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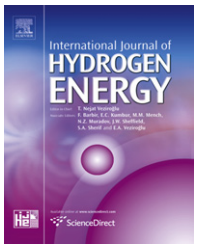

CO electrooxidation on Pt–Ru catalysts supported on carbon nanotubes

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ABSTRACT

CO electrooxidation studies can be done in relation to either the poisoning effect in methanol fuel cells or to be applied as basis for the development of electrochemical CO sensors. In the present work, Pt and PtRu catalysts supported on multiwalled carbon nanotubes, CNTs, are probed with regard to their ability to detect changes in the CO concentration in acidic solutions. Pt and PtRu particles were dispersed onto pretreated CNTs by a modified polyol process using $RuCl_3$ and H_2PtCl_6 as their metallic precursors. The physical characterization and dispersion of the catalytic particles were obtained through SEM and TEM images, and EDX analysis provided the chemical composition. CO oxidation was studied applying electrochemical techniques. For both catalysts, linear relationships were obtained when relating chronoamperometric current densities to different CO concentrations, indicating their possible application as CO sensors'devices materials.

1. Introduction

Carbon monoxide is a gas present in the atmosphere generally in low levels, but it can be a serious problem when the limits established for human life are surpassed. It is mainly produced by the incomplete combustion of fuels. Intensive research is done in relation to different Pt-based catalysts applied to direct alcohol fuel cells [1,2]. In this case, CO-like intermediates formed in the alcohol oxidation reaction can be adsorbed on the electrode surface lowering the cell yield [3–5]. On trying different ways to solve the problem, bi- and tri- metallic catalysts are used; they are combinations of Pt with other metals such as Ru, Ni, Co prepared as bulk alloys [6,7], deposited by different methods [8–12], dispersed onto diverse substrates [8,10,11] or supported on carbon particles [9,10].

Presently, high surface area noble metal electrodes have been supported on different types of carbon particles and by several routes [8,9,13]. Powders of the catalysts are mainly obtained through chemical precipitation from aqueous or organic solutions with a particle size and agglomeration dependent on the nature and the concentration of both, the precursors and the reducing agent [14]. Moreover, nanostructured carbon materials such as carbon nanotubes are being used in the preparation of supported electrodes. Recently, we have developed multiwalled carbon nanotubes, CNTs, which were used as aggregates to polyaniline films for Pt and PtRu composite electrodes for methanol oxidation [11].

The very same materials can be applied to the detection of carbon monoxide in solution. In this respect, the preparation and characterization of Pt and PtRu supported on CNTs electrodes are detailed, and their electrochemical behavior for the

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CO oxidation reaction is presented in relation to their application in CO sensor devices.

2. Experimental

2.1. Preparation of composite electrodes

Carbon-supported catalysts were prepared using lab prepared CNTs pretreated with HNO_3 2.2 M for 20 h [11]. The catalysts were synthetized by a modified polyol technique [14], employing $RuCl_3$ and H_2PtCl_6 as metallic precursors and polyvynilpyrrolidone (PVP), ethylene glycol and sodium borohidride.

The preparation run involved the following steps: (i) a preset amount of CNTs was added to a 3:1 ethylene glycol - water solution and PVP (considering a 0.3 monomers per Pt atom ratio); the mixture was stirred using an ultrasonic bath for 15 min; (ii) the precusor was added in the stoichiometric ratio to obtain a colloidal solution after 15 min ultrasonication; (iii) the nucleation and growth process of the metals was attained fixing the temperature at 140 °C for1 h; (iv) the mixture was cooled down adjusting pH to 8; (v) after filtration, the retained solid was rinsed carefully and afterwards dried in a vaccum stove at 60 C for 12 h.

When preparing PtRu catalysts, an additional step was introduced to favor the Ru(III) reduction process adding $NaHB_4$ because it is a powerful reduction agent that promote the formation of nucleation sites [15]. Thus, after including the Ru precursor and previous to (iv) the addition of a $NaHB_4$ 0.2 M solution to the mixture drop by drop, the whole mixture was stirred, then the system was maintained at 80 C for 1 h.

2.2. Characterization of the composite electrodes

SEM images provided the surface characterization and the dispersion of the catalytic particles, the composition was determined by EDX and the number and size of the catalysts were estimated through TEM images.

