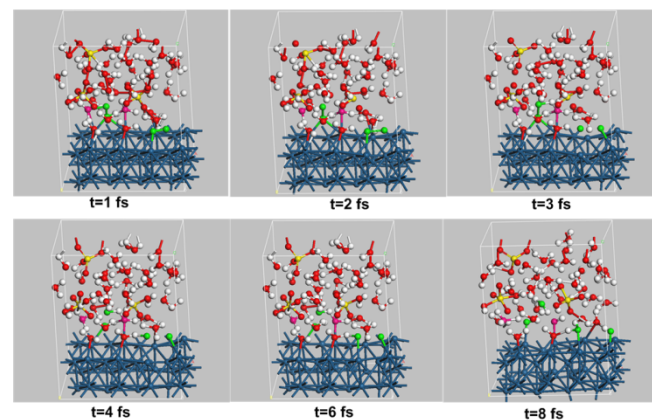


Fig. 4. A cartoon of dynamic configurations at different times/steps for a model containing water with a density of  $2 \text{ g cm}^{-3}$ .

In conclusion, the results indicate that the interface can be characterized by a few layers of orderly distributed molecules. The periodicity in the first layer on the surface of Pt is broken at the boundaries between hydrophilic and hydrophobic domains. In addition, the periodically distributed molecules in the first layer on top of the Pt also form a superlattice. This ordered layer favors oxygen reduction but does not favor hydrogen oxidation. The oxygen reduction path is  $2Pt + O_2 + H_3O^+ + e^- \rightarrow 2Pt-OH + H_2O$  or  $2Pt-OH_2 + O_2 + 2H_3O^+ + 2e^- \rightarrow 2Pt-OH + 4H_2O$ . The hydrogen oxidation path is  $2Pt-H_2 + H_2O \rightarrow 2Pt-H + H_3O^+$ .