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Nanostructured catalysts for fuel cell reactions: Effects of properties on activity

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Abstract – Catalysts properties can be well controlled, allowing analysis of their influence on electroactivity, when adequate synthesis methodologies are employed. The analysis of the effects of chemical, structural and electronic properties of carbon supported Pt-based nanoparticles (PtM/C, M= Fe, Ni, Co, V) on the catalytic activity for the oxygen reduction reaction shows that PtM/C nanocatalysts with similar lattice constant exhibit nearly the same kinetic currents, independently of the second metal nature and content. It is also verified that even though Pt-rich surfaces tend to be more active for oxygen reduction, they might be less tolerant to the presence of methanol.

Proton exchange membrane fuel cells (PEMFC) are considered adequate for vehicle and portable applications and might help to mitigate other power problems. However, there are still a number of issues to be solved to make the generation of electrical power using PEMFCs practical and cost-effective. Independently of the fuel, that might be hydrogen or an alcohol such as methanol or ethanol, the slow kinetics of the oxygen reduction reaction, which takes place at the cathode side of these cells, is still the cause of severe overpotential losses (~0.3-0.4 V under typical operation conditions).

In a general manner, literature data show that Pt-based binary catalysts perform better as catalysts for oxygen reduction than pure Pt. However, the electrochemical activities of nano-sized Pt-based materials are strongly influenced by their physical and chemical properties which are, in many cases, mutually dependent and determined by the synthesis conditions. So, it comes to not surprise to find that the electrocatalytic activities reported in the literature are dependent on the preparation methodology adopted. Different reports have interpreted activities as associated to various physical parameters, such as particle size, Pt enrichment of the surface, distance between Pt atoms, and occupancy of the 5d Pt band.

Thus, the use of synthesis methods that allow controlling chemical composition and physical properties is needed in order to gain a deeper understanding of the role that those properties play on catalytic activities. Preparation methodologies based on the synthesis of colloidal nanoparticles, that are subsequently supported on high surface area carbon, such as microemulsions and modified polyol methods [1-3], are advantageous in order to avoid any influence of the support on particle growth and allow controlling properties, such as chemical composition, particle size, and Pt-Pt distance [1,2].

Using those methods, different PtM/C (M=Fe, Co, Ni, V) nanocatalysts were prepared and their physical properties were obtained by X-ray diffraction and transmission electron microscopy while the electronic characteristics were derived from *in situ* dispersive X-ray absorption spectroscopy studies. When properties are well-controlled, the results of catalytic activity for the electrochemical reduction of oxygen, as evaluated from measurements carried out using the rotating disk electrode technique, can be correlated with them. For instance, the results obtained show that PtM/C nanocatalysts of same particle size and having similar lattice constant exhibit nearly the same oxygen reduction kinetic currents, independently of the second metal nature and content.

When the fuel is an alcohol, such as methanol or ethanol, tolerance to alcohol contamination of the cathode compartment becomes another important factor to determine the cathode performance. Our studies have shown that tolerance depends on the surface chemical composition. In addition, even though a Pt-rich surface increases the kinetic currents of oxygen reduction, it might decrease the catalysts tolerance to alcohol contamination.

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