

Highly efficient cathodic catalysts for polymeric electrolyte fuel cells

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Objectives and Novelty

Fuel cells are devices able to produce energy from an electrochemical reaction and currently play an important role in efficient electricity generation from a free emission perspective.

Among them, there are fuel cells that use a protonic exchange polymeric membrane as an electrolyte (PEMFCs, Polymer Exchange Membrane Fuel Cells) and operate at relative low temperatures (25-100 °C), and therefore, electrocatalysts are needed for their correct operation achieving a power output up to 1000 mW.cm⁻². Also, this type of fuel cells usually uses hydrogen as fuel, which can be obtained from fossil fuels reforming or from renewable sources (as photo-water splitting). Handling, storage and distribution of hydrogen entail some special care as well as adequate facilities to reduce leakage risk and possible accidents. For that reason, despite lower output power production (50-200 mW.cm⁻²), polymeric membrane fuel cells supplied by liquid methanol (DMFCs, Direct Methanol Fuel Cells) appear as an alternative for PEMFCs, mainly for application in portable devices.

Both fuel cells use Pt as a catalyst, which increases their operation cost and hinders their early commercialization. Also, oxygen reduction reaction (ORR) that occurs on the cathode side of PEMFCs/DMFCs, presents a sluggish kinetic on these catalysts, which decrease the global fuel cell performance. On the other hand, in DMFCs take place the so called the methanol crossover, which is a process where the methanol employed as fuel passes across the electrolyte membrane from the anode to the cathode, causing a drastic performance decrease due to the production of mixed potentials as a consequence of the ORR low selectivity for the cathodic catalyst.

This PhD thesis deals with these issues and focusses on the development of highly efficient catalysts toward the ORR with elevated methanol tolerance, for the cathode of PEMFC and DMFC devices. With this aim, several strategies on the design of low-cost catalysts with electrocatalytic activity toward the ORR have been developed.

Results

The current PhD thesis was presented in the form of a compendium of publications [1-11]. Main results of selected publications are summarized in the subsequent paragraphs.

Carbon-supported Pt free catalysts based on Pd and its binary (PdFe/C, PdIr/C) and trimetallic (PdFeIr/C) alloys with Fe and Ir were synthesized. Physicochemical characterization of these materials revealed significant structural and electronic changes when a second or third metal is inserted into the Pd structure, which determines the final performance toward the ORR either in conventional electrochemical experiments as well as in DMFC test station. Pt removal and decrease of Pd loading due to the use of metallic alloys implied a strategic conjunction for searching cheaper catalysts than those traditionally used, with high electroactivity toward the ORR and tolerance to methanol [1,6,9,11].

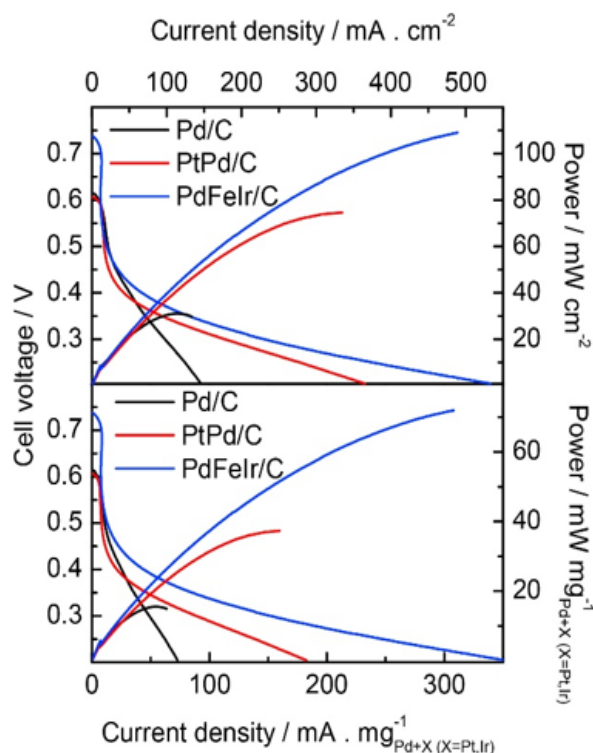


Figure 1. Voltage vs Current and Power vs Current curves for single DMFC. Current and Power are depicted as measured (top panel) and normalized by the mass of noble metals (bottom panel). Cathode catalyst: Pd, PdPt and PdFeIr at loading of 2.0 mg_{metal} cm⁻². Anode: PtRu/C at loading of 1.0 mg_{metal} cm⁻². $T_{cell} = 60$ °C. Anode fed with 2.0 M CH₃OH at 1.5 mL min⁻¹. Cathode fed with humidified O₂ at 50 mL min⁻¹. Reproduced with permission from [11].

In order to decrease the Pt loading in the cathodic catalysts and to increase the methanol tolerance and the catalytic activity toward the ORR, Pt alloys with Cr and Co (Pt₂CrCo) supported on ordered mesoporous carbons (CMK-3) were synthesized and evaluated as cathode. In this regard, searching for a

corrosion resistant carbonaceous support, combined with the usage of metallic alloys (producing a Pt content decrease) and the finding of active phases as a consequence of a suitable reducing thermal

treatment, converge as options employed in this study for achieving efficient DMFC cathodic catalysts [6,10].

