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Molecular and electronic structure of sulfonic acid/platinum cluster systems

R. P. Pereira(1), A. M. Rocco(2)*

(1) Grupo de Materiais Condutores e Energia, Universidade Estadual da Zona Oeste (UEZO), Campo Grande, Rio de Janeiro, RJ, Brasil.
(2) Grupo de Materiais Condutores e Energia, Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ, Brasil <amrocco@eq.ufrj.br>.
* Corresponding author.

Abstract – In the present work, the molecular and electronic structure of Nafion/platinum cluster model systems is studied using Density Functional Theory calculations. The molecular structure of the interacting systems has shown to be strongly influenced by the number of platinum atoms in the cluster. According to the calculations, hydroxide transfer from Nafion to the Pt cluster is energetically equivalent to the proton transfer, with energy differences increasing with the cluster size. Integrated electronic density exhibits a partial charge localization coherent with a H^+ or OH^- transfer mechanism.

Fuel Cells (FC) are devices in which the chemical energy is converted into electrical energy to be used as power source in stationary, vehicular and mobile applications, without pollutant emissions [1]. The efficiency of FC devices depends on several parameters involving cathode, anode and electrolyte. Particularly, in Proton Exchange Membrane (also Polymer Electrolyte Membrane) fuel cells (PEMFC), a proton conductive membrane is used as electrolyte. Most of the PEMFC prototypes and commercial devices are based on Nafion, a perfluorosulfonic acid membrane with conductivity of 10^{-3} to 10^{-2} $\Omega^{-1}cm^{-1}$ [2]. The description of the interaction between Nafion and platinum (the catalyst used in cathode and anode) is a key knowledge for the control and optimization of PEMFC devices and this work aims to be a contribution on this subject.

Geometry optimization calculations were performed for perfluoro(2-ethoxyethane) sulfonic acid (PES) model systems interacting with small platinum clusters, in order to describe these interactions using both molecular and electronic structure. Calculations based on the Density Functional Theory (DFT) were carried out using NWChem software [3], with the hybrid B3LYP functional and 6-31G(d,p) basis set for all atoms.

The molecular structure of Nafion/Pt systems evidenced two possible ion transferences involving the sulfonic acid and the metal cluster: (i) a proton transfer and (ii) a hydroxide transfer. Figure 1 depicts the proton transfer in a PES/Pt_4 system, as described by DFT calculations.

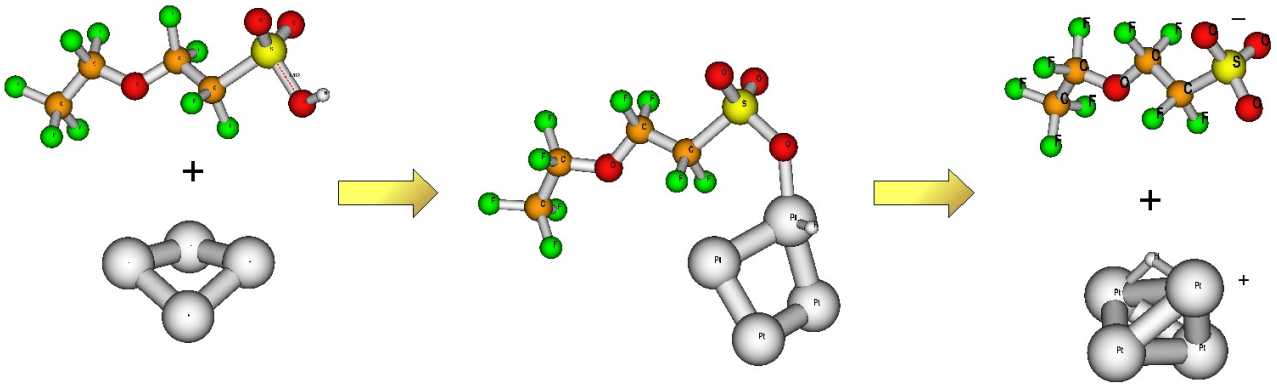

Figure 1. Proton transfer in a PES/Pt_4 system (the central structure represents a stable intermediate).

At least one stable structure was found during the proton transfer from Nafion (-SO_3H) to the Pt cluster (Pt_nH^+) for each system, and these structures exhibited a strong dependence on the number of Pt atoms in the cluster. Study of the molecular and electronic structure of these intermediates reveals a dependence of the Pt cluster size on the energy required for the proton transfer, as well as for hydroxide transfer, which exhibits a similar behavior.

References

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