

## ELECTROCATALYSIS IV: FUNDAMENTAL AND APPLIED ASPECTS OF ELECTROCATALYTIC PROCESSES, BIO-ELECTROCATALYSIS AND KINETIC INSTABILITIES

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Figure 1. Highlights of the scientific production between 2010 and 2013. The cover pages appeared in the following periodics are included: *J. Phys. Chem. C* 114, 2010, issue 43; *Phys. Chem. Chem. Phys.* 13, 2011, issue 2; *Idem* 14, 2012, issue 23; and *Electrocatalysis* 4, 2013, issue 2

The goal of the project consists of the study of electrocatalytic processes taking place in energy conversion and storage systems, particularly the ones involving reactions in fuel cells, including bioactive electrodes. Attention will be paid to the study of the oxygen reduction reaction and of the oxidation of alcohol molecules and hydrogen deliberately contaminated with traces of carbon monoxide. The investigation will also include the study of kinetic instabilities usually observed, for instance, during the electro-oxidation of small organic molecules such as formic acid, methanol, and ethylene glycol. It will be studied some fundamental aspects of the electrocatalysis as well as the kinetic instabilities of such reactions on massive pure metals (both single crystals and polycrystalline) and metallic alloys, and carbon dispersed electrocatalysts. In this case, it will be employed nanoparticles of pure noble metals, alloys, core-shell structures formed by a transition metal covered by monolayers of noble metals, and metallic oxides. Finally, the development of biomaterials for low temperature bio fuel cells will be also considered, with emphasis on the immobilization of enzymes such as cloroperoxidase, peroxidase, lacase, tirosinase e glicose oxidase. Further development might also include operational systems of gas diffusion electrodes, on which the study of electrocatalysed reactions of fundamental and practical interest will be carried out.

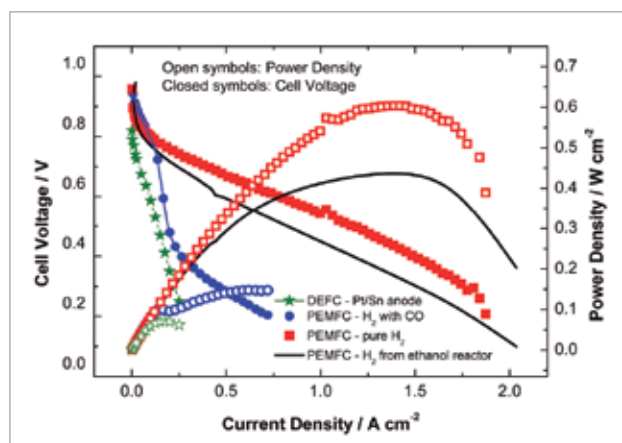


Figure 2. Stabilized polarization and power density curves of PEMFCs with anodes operated under  $H_2$  coming from an ethanol dehydrogenation reactor compared to pure  $H_2$ ,  $H_2$  with 100 ppm CO, and a pure ethanol. Cathode: pure Oxygen.  $T = 70^\circ C$ . More details in: Sato et al. 2015. *J. Power Sources*. **294**: 269-573

## SUMMARY OF RESULTS TO DATE AND PERSPECTIVES

New insights have been achieved regarding the understanding of fundamental aspects of the reactions and processes, as well as on the improvements of the catalytic performances. In this way, studies on the electrocatalysis of the oxygen reduction reaction were conducted either in acid and alkaline electrolytes, employing a number of nanostructured carbon-supported Pt-based (PtM/C) electrocatalysts, where M were Ni, Co, Fe, etc., with special structures such as hollows and core-shells, and different catalyst supports such as non-noble metal carbides and oxides. In addition, the electrocatalysis of alcohol oxidations such as methanol, ethanol, glycerol, were investigated aiming at applications on acid and alkaline fuel cell systems. Electrocatalyst materials were nanocrystalline and polycrystalline bulk metals (Pt, Pd, and Au). Several types of carbon-dispersed nanoparticles (PtRu/C, PtRh/C, PtSnOx/C, PtWOx/C, etc) were also considered. In these systems, different types of oscillatory kinetics have been commonly investigated for obtaining kinetic parameters under far-from-equilibrium reaction regimes. In the bioelectrocatalysis area, works to study the electron transfer reactions mediated by triphenylen-derived compound and the pseudomonas aeruginosa bacteria for the electrocatalysis of the glycerol oxidation were carried out. Finally, the electrocatalysis of the cathodic and anodic reactions on proton exchange membrane fuel cells (PEMFC) were investigated focusing practical and fundamental aspects of the oxygen reduction reaction and hydrogen oxidation reaction in the presence of contaminants such as CO and sulfur.

Figure 1 shows, in an illustrative way, some of the main results obtained in the project, including four cover pages that appeared in specialized journals. The academic production achieved inserted in Fig. 1 clearly show that the project was completed very successfully. The quality of the scientific production is attested by the large number of articles published in journals of high scientific impact such as Chemical Sciences, Chemical Communications, Applied Catalysis B, Journal of Physical Chemistry, Journal of Power Sources, Electrochemistry Communications, Electrochimica Acta, PLoS One, among others. Typical results obtained on PEMFCs are illustrated in Figure 2.

## MAIN PUBLICATIONS

- Cantane DA, Oliveira FER, Santos SF, Lima FHB. 2013. Synthesis of Pt-based hollow nanoparticles using carbon-supported Co@Pt and Ni@Pt core-shell structures as templates: Electrocatalytic activity for the oxygen reduction reaction. *Applied Catalysis. B.* **136-137**: 351-360.
- Garcia AC, Lima FHB, Ticianelli EA, Chatenet M. 2013. Carbon-supported nickel-doped manganese oxides as electrocatalysts for the oxygen reduction reaction in the presence of sodium borohydride. *Journal of Power Sources.* **222**: 305-312.
- Nikkuni FR, Ticianelli EA, Dubau L, Chatenet M. 2013. Identical-location transmission electron microscopy study of pt/C and pt-Co/C nanostructured electrocatalyst aging: effects of morphological and compositional changes on the oxygen reduction reaction activity. *Electrocatalysis.* **4**: 104-116.
- La Rottaz CE, Gonzalez ER. 2013. Synthesis and characterization of chemical modified carbon-chitosan composites applied to glucose oxidase fuel cells. *Journal of the Electrochemical Society.* **160**: G37-G45.
- Prieto MJ, Tremiliosi G. 2013. Surface restructuring of Pt films on Au stepped surfaces: effects on catalytic behaviour. *Physical Chemistry Chemical Physics.* **15**: 13184-13189.
- Angelucci CA, Varela H, Tremiliosi-Filho G, Gomes JF. 2013. The significance of non-covalent interactions on the electro-oxidation of alcohols on Pt and Au in alkaline media. *Electrochemistry Communications.* **33**: 10-13.
- Sitta E, Batista BC, Varela H. 2011. The impact of the alkali cation on the mechanism of the electro-oxidation of ethylene glycol on Pt. *Chem. Commun.* **47**: 3775-3777.

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