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Preparation of Pt electrocatalysts by galvanic displacement

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Pt-based electrocatalysts were prepared by spontaneous deposition (galvanic displacement) of Pt on carbon-supported Ni, Sn, and NiSn electrocatalysts. The spontaneous deposition of Pt was performed by stirring of an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in the presence of Ni/C, Sn/C, and NiSn/C for 1 h at room temperature and open atmosphere. The obtained materials were characterized Energy-dispersive X-ray Analysis (EDX), x-ray diffraction (XRD), transmission electron microscopy (TEM), and cyclic voltammetry, and were tested for ethanol electro-oxidation using chronoamperometry. X-ray diffractograms of Ni/C and Sn/C showed that a Ni(fcc) phase and metallic Sn were formed, respectively. For NiSn/C, the presence of metallic Sn and NiSn phases was observed. After the spontaneous deposition of Pt, the x-ray diffractograms of the obtained materials did not show the presence of the crystalline phases of Pt; however, EDX analysis showed the presence of Pt in these materials. The materials obtained after spontaneous deposition of Pt showed a superior activity for ethanol electro-oxidation compared with the starting materials.

1. Introduction

Direct ethanol fuel cells (DEFCs) are attractive as power sources for mobile and portable applications. Compared with hydrogen-fueled fuel cells, which need a reforming system or have problems of hydrogen storage, DEFCs use a liquid fuel, thus simplifying the fuel system. Also, ethanol offers an attractive alternative as fuel because it is produced in large quantities from biomass. However, the electro-oxidation of ethanol to CO_2 and water is very difficult because of the C–C bond breaking, which leads to the formation of intermediates, like acetaldehyde and acetic acid, that poison the Pt anode catalysts. In this manner, the complete electro-oxidation of ethanol to CO_2 and water remains a great challenge (Antolini, 2007). PtSn/C electrocatalysts have been shown the best performances for ethanol electro-oxidation in acid medium; however, their activities depend greatly on the preparation procedure (Antolini, 2007; Spinacé *et al.*, 2006). Also, because of the high cost of Pt, it is interesting to have all the Pt atoms at the surface of the nanoparticles in order that they can be actively involved in the

anodic oxidation of ethanol [3,4]. Bambagioni *et al.* (2009) studied the ethanol oxidation in alkaline media using electrocatalysts obtained by spontaneous deposition of Pd on Ni–Zn materials and observed an excellent electrocatalytic performance of these materials. Pasricha *et al.* (2009) prepared porous Pt nanoparticles by transmetalation reaction between sacrificial Ni nanoparticles and H_2PtCl_6 . The obtained materials showed excellent catalytic activity for hydrogenation reactions. The spontaneous deposition of a noble metal on a nonnoble metal is normally performed under inert atmosphere and/or removing the oxide film of the surface of nonnoble metal with reducing agents prior to the galvanic exchanging reaction (Bambagioni *et al.*, 2009; Mohl *et al.*, 2010; Pasricha *et al.*, 2009). It is known that nickel has a high corrosion resistance because of the very thin surface nickel oxide film inhibiting the galvanic replacement reaction (Mohl *et al.*, 2010); however, x-ray photoelectron spectroscopy (XPS) analyses of PtNi/C and PtSn/C catalysts showed that some Ni(0) and Sn(0) continue to exist in these samples, despite the major part of Ni and Sn found as oxide species (Park *et al.*, 2002; Zhou *et al.*, 2005). Thus, the objective

of this work was to evaluate the possibility of preparing Pt-based electrocatalysts just performing the spontaneous deposition of Pt by stirring an aqueous solution of H_2PtCl_6 in the presence of Ni/C, Sn/C or NiSn/C under room temperature and open atmosphere. The obtained materials were tested for ethanol electro-oxidation in acid medium.

2. Experimental

2.1 Preparation and characterization of the Pt-based electrocatalysts

Sn/C, Ni/C, and SnNi/C (Sn:Ni atomic ratio of 50:50) were prepared with 20 wt% of metal content. Ni/C was prepared by wet impregnation $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ on the carbon support (Vulcan XC72) and reduction at 400°C under H_2 atmosphere. Sn/C and SnNi/C were prepared by borohydride reduction of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. The spontaneous deposition of Pt was performed by stirring (300 rpm) an aqueous solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (30 mg Pt/50 ml H_2O) in the presence of 200 mg of Ni/C, Sn/C or NiSn/C at room temperature and open atmosphere for 1 h (in these conditions, assuming that all Pt(IV) ions were spontaneously reduced and deposited on the carbon-supported materials, the obtained Pt-based electrocatalysts could reach about 15 wt% of Pt loading). After this, the solid was filtrated, washed with excess of water and dried at 70°C for 2 h.

The Pt:Sn and Pt:Sn:Ni atomic ratios were obtained by EDX analysis using a Jeol scanning electron microscope with a 20 keV electron beam and provided with a microanalyzer. The content of Pt (wt%) was determined using a calibration curve.

