Thesis Review. Electrocatalysts for direct alcohol fuel cells

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Objectives and novelty

Highly porous carbon supports play a key role on the performance of fuel cell electrocatalysts. Carbon black is the most commonly used material for these applications, in particular Vulcan XC-72R, which combines good electrical conductivity and high surface area. Carbon nanocoils (CNCs) have recently received great attention as catalytic support in fuel cell electrodes due to the combination of their good electrical conductivity, derived from their graphitic structure, and a wide porosity that allows the diffusional resistances of reactants/products to be minimized.

In this work, the catalytic graphitization was proposed as the synthesis procedure for CNCs; this way, carbon materials containing graphitic structures can be obtained at low temperature. A study of the physicochemical properties of carbon nanocoils, giving particular attention to the variation of these characteristics depending on the synthesis conditions was carried out. Furthermore, it was reported for the first time a study of different oxidation treatments on carbon nanocoils, in order to modify their surface chemistry, increase the specific surface area and develop a higher porosity.

As an application, CNCs were used as support material for electrocatalysts to be used in fuel cells. Mono and bimetallic catalysts supported on the as-prepared carbon nanocoils. The influence of the support (compared with the commercial carbon black Vulcan XC-72R) and the synthesis method on the electrocatalysts' properties for CO and alcohol oxidation were studied. It was reported for the first time the influence of different preparation methods on the behaviour of Pt based electrocatalysts in the ethanol oxidation reaction.

On the other hand, the improvement of the catalysts can either be reached by the development of inherently more active binary or ternary alloy catalysts or by improving the "Pt economy" of known alloys. The latter may be achievable by effectively removing the "un-used" Pt from the core of the metal nanoparticles by fabrication of core-shell electrocatalysts, in which Pt or Pt alloy is distributed on the surface of a nanoparticle core composed of another (ideally less expensive) metal. For this reason, a first attempt to explore new and novel configurations for the development of active and stable catalysts with a core-shell nanostructure for the electrooxidation of alcohols in DAFCs was executed.

Results

The synthesis of carbon nanocoils (CNC) was studied varying the molar ratios of the reactants used. The synthesis involved the heat treatment of composites formed by a carbon precursor (resorcinol-formaldehyde gel), silica, and a transition-metal salt (a mixture of cobalt and nickel salts). The characterization of these materials by means of different techniques allowed determine the textural and structural properties and the morphology of the synthetic carbon materials, confirming their high surface area, well-defined porosity, and good crystallinity. The surface of carbon nanocoils can be modified by using different oxidation agents in liquid phase. CNC-3 was chosen, and carboxylic groups, lactones, phenols and quinones were created, increasing their number with the severity of the treatments. Carboxylic groups are stable only at low temperatures and increase the wettability of the carbon, facilitating the interaction of the metal precursor and the carbon during the impregnation stage. On the other hand, phenols and quinones are stable at high temperatures and act as metal anchoring sites, which hinder the redistribution and agglomeration of metal during the reduction stage.

