



Short communication

Development of Pd and Pd–Co catalysts supported on multi-walled carbon nanotubes for formic acid oxidation

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ABSTRACT

Pd–Co and Pd catalysts were prepared by the impregnation synthesis method at low temperature on multi-walled carbon nanotubes (MWCNTs). The nanotubes were synthesized by spray pyrolysis technique. Both catalysts were obtained with high homogeneous distribution and particle size around 4 nm. The morphology, composition and electrocatalytic properties were investigated by transmission electron microscopy, scanning electron microscopy–energy dispersive X-ray analysis, X-ray diffraction and electrochemical measurements, respectively. The electrocatalytic activity of Pd and PdCo/MWCNTs catalysts was investigated in terms of formic acid electrooxidation at low concentration in H₂SO₄ aqueous solution. The results obtained from voltamperometric studies showed that the current density achieved with the PdCo/MWCNTs catalyst is 3 times higher than that reached with the Pd/MWCNTs catalyst. The onset potential for formic acid electrooxidation on PdCo/MWCNTs electrocatalyst showed a negative shift ca. 50 mV compared with Pd/MWCNTs.

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1. Introduction

The electrochemical oxidation of small organic molecules has been widely studied due to their potential utilization as fuel in energy conversion systems. The main reason is related to their low toxicity, facility of storage, handling and primarily their energy density. Moreover, due to their simple molecular structure they should undergo a more straightforward reaction mechanism than other possible organic fuels [1–4].

In this context, formic acid, a non-toxic and non-explosive liquid at room temperature, has shown potential applications in small portable fuel cell applications [5,6]. The mechanism of formic acid electrooxidation on Pt and select Pt-group metal surfaces in acid solution follows the so-called dual pathways dehydrogenation and dehydration [7]. Numerous studies have shown for instance that Pd catalysts accomplish higher activity for formic acid oxidation than Pt [8,9]. Palladium is a metal known for its ability to catalyze CO oxidation and other hydrocarbons as well [10]. It has an electronic configuration identical to platinum and forms a not so strong, bond to most absorbates. The key differences are: Pd-*d*-bands are closer to the cores than platinum, and

there is less *d* electron density available for bonding. This leads to weaker interactions with π bonds, which allows unique chemistry to occur. Pd has higher oxidation potential than Pt, and the Pd oxides are more stable [11]. Weak inter-atomic bonds between palladium atoms compared to platinum or nickel lead to easy formation of subsurface species, whose role is still uncertain. Also, palladium has a very similar lattice constant to that of platinum [11].

On the other hand, it is well known that the type of carbon support affects the performance and stability of the catalysts. Carbon supported palladium catalysts have become a very important area in DFAFC (direct formic acid fuel cell) catalyst research in recent years, showing good activity along with the potential for more efficient palladium metal utilization and lower metal loadings [12–17]. In this context, Ha et al. synthesized Pd particles dispersed on Vulcan XC-72[®] carbon support and the results were compared with those obtained from pure palladium in DFAFC [12]. Even in the light of these and other, it is clear that in order to achieve an improved performance in terms of activity and stability of the Pd catalysts, a promising approach consists in the addition of metal or metal oxide promoters [18]. Carbon nanotubes (CNTs) are of interest as catalyst supports for applications in fuel cells due to their unique electrical and structural properties [19,20]. Multi-walled carbon nanotubes (MWCNTs) have been used as the support of the cathode electrocatalyst and showed a better performance in DEFCs (direct

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ethanol fuel cells) due to the higher nanoparticle dispersion than that electrocatalysts supported on carbon black [21–25].

In this study MWCNTs were prepared by the spray pyrolysis technique and used to supporting Pd-based electrocatalysts. Some authors have supported alloy catalysts by low temperature aqueous route on high surface area carbon with nanometer size particles, stability and superior electrocatalytic properties [26,27]. In this work, the novel materials were synthesized by impregnation method on MWCNTs at low temperature. The physicochemical properties of Pd-electrocatalysts were evaluated by transmission electron microscopy (TEM), scanning electron microscopy coupled to energy dispersive X-ray (SEM–EDX) and X-ray diffraction (XRD). The electrooxidation of 0.1 M formic acid was investigated in order to show the high catalytic activity of our materials and a comparison with the performance of the Pd/XC-72 commercial electrocatalyst was done.

2. Experimental

2.1. Synthesis and functionalization of MWCNTs

MWCNTs were synthesized using the spray pyrolysis technique. The detailed procedure of preparation has already been reported [28]. The MWCNTs were cleaned by immersion in concentrated HNO₃ in an ultrasonic bath for 1 h. After that, they were refluxed for 12 h at 80 °C. The solution was filtered and washed with plenty of distilled water. In order to promote their functionalization, the MWCNTs were immersed in a HNO₃/H₂SO₄ (1:4, v/v) solution for 5 h at 60 °C under refluxing and stirred conditions. Later, the wet powder was washed with deionized water until the pH of the filtrated solution was 7. Finally, the powder obtained was dried overnight at 60 °C.