The x-ray diffraction (XRD) analyses were carried out in a Miniflex II model Rigaku diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). The diffractograms were recorded at 2θ in the range 20° – 90° with a step size of 0.05° and a scan time of 2 s per step.

Transmission electron microscopy (TEM) and EDX elemental mapping were carried out using a JEOL JEM-2100 electron microscope operated at 200 kV.

2.2 Electro-oxidation of ethanol

Chronoamperometry experiments were carried out to examine the electrochemical activity and stability of the electrocatalysts. The reference electrode was a RHE and the counterelectrode was a platinumized Pt plate. Chronoamperometry experiments were performed with a Microquimica (model MQPG01) potentiostat/galvanostat using 1.0 mol/l of ethanol in 0.5 mol/l H_2SO_4 solution saturated with N_2 at 0.5 V and at room temperature.

3. Results and discussion

In the preparation of Pt–Ni/C electrocatalyst, after its separation by filtration, the presence of Ni(II) ions in the filtrate using dimethylglyoxime (Vogel, 1979) was observed, which suggest a galvanic

exchange reaction (Equation 1) between carbon-supported Ni nanoparticles (Ni/C) and H_2PtCl_6 [3–5].



The presence of Ni(II) ions was also observed in the filtrate of Pt–SnNi/C electrocatalyst. The Pt:Sn and Pt:Sn:Ni atomic ratios and the Pt loading (wt%) of the obtained Pt-based electrocatalysts are shown in Table 1.

EDX analysis (Figure 1) showed the presence of Pt in all prepared electrocatalysts and the mass of Pt present in these materials was in the range of 1.5–2.5 wt%, showing that only 10–15 wt% of Pt(IV) ions present in the solution were spontaneously deposited on the starting materials.

TEM micrograph and the corresponding EDX elemental mapping of Ni, Sn, and Pt of the Pt–SnNi/C electrocatalysts are shown in Figure 2.

TEM image revealed that the Pt–SnNi/C electrocatalyst is not very homogeneous with some regions showing dispersed nanoparticles and others containing agglomerates. From the EDX elemental mapping images of Ni and Sn, it was observed that the signal intensities and distributions of these elements are very similar. As expected, low Pt signal intensity was observed because of its low content in

Electrocatalyst	Atomic ratio			Pt loading (wt%)
	Pt	Sn	Ni	
SnNi/C	—	48	52	—
Pt–Ni/C	06	—	94	1.5
Pt–Sn/C	07	93	—	2.2
Pt–SnNi/C	07	58	35	2.4

Table 1. Pt:Sn:Ni atomic ratios and Pt loading (wt%) of the obtained Pt-based electrocatalysts.

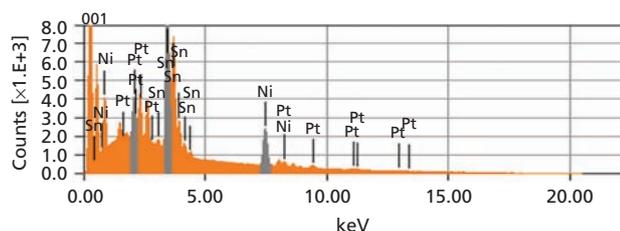


Figure 1. EDX spectrum of the Pt–SnNi/C electrocatalyst (the gray peaks correspond to Pt–M, Sn–L, and Ni–K lines used to determine the Pt:Sn:Ni atomic ratio).

the sample; however, the Pt distribution occurred principally in Sn- and Ni-rich regions.

The x-ray diffractograms of Ni/C, Sn/C, and SnNi/C and the resulting Pt–Ni/C, Pt–Sn/C, and Pt–SnNi/C are shown in Figure 3.

In all diffractograms, a large peak at about $2\theta = 25^\circ$ was observed, which was associated with the carbon support Vulcan XC72. The diffractogram of Ni/C showed the peaks at about $2\theta = 44^\circ$, 52° , and 77° assigned to (111), (200), and (220) planes, respectively, of

the face-centered cubic (fcc) Ni phase (Chopra *et al.*, 2010). Sn/C material showed diffraction peaks at about $2\theta = 30^\circ$, 32° , 43° , 44° , 55° , 62° , 63° , 64° , 72° , 73° , 79° , and 89° which were ascribed to the (200), (101), (220), (211), (301), (112), (400), (321), (420), (411), (312), and (431) planes, respectively, of metallic Sn (Yu *et al.*, 2010), whereas the x-ray diffractogram of the SnNi/C material seems to show the presence of metallic Sn and SnNi phases (Chou and Schaak, 2007; Wang *et al.*, 2010). For all obtained Pt-based electrocatalysts, the x-ray diffractograms did not show the presence of the crystalline phases of Pt (Lee *et al.*, 2011) revealing that Pt particles could be amorphous or too small to be detected by XRD.

