



Theoretical quantum-chemical study of the interaction of Mo⁶⁺-porphyrin with O₂

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Abstract - The fuel cells are considered as an alternative to substitute current energy sources. The present catalysts are not able to break the bond of O₂, the way they do with H₂. Some research work shows that the metalloporphyrins can help the current catalysts in the electrocatalysis of O₂. In this context calculations were performed with the DFT method e functional B3LYP in the form of PCM solvation PCM with metalloporphyrins of Mo⁶⁺ to act in the break of O₂. The results show that a break of O₂ does not occur, but the electrocatalysis and the transport of O₂ can be facilitated.

One of the most important reactions in a fuel cell of Proton Exchange Membrane (PEM) is the oxygen reduction reaction (ORR) [1]. The oxygen reduction reaction is considered as one of the most important electrocatalytic reactions because of its role in electrochemical energy converters. One of the alternatives to improve the efficiency of use of ORR is the use of metalloporphyrins. Collman [2] have proved that the porphyrin dimers can act in the reaction of reduction of oxygen; however there are no theoretical studies of the performance of monomers in cells of the PEM-type. This work has as objective to show the interaction of Mo⁶⁺-porphyrin with the O₂-molecule through direct mechanism or the mechanism of 4-electrons.

The calculations were performed in Gaussian 2003TM software, using the DFT methodology (Density Functional Theory) and the functional B3LYP. for the atom of Molybdenum was used the base lan12dz, for the H atoms the base 3-21G⁺, for other atoms of the porphyrin, like C and N was used the base 3-21G. To simulate the solvation was used the Polarizable Continuum Model - PCM, and as solvent water, adopted to the temperature of 350 K and pressure of 1 atm, conditions that a PEMFC cell-type can operate with good humidification of all Membrane Electrode Assemblies (MEA). The atomic charges loads were analyzed with the NBO-method (Nature Bond Orbitals).

Two models were used: Mo⁶⁺-porphyrin (Figure 1) and Mo⁶⁺-porphyrin with an O₂-molecule, H₃O⁺-ions and four electrons (Figure 2), with the conditions described above, as in Figure 1 and Figure 2. Experimental data show that the distance of a double bond in O₂ is 1.21 Å. After interaction with the Mo⁶⁺-porphyrin the bound showed the value of 1.200 Å, showing that the Mo⁶⁺-porphyrin interacts with O₂. The angle of NMN Mo⁶⁺-porphyrin was 179.50, demonstrating that metal is in the macrocycle. After the interaction with O₂ the value 175.00 shows that there was a slight decrease in the angle of Mo⁶⁺-porphyrin.

The O₂-molecule after the interaction with Mo⁶⁺-porphyrin, the oxygen atoms passed the charge 0.0497 (OI) and -0.0960 (OII) to -0.130 and -0.516, respectively, which indicate that O₂ receives negative charge after the interaction with the porphyrin, which indicates facilitation in the process of electrocatalysis, because there was an absorption of negative charge at O₂. The NBO reveal that there is a connection between O₂ and Mo, but the donor-acceptor effect indicates a strong interaction $\eta_{\text{O}} \rightarrow \eta_{\text{Mo}}$, which facilitate the transport of mass, because the O₂ is close to porphyrin and is more easily transported to the catalyst, which would increase the performance of a PEM-cell.

The results prove that Mo⁶⁺-porphyrin can act in cells of the PEM-type, the interaction does not alter significantly the length of the O₂ bonds and leaves the O₂ catalytically active and also can carry the O₂ to the catalyst.

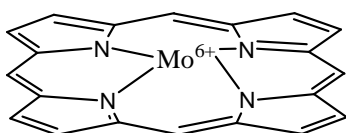


Figure 1. Mo⁶⁺-porphyrin

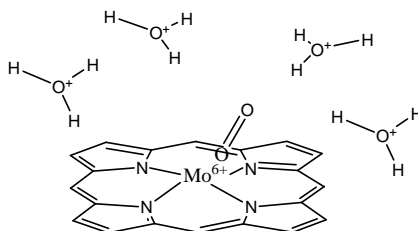


Figure 2. Mo⁶⁺-porphyrin with O₂

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