2.2. Preparation and physicochemical characterization of Pd and Pd–Co catalysts

Pd-based catalysts were prepared by the impregnation on MWCNTs and reduced by the action of NaBH₄. The procedure for the synthesis of Pd/MWCNTs was as follows: MWCNTs were first dispersed in deionized water by treated in an ultrasonic bath for 60 min. After that, the nanotubes were added into (NH₄)₂PdCl₆ (Stream Chemicals, 99%) aqueous solution. NaBH₄ (Sigma–Aldrich, 98.5%) was slowly dropped into this mixture and vigorously stirred for 1 h. The molar ratio between the metal and the reducing agent was 1:5. The resulting solution was filtered, washed and dried overnight at 60 °C. The same method for preparation of PdCo/MWCNTs was carried out. In this case however, previous to the NaBH₄ addition to the mixture of (NH₄)₂PdCl₆–MWCNTs, CoN₂O₆·6H₂O (Acros Organic, 99%) was added to the aqueous solution. In order to remove the excess of cobalt in PdCo/MWCNTs, a treatment with 0.1 M HCl was accomplished.

The obtained powders were characterized by X-ray diffraction (XRD) measurements on an X-pert MPD Phillips Diffractometer using Cu K α radiation operating at 43 kV and 30 mA. The peak profile of the (2 2 0) reflection in the face-centered cubic structure was obtained by using the Marquardt algorithm and used to calculate the crystallite size utilizing the Debye–Scherrer equation [29]. A JEOL JSM 5800-LV scanning electron microscope (SEM) on the other hand, was used for SEM–energy dispersive X-ray (EDX) analysis of the catalysts. The morphology of catalysts was investigated using a Philips Model CM200 transmission electron microscope (TEM) operated at 200 kV.

2.3. Half-cell experiments

Electrochemical experiments consisted in cyclic voltammetry (CV) and linear sweep voltammetry (LSV) using a BAS Epsilon

Potentiostat/Galvanostat (Bioanalytical Systems). A glassy carbon electrode (3 mm diameter) was used as working electrode in a standard three-electrode glass cell, using a Hg/Hg₂SO₄ electrode and a Pt wire as reference and counter electrode, respectively. Potentials in the text are referred to the NHE (normal hydrogen electrode).

The working electrode, which was used as substrate of catalyst inks, was prepared by polishing until a mirror-finished with 0.05 μ m alumina powder followed by rinsing in water. Later, 1 mg of catalyst was dispersed in 200 μ l of isopropyl alcohol in an ultrasonic bath for 40 min; afterwards, 20 μ l of Nafion® 5% solution were added and continuously stirred for 20 min. Two aliquots of 1.5 μ l of the electrocatalytic ink were deposited onto glassy carbon disks and dried under a nitrogen flow. For comparison, a commercial Pd/XC-72 catalyst was used (Electrochem®, 10 wt.%). The electrode was also prepared according to the procedure described above.

All electrolytes were prepared with deionized water ($\rho \geq 18 \text{ M}\Omega \text{ cm}$). The formic acid electrooxidation was investigated in 0.1 M in 0.5 M H₂SO₄, which was employed as electrolyte. Before each experiment, the electrode was cycled for 5 min at 20 mV s⁻¹ between 0.08 and 1.2 V in 0.5 M H₂SO₄ under N₂ atmosphere in order to clean the surface. Afterwards, CV experiments were carried out in the presence of 0.1 M formic acid. LSV curves of 0.1 M formic acid were recorded at different scan rates (20, 40, 60, 80 and 100 mV s⁻¹). The experiments were carried out under research-grade N₂ atmosphere (Infra, 99.999% pure) and the temperature was kept in all cases at 30 °C.

3. Results and discussion

3.1. Physicochemical characterization

X-ray diffraction patterns collected from Pd/MWCNTs and PdCo/MWCNTs catalysts are presented in Fig. 1. The maximum peak located at 26° corresponds to the graphite (0 0 2) plane of MWCNTs support [30]. The other principal peaks exhibit the characteristics of a single face-centered-cubic (fcc) crystallographic structure of Pd (JCPDS, Card No. 5-681), corresponding to the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1) located at 40°, 47°, 68° and 82°, respectively. Although not exists an obvious shift of these four diffraction peaks for the PdCo material with respect to the corresponding peaks in the Pd catalyst, a lattice contraction caused by the incorporation of Co into the Pd fcc structure is revealed by a lower value in the lattice parameter of PdCo catalyst. This Pd lattice compression or reduction of bond lengths between metals can be induced by the

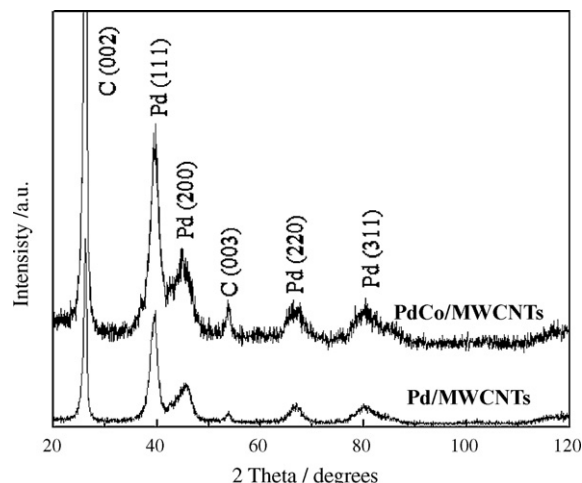


Fig. 1. XRD patterns of Pd/MWCNTs and PdCo/MWCNTs.

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