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Pt, PtNi and PtCoNi film electrocatalysts prepared by chemical vapor deposition for the oxygen reduction reaction in 0.5 M KOH

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ABSTRACT

Pt, PtNi and PtCoNi films were deposited by metal–organic chemical vapor deposition (MOCVD) upon glassy carbon rods. Physical characterization was performed by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. It was found that films consisted of crystalline and nanometric particles with more than one phase as a result of the interactions among reactants, intermediate and product species during the chemical vapor deposition process. The electrochemical set-up to test the films for the oxygen reduction reaction was a three-electrode cell where the reference electrode was Hg/HgO/0.5 M KOH, the working electrodes were the films upon glassy carbon rods. The films were tested in 0.5 M KOH electrolyte; polarization curves were obtained by using the rotating disk electrode technique to evaluate the electrocatalytic activity of the prepared films. The kinetic parameters of Pt, PtNi and PtCoNi electrocatalysts were calculated. PtCoNi showed the best performance for the oxygen reduction reaction due to a synergetic effect of alloying Pt with transition metals.

1. Introduction

Oxygen reduction reaction (ORR) is a key step in cathodes of fuel cells due to its relatively high overpotential, around four times of that one for hydrogen oxidation, the anodic reaction [1,2]. The majority of research in oxygen electrocatalysis on supported platinum electrodes has focused on the study of oxygen reduction in acid media. This is due to the fact that acid electrolytes are mainly used in fuel cell systems. Platinum is also the material of choice for technical application in alkaline fuel cells because of its high electrocatalytic activity and chemical stability. It is known that the oxygen reduction overpotential is lower in alkaline than that in acid solutions [3]. Concentrated KOH solution is used in alkaline fuel cells and in metal-air batteries. It has been found from practical applications that the oxygen reduction kinetics is more rapid in alkaline electrolytes than in acids and a wide range of electrocatalysts can be used in alkali, including Ag, Ni, metal oxides and spinels as well as noble metals [4]. In search of electrocatalysts with lower cost, to replace platinum as much as possible with metals of higher abundance, a variety of proposals has arisen for this application including mainly Pt alloys with transition metals prepared by several techniques that showed interesting results of electrocatalytic activity for the ORR [5–10].

Chemical vapor deposition (CVD) is a versatile process, suitable for the manufacturing of coatings, powders, fibers and monolithic components. With CVD, it is possible to produce most metals, many nonmetallic elements such as carbon and silicon as well as a large number of compounds including carbides, nitrides, oxides, intermetallics and many others. This technology is now an essential factor in the manufacture of semiconductors and other electronic components, in the coating of tools, bearings and other wear-resistant parts and in many optical, optoelectronic and corrosion applications [11]. In spite of CVD versatility, there are not many proposals of electrocatalysts prepared by this process [12–14]. CVD is by definition a chemical process; various process parameters, such as reaction temperature, reactor pressure and precursor chemistry (which can be metal–organic) as well as the nature of the substrate, affect film growth and microstructure [15].

The aim of this work was to prepare electrocatalysts of Pt, Co and Ni by using the CVD process and to evaluate their performance for the ORR in alkaline media.

2. Experimental

2.1. Films deposition

The precursors for CVD experiments were cobalt (II), nickel and platinum acetylacetonates as supplied by Aldrich. CVD of all films was carried out in a low pressure, horizontal hot-wall quartz reactor. Prior to film deposition, the reactor was purged with argon gas (Praxair 99.999%) at a flow rate of 100 $cm^3 min^{-1}$ for 30 min. The precursors, which are subliming solids, were vaporized at 423–473 K. Argon was used as carrier gas with a flow rate of 180 $cm^3 min^{-1}$, which was maintained steady by using an electronic mass-flow controller. Reactor pressure was 1 mmHg.

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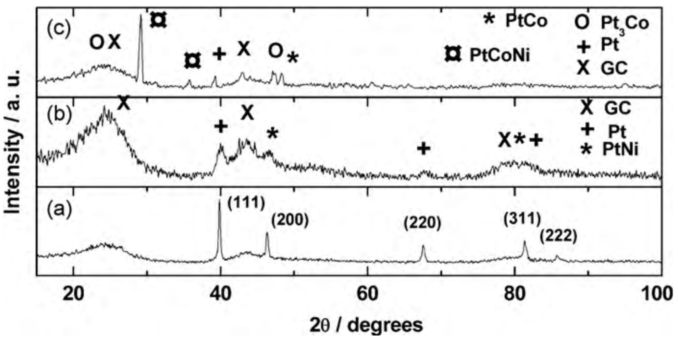

Fig. 1. DRX patterns of (a) Pt, (b) PtNi and (c) PtCoNi films prepared by CVD.