Electrochemical techniques such as stripping voltammmetry and chronoamperometry were also used, in a conventional three electrode cell at 25 C. The counter electrode was a large Pt sheet and the reference electrode was Ag/AgCl. All potential values in the text are referred to the reversible hydrogen electrode, RHE. The working electrodes were Pt/CNTs and PtRu/CNTs catalysts. The electrodes were prepared on a glassy carbon disc where the catalyst suspension was set with a micropipette. When it dried, a Nafion polymer solution was added covering the entire disc.

CO stripping measurements were performed in saturated CO H_2SO_4 0.5 M solutions. CO was adsorbed at E = 0.05 V for 20 min; then N_2 was bubbled to remove CO from the solution. The CO electrooxidation was achieved by voltammetry.

Chronoamperometric measurements were used to determine the steady current for different CO concentrations. An experimental routine was applied to reach the adsorption potential. First, a $CO–N_2$ mixture with controlled concentrations was bubbled in the cell solution for 3 min; then, CO was adsorbed at E = 0.05 V for 7 s. Finally, through an anodic sweep at high sweep rate, v = 0.5 V s^{-1}, the adsorption potential is changed to its end value in the 0.55–0.65 V potential range.

Real areas were determined by considering the anodic charge involved in the CO-stripping peak by assuming that CO is linearly adsorbed on one Pt site and taking into account that 420 μC is equivalent to 1 cm^2.

3. Results and discussion

3.1. Preparation and characterization of the supported electrodes

The carbon supported electrodes were prepared as described in the experimental section. Fig. 1 shows their SEM and EDX results for Pt/CNTs and PtRu/CNTs catalysts, respectively. The micrographs reveal a rather uniform dispersion of the supported catalyst. The catalysts metallic composition was

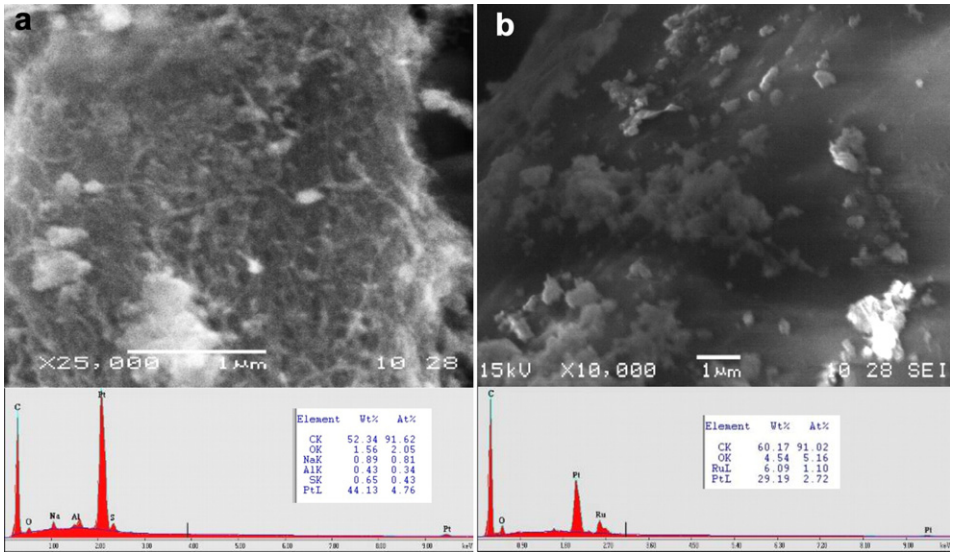

Fig. 1 – SEM images and EDX analysis for (a) Pt/CNTs and (b) PtRu/CNTs catalysts.