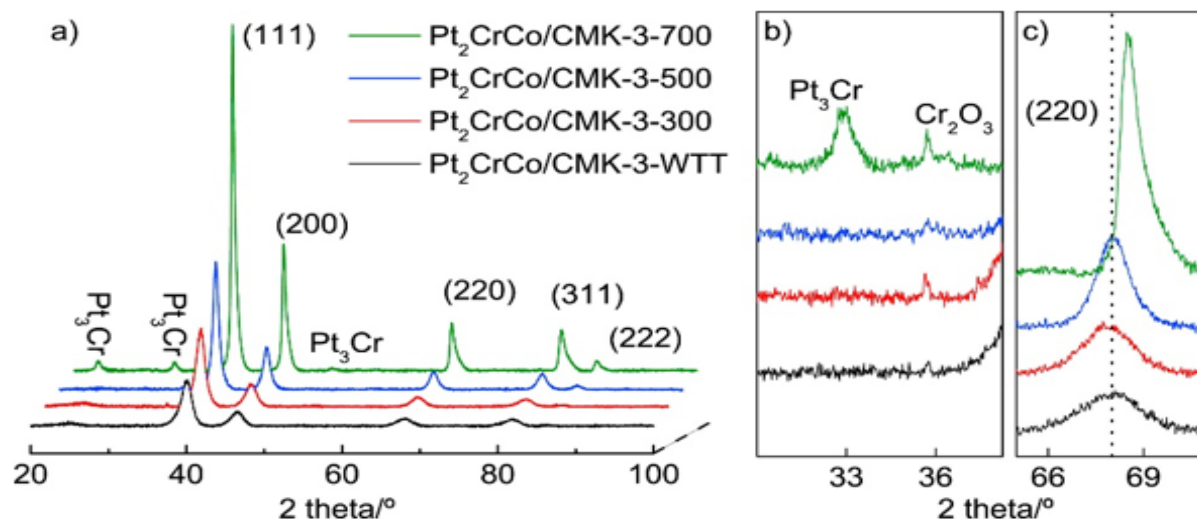


Figure 2. X-ray diffraction patterns of $\text{Pt}_2\text{CrCo}/\text{CMK-3}$ electrocatalysts. Reproduced with permission from [10].

Finally, several carbonaceous and graphene materials (MGs) were developed with the purpose of obtaining carbon metal-free catalysts that. These MGs were obtained by chemical reduction of graphene oxide (GO) employing different reducing agents that allowed the graphene network doping, and thus, the increase and modulation of the ORR activity in alkaline electrolyte. The electrochemical stability and the catalytic activity toward the ORR in the presence and the absence of methanol were evaluated through the rotating ring-disk electrode (RRDE) and Raman spectroelectrochemistry techniques, while the catalyst performance as cathodic material was estimated in a DMFC test station [2-4,8].

Conclusions

In summary, this PhD attempts to contribute to the development and progress of the fuel cells technology, improving the design and performance of materials for the cathode of these energy conversion electrochemical devices.

Several strategies to overcome the limitation of PEMFC and DMFC cathode have been suggested. Metal-free and Platinum-free catalysts with enhanced catalytic activity toward the ORR and high tolerance to the methanol crossover were successfully achieved and evaluated by a series of conventional and non-conventional spectroelectrochemical techniques.

Therefore, the aim of the present PhD Thesis is not only to provide new fundamental advances in the electrocatalysis field, but also to understand the reactions occurring at the cathode electrode, which may help to improve the fabrication of novel catalysts in order to increase the performance and to decrease the cost of DMFCs.

Related Publications

[1] Rivera-Gavidia LM, Sunga M, Rodríguez JL, Pastor E,

García G, Pd-based carbon supported catalysts for oxygen reduction reaction. *Int J Hydrogen Energ*, HE-D-19-04589. (Aceptado).

[2] Rivera-Gavidia LM, Arévalo MC, Kalbac M, Sunga M, Bousa M, Vales V, Pastor E, García G, S- and N-Doped Graphene-based catalysts for the Oxygen Evolution Reaction. *Electrochim Acta*. ITM19-T-16. (En proceso de publicación).

[3] Rivera-Gavidia LM, Fernández de la Puente I, Hernández-Rodríguez MA, Celorrio V, Sebastián D, Lázaro MJ, Pastor E, García G, Bi-functional carbon-based catalysts for unitized regenerative fuel cells. *J. Catal. JCAT-19-1574*. (En proceso de publicación).

[4] Arteaga G, Rivera-Gavidia LM, Martínez SJ, Rizo R, Pastor E, García G, Methanol Oxidation on Graphenic-Supported Platinum Catalysts, *Surfaces*, 2019; 2, 16-31.

[5] Rodríguez González MC, Gavidia-Rivera LM, Pastor E, Hernández Creus A, García G, A facile method for the fabrication of hierarchical nanosized metal catalysts, *J. Catal*, 2018; 366, 1-7.

[6] Rivera-Gavidia LM, García G, Pastor E, Novel graphene materials for the oxygen reduction reaction. *Current Opinion in Electrochemistry*, 2018; 9, 233-239.

[7] Moghadam Esfahani RA, Rivera Gavidia LM, García G, Pastor E, Specchia S, Highly active platinum supported on Mo-doped titanium nanotubes suboxide ($\text{Pt}/\text{TNTS-Mo}$) electrocatalyst for oxygen reduction reaction in PEMFC, *Renew. Energy*, 2018; 120, 209-219.

[8] Rivera- Gavidia LM, Fajardo S, Arévalo MC, García G, Pastor E, S- and N-Doped Graphene Nanomaterials for the Oxygen Reduction Reaction, *Catalysts*, 2017; 7: 278-280.

[9] Rivera Gavidia LM, Sebastián D, Pastor E, Aricò AS, Baglio V, Carbon-Supported Pd and PdFe Alloy Catalysts for Direct Methanol Fuel Cell Cathodes, *Materials*, 2017; 10: 580-594.

[10] Rivera-Gavidia LM, García G, Celorrio V, Lázaro MJ, Pastor E, Methanol tolerant Pt_2CrCo catalysts supported on ordered mesoporous carbon for the cathode of DMFC, *Int J Hydrogen Energ*, 2016; 41,19645-19655.