Substrates were glassy carbon (GC) rods, 5 mm in diameter, 10 mm length, polished with emery paper No. 1000 in the transversal surface which was the film receptor. The substrate (growth) temperatures were in the 673–723 K range. The deposition time for all films was 20 min.

2.2. *Structural and morphological characterization*

The as-deposited films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD was carried out in a Siemens D-5000 diffractometer (Cu Kα radiation, $\lambda = 0.15418$ nm). Particle size was calculated by using X-Powder software (trial version). Surface morphology was observed and thickness film was estimated with a JEOL JSM-6300 scanning electron microscope, equipped to perform elemental chemical analysis by energy dispersive analysis by X-rays (EDAX). Transmission electron microscopy images were obtained by using a JEOL JEM-2000 FXII microscope to have a deeper sight of the films, to support particle size calculation and to confirm crystallinity analysis.

2.3. *Electrochemical experiments*

To prepare the working electrodes, the GC rods with the as-deposited films were mounted into concentric Teflon cylinders holders. Insulated epoxy resin was used to seal the gap between the Teflon holder and the GC rods. Ohmic contact was made with silver epoxy paste (Spi supplies).

To perform the electrochemical measurements, a typical three compartments electrochemical cell was used. A pre-calibrated house-made Hg/HgO electrode (0.194 V vs. NHE) was set as reference electrode and a platinum mesh was the counter electrode. A 0.5 M KOH solution was used as the electrolyte which was prepared by dissolving KOH pellets (Aldrich) in bidistilled water. Before electrochemical experiments, the electrolyte was deoxygenated by bubbling N_2 (Praxair 99.999%) during 30 min. Cyclic voltammetry was performed to working electrodes with a scanning rate of 50 mV s^{-1} until voltammograms were reproducible. To perform ORR measurements, the electrolyte was saturated with O_2 (AGA 99.999%). Linear voltammetry was carried out by using the rotating disk electrode (RDE) technique to evaluate the electrocatalytic performance of CVD films for the ORR. The electrochemically active surface area of the catalysts was calculated by using the hydrogen adsorption method [16,17], from the cyclic voltammogram of each catalyst, the charge associated with the cathodic deposition of hydrogen atoms was calculated by integration of the area under this region and subtracting the double layer contribution. A hydrogen monolayer adsorption charge of 210 μC cm^{-2} was assumed. A Potensiostat/Galvanostat EG&G Model 273A and a unit for rotation speed control (EG&G Model 636) were employed for the electrochemical experiments.

3. Results and discussion

3.1. *XRD, SEM and TEM analysis*

Fig. 1 shows XRD patterns of as-deposited Pt, PtNi and PtCoNi films. XRD reflections were assigned according to Joint Committee of Powder Diffraction Standards (JCPDS). A broad reflection at $2\theta \cong 26.5^{\circ}$ observed in all diffraction patterns corresponds to (0 0 3) plane of GC hexagonal structure. XRD patterns in Fig. 1 show that for PtNi and PtCoNi films more than one phase can be observed. XRD pattern of PtNi film shows reflections for GC support, also, those for planes of fcc Pt and three peaks at $2\theta \cong 44.5^{\circ}$, 46.5° and 80° corresponding very likely to Pt_3Ni phase (PDF card not available). Finally, XRD pattern of PtCoNi film shows reflections for (1 0 0) and (2 0 0) planes of Pt_3Co at $2\theta \cong 23^{\circ}$ and 47°, respectively. A peak at $2\theta \cong 48.5^{\circ}$ corresponds to (1 1 1) plane for PtCo. Two more reflections at $2\theta \cong 29^{\circ}$ and 61°, probably for PtCoNi alloy but PDF card was not available to confirm this observation.

