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Electrocatalysis of oxygen reduction on CoNi-decorated-Pt nanoparticles: A theoretical and experimental study

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ABSTRACT

A CoNi-decorated-Pt (40:40:20 wt%) electrocatalyst was theoretically studied and experimentally validated for the oxygen reduction reaction (ORR) in acid media. To predict the activity of the electrocatalyst a $Co_{16}Ni_{16}$-decorated-Pt_3 cluster was employed. The O and O_2 adsorption energies were used as descriptors of the catalytic activity for the ORR. All calculations were performed using the density functional theory approach as implemented in the deMon2k code. A combined synthesis of high energy milling-galvanic displacement was performed to produce the CoNi-decorated-Pt electrocatalyst. The physical characterization of the electrocatalyst was developed using X-ray diffraction (XRD) for the phases identification, energy disperse X-ray spectroscopy (EDX) for compositional analysis and scanning transmission electron microscopy (STEM) to determine morphology and particle size of the synthesized electrocatalyst. Cyclic voltammetry and rotating disk electrode techniques were used for the electrochemical characterization of the synthesized electrocatalyst. The O and O_2 adsorption energies showed that CoNi-decorated-Pt ($Co_{16}Ni_{16}$–Pt_3 cluster) electrocatalyst represents an attractive candidate for the ORR. STEM micrographs showed homogeneous nanocrystalline particles of 5–10 nm size. The CoNi-decorated-Pt nanoparticles presented high specific activity, 40% above of the determined from Pt/C and similar mass activity from the same commercial Pt/C, used as comparison. Electrochemical results confirm the feasibility of a combined synthesis method to produce nanocatalysts which exhibit similar catalytic activity than that of commercially available Pt/C electrocatalyst.

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Introduction

Proton exchange membrane fuel cells (PEMFCs) are electrochemical energy conversion devices which have attracted considerable interest as power sources for mobile and stationary applications [1,2]. However, their commercialization is severely hampered both by the fact that oxygen reduction reaction (ORR) is slow and by the extremely high cost of platinum [3,4]. To overcome these disadvantages, M@Pt (M = Fe, Co, Ni, Cu, Pd, etc.) bimetallic catalysts were explored as the first alternatives to pure Pt catalysts for the oxygen reduction reaction (ORR) [5,6]. Later, multi-metallic electrocatalysts were also reported [7]. For example, bimetallic cores containing a Pt shell have also been investigated to enhance electroactivity towards the ORR [8,9]. The latest trend focuses on novel structures produced by several synthesis methods that favor controlling the structure at the atomic level and that are able of tuning catalytic properties [10]. However, other synthetic methods less sophisticated such as high energy milling (HEM) also have demonstrated being highly efficient in the fabrication of electrocatalysts for the ORR [11–13]. Up to now, the preparation of catalysts using HEM as the unique synthesis method has been reported [11–13]. Nevertheless our procedure of synthesis implies two different techniques, the HEM technique that was employed for obtaining nanosized particles of non-noble metals (Co and Ni) and galvanic displacement for decorating the Co and Ni mix with chemically deposited Pt.

On the other hand, recent advances in density functional theory (DFT) show that design of computer-based catalysts can be archived. These calculations allow to obtain interaction energies of molecules or atoms with metal surfaces with the sufficient accuracy to describe trends in the catalytic activity of systems which contain transition metals [14]. Regarding the ORR, several studies have been performed to correlate theoretical and experimental studies. The descriptors of the catalytic activity towards the ORR commonly used are the adsorption energies of adsorbates (O, O_2, OH and others) and the d-band center energy [15–17]. It has been observed that the predictor values are closely related with the specific and mass activity obtained experimentally. In 2004, it was demonstrated that from the theoretical O and OH adsorption energies, the trends in the oxygen reduction rate for a large number of different transition metals could be predicted [15]. In another study, a kinetic model was performed that gives the rate of the ORR at a given potential as a function of a single parameter (oxygen adsorption energy) characterizing the catalyst surface. The model of the catalytic activity as a function of the adsorption energy of the oxygen leads to a volcano-shaped dependence. With this model accurately predicted trends for the catalytic activity toward the ORR can be obtained [16]. More recently, the graph of the catalytic activities of different catalysts as a function of the calculated oxygen adsorption energy results in a simple volcano relationship and it was confirmed again that the oxygen adsorption energy is a good descriptor for the catalytic activity [17]. With the combination of theoretical and experimental results, has been shown that the best catalysts should exhibit an O binding energy of roughly 0.2 eV weaker than that of Pt [16,17]. Due to the great accuracy of DFT calculations several theoretical studies on electrocatalysts have been developed considering surfaces [18,19] and nanoparticle models [19–21] and the adsorption energies of the intermediaries theoretically calculate served as predictors for the ORR.

In this theoretical-experimental study we developed a CoNi-decorated-Pt (40:40:20 wt%) electrocatalyst. To predict the catalytic activity of the electrocatalyst, a $Co_{16}Ni_{16}$-decorated-Pt_3 cluster model was employed in the theoretical part. The metal ratios in this cluster are proportional to the metals in the synthesized electrocatalyst. The O and O_2 adsorption energies on $Co_{16}Ni_{16}$-decorated-Pt_3 cluster obtained with DFT calculations were considered as descriptors of catalytic activity. In the experimental part of this study, the CoNi-decorated-Pt electrocatalyst was fabricated with a combined synthesis procedure of high energy milling and galvanic displacement. Physical characterization was employed to determine composition and particle size whereas electrochemical characterization was performed to determine specific and mass activities. The obtained results were compared with commercially available carbon supported Pt/C for the ORR.

To the best of our knowledge this work represents one of the few studies where a very extensive investigation bridging theoretical and experimental results is performed with the aim to propose a novel electrocatalyst characterized by similar catalytic activity as the one of commercially available Pt/C electrocatalysts.

The manuscript is organized as follows. In the next section details of the employed theoretical methods and experimental procedures are given. In Section Results the obtained results are presented and discussed. Finally in the last section the conclusions are summarized.

Methodologies

Computational details

All calculations were performed using the linear combination of Gaussian type orbital Kohn–Sham auxiliary density functional theory (LCGTO-KS-ADFT) with the deMon2k program [22,23]. The exchange correlation potential was numerically integrated on a fine grid [24,25]. The Coulomb energy was calculated by the variational fitting procedure proposed by Dunlap, Connolly and Sabin [26,27]. For the exchange and correlation functional, we employed the PBE98-PBE96 functional, which uses a combination of PBE98 exchange functional [28] and PBE96 correlation functional [29]. The platinum atom has been described using an 18 electron quasi-relativistic effective core potential (QECP|LANL2DZ) and the corresponding valence basis set [30] whereas the cobalt, nickel and oxygen atoms were described with an all-electron double zeta valence plus polarization (DZVP) basis set optimized for GGA functionals [31]. For all calculations the GEN-A2* auxiliary function set was employed [31]. The restricted open-shell Kohn–Sham (ROKS) methodology was employed to avoid spin contamination [32].

In this investigation, a $Co_{16}Ni_{16}$-decorated-Pt_3 cluster was modeled to represent the ratios of the CoNi-decorated-Pt