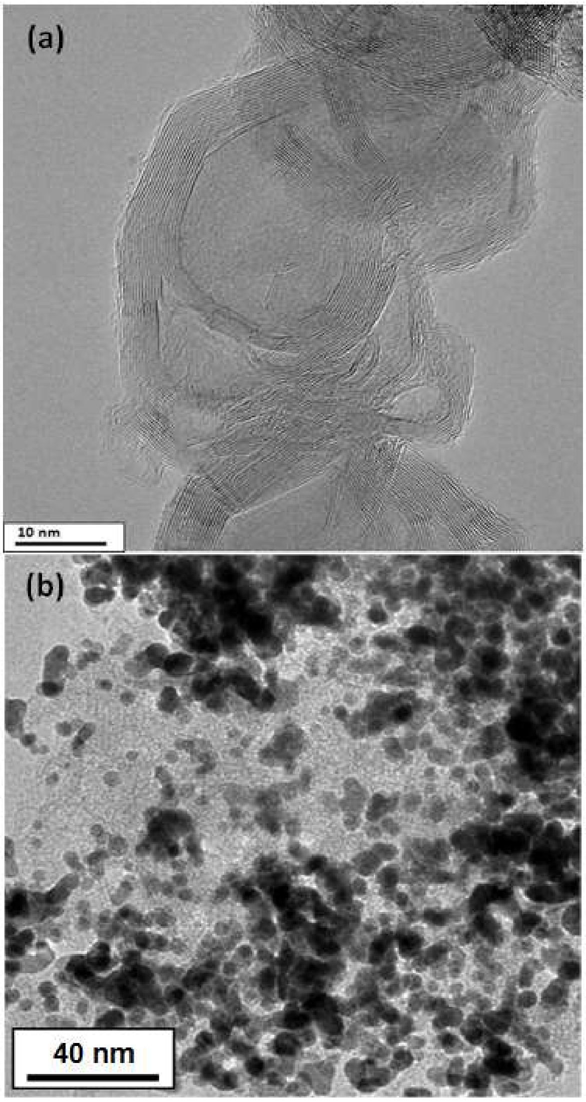

Figure 1. HRTEM image of CNC-3 NcTa2 (a); and TEM image of a Pt/CNC electrocatalyst (b).

From the functionalization study, the material treated with concentrated nitric acid at room temperature for 2h (CNC-3 NcTa2) was selected to prepare supported platinum and platinum-ruthenium catalysts by different synthesis procedures. The same routes were used to prepare nanoparticles supported on Vulcan for comparison. In general terms, higher average particle sizes were obtained using CNC as support, due to the lower number of nucleation sites (in graphitized carbons, only the surface defects can function as nucleation sites). A strong influence of the synthesis method and the carbon support was found on the particle size. CO oxidation on Pt and Pt-Ru electrocatalysts was favoured by using CNC as support; CO_{ads} oxidation peaks were obtained at lower potentials than using Vulcan. However, in the case of Pt, this improvement did not aid methanol oxidation, obtaining higher current densities when Vulcan was used as support. This could be attributed to a higher formation of by-products on CNC samples (observed by Differential Electrochemical Mass Spectroscopy analysis) that could poison the metal particles to a large extent. On the contrary, an improvement in the ethanol oxidation reaction was produced when CNC were used as support. As the key step in the EOR is the cleavage of the C-C bond, it can be deduced that Pt-CNC interactions favour this reaction.

By growing metallic films on a foreign substrate, the structure of the *d*-band, which plays an important role in the catalytic activity of metal, can be modified. For this reason, Au-Pd core-shell structured nanoparticles were prepared. The influence of the Pd-shell thickness was studied, as well as the influence of the support. As the nanostructures were already formed, this approach allowed decoupling effects of the support on particle growth from specific chemical interactions linked to the reactivity of the metallic centres; Vulcan and In-doped SnO_2 electrodes (ITO) were used. It was demonstrated that the reactivity of Au-Pd core-shell nanostructures towards CO and HCOOH oxidation is not only determined by the composition and structure of Pd overlayer, but also by the interaction with the support. Analysis of the CO stripping voltammograms in acid solution concluded that the CO coverage is strongly linked with the average lattice strain of core-shell particles, while the carbon support affects the onset potential for CO oxidation. HCOOH oxidation also exhibits a strong dependence on the support. Particles supported on Vulcan exhibit a significantly slower deactivation rate in chronoamperometric measurements, in comparison to those assembled on ITO. Furthermore, core-shell nanoparticles with thicker Pd layers, presented higher current densities than pure Pd nanoparticles for HCOOH oxidation.