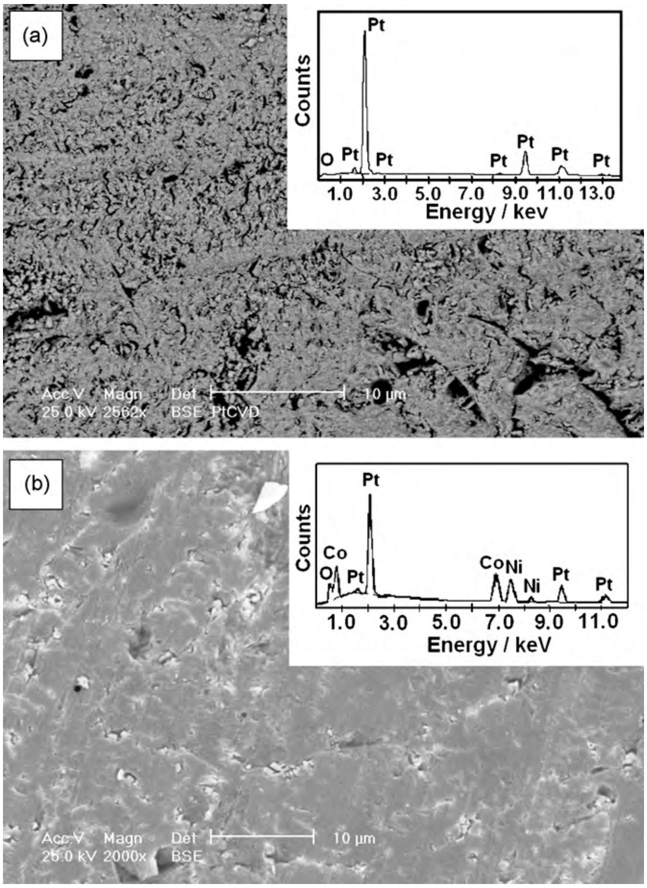

Fig. 2. SEM images of (a) Pt and (b) PtCoNi films. Insets are EDAX spectra of chemical analysis.

The presence of more than one phase in XRD patterns of as-deposited films could be explained as it has been pointed out by several authors; chemical vapor co-deposition of multi-component films with separate source precursors is the most common practice for depositing multi-component films [18–22], however, this route can be complex because of interactions among reactant, intermediate and product species on the surface substrate and in the gas phase [18,21,23]. The films oxygen content (as confirmed later by EDAX) is due to the fact that film top surface is oxidized by air. Oxygen content can vary through film thickness [24,25].

Fig. 2 shows the Pt and PtCoNi films morphology in micrographs obtained by SEM. Surface of these films is rather rough. This observation suggests that film growth involves a high nucleation density and proceeds by coalescence of small grains, leading to rather substantial roughness. Insets in Fig. 2 are EDAX spectra of each film.

Particle size and EDAX analysis of film catalysts are given in Table 1. It can be observed that all films have nanometric particle size. Chemical composition indicates more than one phase for each film, except Pt, supporting what was observed by XRD analysis.

Table 1
Particle size and chemical analysis by EDAX of Pt, PtNi and PtCoNi film electrocatalysts.

Electrocatalyst	Particle size/nm	Co	Ni	Pt	O
Pt	30			94.78	5.22
PtNi	15		15.12	70.32	14.56
PtCoNi	16	22.15	18.15	33.95	25.95

Table 2
Kinetic parameters for the ORR in KOH 0.5 M @ 298 K on Pt, PtNi and PtCoNi film electrocatalysts.

Electrocatalyst	E_{oc} /V	$-b$/V dec^{-1}	I_o/ mA cm^{-2}	Potential/V @ $i = -0.4$ mA cm^{-2}
Pt	0.244	0.108	5.34×10^{-4}	-0.078
PtNi	0.251	0.115	4.61×10^{-4}	0.062
PtCoNi	0.262	0.127	2.69×10^{-3}	0.094

Films thickness was estimated by cross-sectional SEM (micrographs not shown) and was about 180–250 nm, in accordance with other films reported elsewhere [24,25].

Fig. 3 shows a TEM image of PtCoNi film obtained at 200 kV and 400,000×. Particles of nanometric size can be observed, consistently with results obtained by XRD analysis. In Fig. 3, agglomerated particles are distinguishable, confirming what was observed through SEM analysis. Inset in Fig. 3 is an electron diffraction pattern with concentric rings which confirms that this film is polycrystalline.

3.2. Electrochemical characterization

Cyclic voltammetry was performed for electrode activation and to calculate normalized surface area of catalysts. Active area was higher than geometric surface area, 0.52, 0.41 and 0.44 cm^2 for Pt, PtNi and PtCoNi, respectively. Oxygen reduction current–potential curves were obtained at six rotation frequencies (between 100 and 1600 rpm) with a 20 mV s^{-1} scan rate. Fig. 4 shows typical RDE curves for the ORR on Pt, PtNi and PtCoNi film electrocatalysts at 1600 rpm in 0.5 M KOH at 298 K. ORR density currents commenced at ca 0.2 V and tend to diffusion limits around −0.2 V. Density currents of PtNi and PtCoNi begin to increase at a more positive potential than that for Pt film by ca. 20 and 30 mV, respectively, indicating an enhanced ORR activity for these electrocatalysts. In Pt film voltammogram there is a small decay of density current at a potential value prior to the hydrogen evolution reaction. Evidently, the number of surface sites that are needed for O_2 molecules to undergo reduction is decreasing due to hydrogen electrosorption. For PtCoNi film polarization curve, it can be observed some instability of density current in almost all the potential range. This could have been caused by bubbling of oxygen gas. In Fig. 4, it can be observed an enhanced electrocatalytic activity for Pt < PtNi < PtCoNi.

To analyze ORR kinetics, mass-transfer corrected Tafel plots were constructed. Two regions with different slopes are seen in Fig. 5 for Pt, PtNi and PtCoNi films. Table 2 shows kinetic parameters for the ORR upon films prepared in this study. Exchange current densities I_o (mA cm^{-2}) were obtained by the extrapolation of Tafel curves at low current density to thermodynamic potential of the O_2/OH^- couple in 0.5 M KOH (0.401 V vs. NHE).