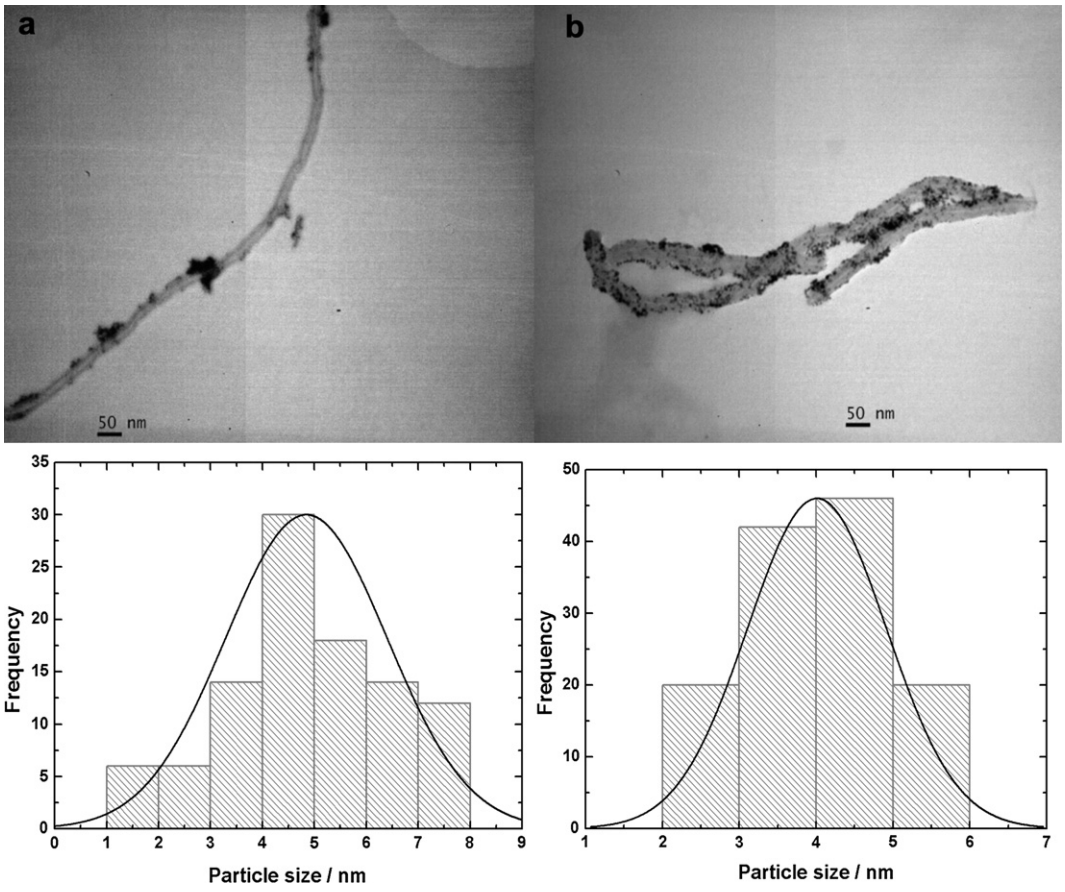

Fig. 2 – TEM images and histograms of the resulting particle distribution for (a) Pt/CNTs and (b) PtRu/CNTs catalysts.

established by EDX analysis, being 44% Pt and 29%Pt and 6%Ru for Pt/CNTs and PtRu/CNTs, respectively.

Fig. 2 shows TEM images for both catalysts. A quite regular distribution of metallic particles on the CNTs walls can be appreciated. It should be pointed out that the reaction process proceeds via dissolution, with the polyol acting simultaneously as a solvent, a reducing agent and to some extent as a protective agent [14]. When it is applied to obtain precious metals powders as in the present case, a coagulation of the particles during their growth can also occur. The histograms of the metal particle size distribution and the corresponding curves are also presented in the same Fig. 2; from these graphs, the mean diameters are ca. 4 nm for Pt/CNTs and 5 nm for PtRu/CNTs. As the particles are nearly spherical and show a low degree of agglomeration, the contribution of the surface area of each metallic particle group with the size distribution to the total one can be calculated. Hence, the surface area is determined predominantly by the particles located between 4 and 8 nm for Pt/CNTs and 4 and 6 nm for PtRu/CNTs.

Surface areas determined from the CO stripping voltammograms (Fig. 3) are 3.5 and 5.6 cm^2 for Pt/CNTs and PtRu/CNTs, respectively.

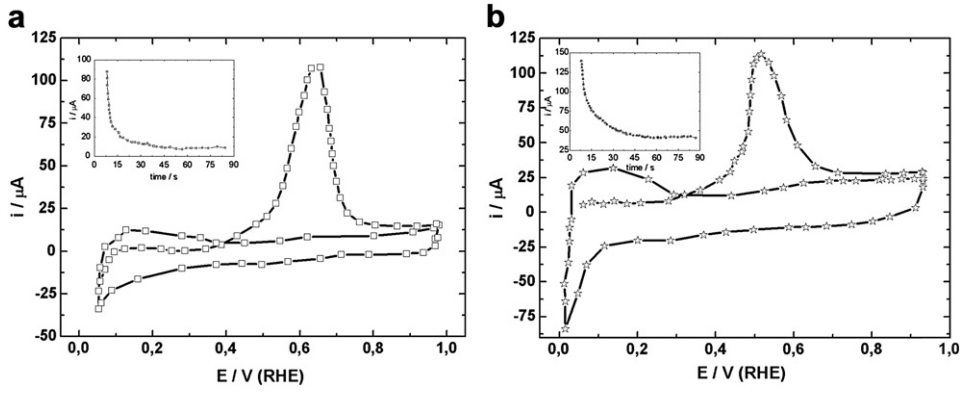

Fig. 3 – CO-stripping curves for (a) Pt/CNTs and (b) PtRu/CNTs catalysts in H_2SO_4 0.5 M at 298 K, with a sweep rate of 0.01 V s^{-1}. The inset shows chronoamperometric measurements at the peak potentials.