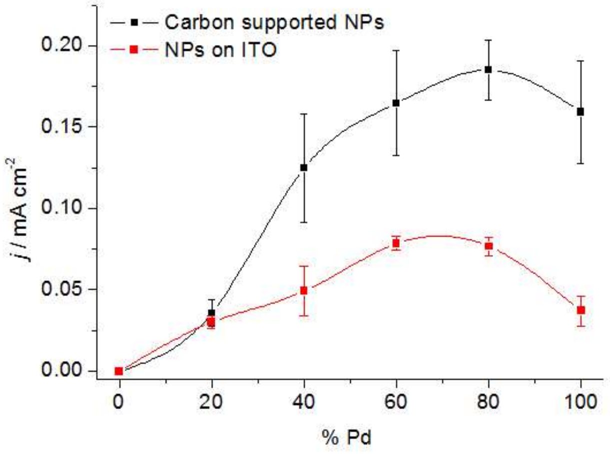

Figure 2. Current density at 750 seconds associated with HCOOH oxidation at 0.60 V (vs. RHE), on the various metallic nanostructures assembled on ITO (red) and supported on Vulcan (black), in 0.5 M H_2SO_4 + 2 M HCOOH.

Conclusions

The properties of CNC as well as their surface chemistry can be tuned by an adequate choice of synthesis conditions, favouring the formation of surface oxygen groups. Platinum-based catalysts have been supported on CNCs through different synthesis methods and their catalytic activity has been proven. These results prove that CNCs are promising candidates as alternative to replace Vulcan in order to improve the performance of the direct alcohol fuel cells.

In addition, it can be affirmed that the reactivity of Au-Pd core-shell nanostructures toward CO and HCOOH electro-oxidation is not only determined by the composition and structure of Pd overlayer but also by interaction with the support.

Related publications

[1] Celorrio V, Calvillo L, Martínez-Huerta MV, Moliner R, Lázaro MJ, Study of the synthesis conditions of carbon nanocoils for energetic applications, Energy&Fuels 2010: 24, 3361-3365.

[2] Lázaro MJ, Calvillo L, Celorrio V, Perathoner S, Moliner R. Study and application of Vulcan XC-72 in low temperature fuel cells (Chapter of the Book Carbon Black: Production, Properties and Uses). F. Columbus (Eds.). ©2011 Nova Science Publishers, Inc. Chapter 2, pp 41-68.

[3] Celorrio V, Calvillo L, Pérez-Rodríguez S, Lázaro MJ, Moliner R, Modification of the properties of carbon nanocoils by different treatments in liquid phase, Microporous and Mesoporous Materials 2011; 142, 55-61.

[4] Lázaro MJ, Celorrio V, Calvillo L, Pastor E, Moliner R, Influence of the synthesis method on the properties of Pt catalysts supported on carbon nanocoils for ethanol oxidation, Journal of Power Sources 2011; 196, 4236-4241.

[5] Montes de Oca MG, Plana D, Celorrio V, Lázaro MJ, Fermín DJ, Electrocatalytic properties of strained Pd nanoshells at Au nanostructures: CO and HCOOH oxidation, Journal of Physical Chemistry C 2012; 116, 692-699.

[6] Celorrio V, Montes de Oca MG, Plana D, Moliner R, Lázaro MJ, Fermín DJ, The effect of carbon supports on the electrocatalytic reactivity Au-Pd core-shell nanoparticles, Journal of Physical Chemistry C 2012; 116, 6275-6282.

[7] Celorrio V, Montes de Oca MG, Plana D, Moliner R, Fermín DJ, Lázaro MJ, Electrochemical performance of Pd and Au-Pd core-shell nanoparticles on surface tailored carbon black as catalyst support, International Journal of Hydrogen Energy 2012; 37, 7152-7160.

[8] Celorrio V, Calvillo L, Moliner R, Pastor E, Lázaro MJ, On the enhancement of activity of Pt and Pt-Ru catalysts in methanol electrooxidation by using carbon nanocoils as catalyst support, submitted to Journal of Power Sources.

Full Thesis can be downloaded from:
http://digital.csic.es/handle/10261/58189