According to Table 2, PtCoNi shows the best performance with the highest current density and the lowest overpotential (last column in Table 2). It is well known that alloying Pt with transition metals causes an enhanced activity for the ORR. Several investigations have been carried out to determine the role of alloying for the ORR. Alloying is believed to retard the formation of the OH (ads) electrode surface poison [26–30].

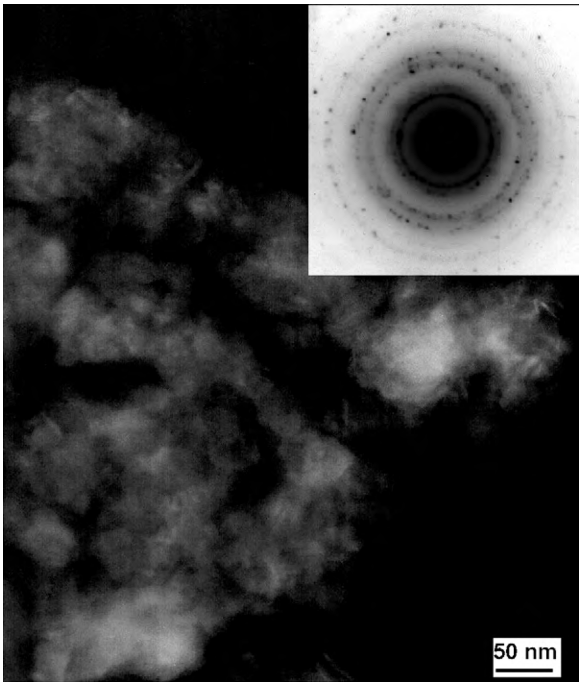

Fig. 3. TEM image of PtCoNi film. Inset presents the electron diffraction pattern.

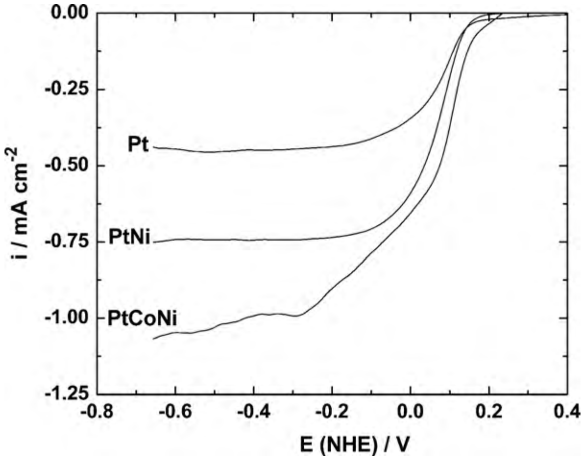

Fig. 4. Polarization curves for the ORR on Pt, PtNi and PtCoNi films in 0.5 M KOH at 1600 rpm.

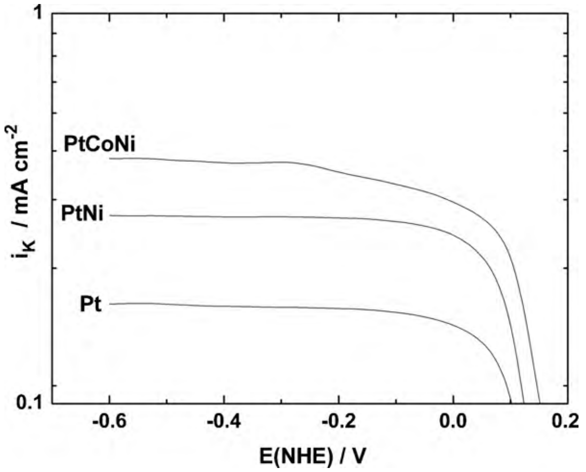

Fig. 5. Tafel plots for the ORR on Pt, PtNi and PtCoNi films in 0.5 M KOH.

4. Conclusions

Electrocatalysis for the ORR in 0.5 M KOH was studied upon films of Pt, PtNi and PtCoNi prepared by metal–organic chemical vapor deposition. All films showed to be crystalline with nanometric size. XRD patterns of PtNi and PtCoNi showed that, with the deposition process utilized in this study, these films consisted of more than one phase due to the complex route that can arise when depositing multi-component films with separate precursors as a result of interactions among reactant, intermediate and product species on substrate surface and in the gas phase. Therefore, in order to obtain only the desired phases the deposition process is being redesigned accordingly for the next experimental stage. All films in this research showed an acceptable catalytic activity in alkaline electrolyte and PtCoNi showed the highest activity for the ORR due to a synergetic effect of alloying Pt with transition metals.

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