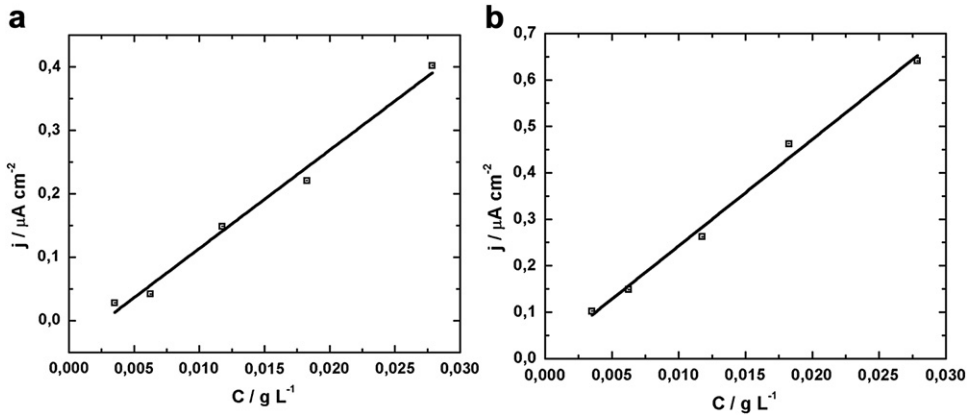

Fig. 4 – Relationship between the stabilized current density and the concentration of CO in solution for (a) Pt/CNTs and (b) PtRu/CNTs.

3.2. *CO electrooxidation*

CO stripping voltammograms are showed in Fig. 3. The onset and peak potentials for CO electrooxidation on PtRu/CNTs were significantly lower than those corresponding to Pt/CNTs catalyst. The potential values are 0.38 V and 0.43 V for the onset ones and 0.55 V and 0.66 V for the peak potentials. The special surface characteristics of the activated CNTs and the abundant active sites on the nano-catalysts particles are regarded as possible reasons for their CO catalytic activity. In addition, the catalytic PtRu sites offer the conditions to adsorb CO and H_2O and promote the generation of active oxygen species, favoring both the onset potential and the oxidation reaction [16,17].

The chronoamperometric response of the electrodes was recorded in the presence of different CO concentrations in the acidic solutions showing a sharp decrease from the starting point (Fig. 3). This behavior was attributed to the exceptionally high surface coverage of CO at the beginning of the electrooxidation reaction. It was reported that depending on the particle size, the shape of the transient currents changes [13]. In this case, the oxidation of CO is so fast that no current maximum is observed. The current decay is rapid for both catalysts, being the steady current values higher for PtRu/CNTs electrodes and reaching ca. 10% and the 30% of the initial values in 3 min for Pt/CNTs and PtRu/CNTs, respectively.

Fig. 4 shows the relationship between the stationary currents and the CO concentration for both electrodes. Linear equations such as $j(\mu A\ cm^{-2}) = 15.4916\ c\ (g\ L^{-1}) - 0.0414$, with a correlation coefficient of 0.98518 for Pt/CNTs and $j(\mu A\ cm^{-2}) = 22.9197\ c\ (g\ L^{-1}) + 0.0135$, with a correlation coefficient of 0.98942 for PtRu/CNTs were established. This fact qualifies both catalysts as promising sensor materials.

It is worth to point out that the superior dispersion characteristics of the nanosized metallic particles on CNTs ascertain a good interaction between the support material and the metal catalyst. Thus, a beneficial electron transfer among the metal catalyst and the carbon support occurs during the electrochemical reaction leading steady currents that show linear relationships with the CO concentration.

4. Conclusions

- Pt and PtRu electrodes prepared by the polyol technique possess nanosized particles uniformly distributed on the CNTs used as support material.
- CO electrooxidation is favored when using PtRu/CNTs electrodes.
- Both Pt/CNTs and PtRu/CNTs electrodes can detect changes in the CO concentration resulting in linear relationships between CO concentration and CO electrooxidation current.

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