The cyclic voltammograms (CVs) in acid solution for Ni/C, Sn/C, NiSn/C, and Pt-based electrocatalysts are shown in Figure 4.

The CVs of the obtained Pt-based electrocatalysts do not have a well-defined adsorption–desorption of hydrogen region (0–0.4 V) as observed for the Pt/C electrocatalysts (Lee *et al.*, 2011). However, when compared with the CVs of the starting materials, the CVs of the obtained Pt-based electrocatalyst showed the region of hydrogen adsorption–desorption a little more defined than the ones observed for the starting materials, which could be because of the presence of Pt in the surface of these materials. Similar results were observed when Pt overlayers were deposited on carbon-supported Ir nanoparticles (Lee *et al.*, 2011).

The chronoamperometry experiments were carried out to examine the performance and stability of the electrocatalysts (Guo and Jing, 2010). Figure 5 shows current density–time responses for ethanol electro-oxidation measured at a fixed potential of 0.5 V, which is in the potential range suitable for practical applications in a DEFC (0.1–0.7 V).

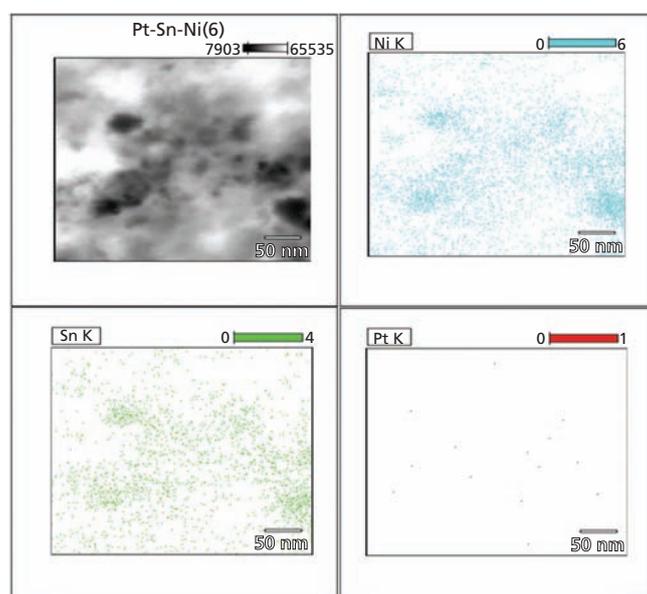


Figure 2. TEM and EDX elemental mapping images of Ni, Sn, and Pt of the Pt–SnNi/C electrocatalyst.

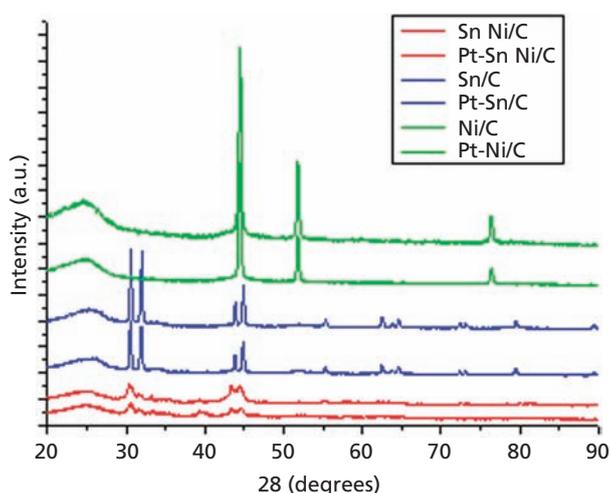


Figure 3. X-ray diffractograms of Ni/C, Sn/C, SnNi/C, and the corresponding Pt-based electrocatalysts.

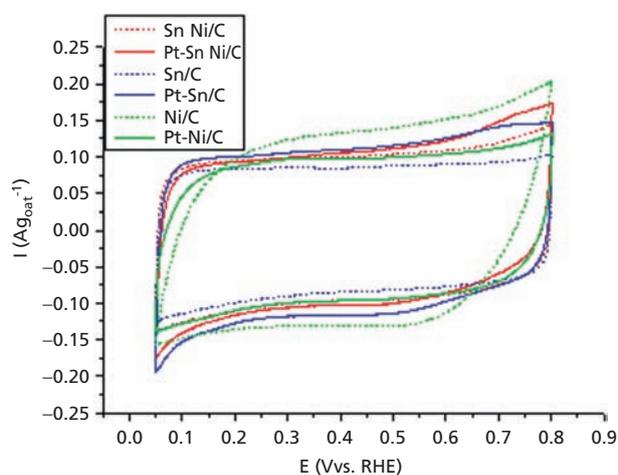


Figure 4. Cyclic voltammograms of Ni/C, Sn/C, SnNi/C, and the corresponding Pt-based electrocatalysts in 0.5 mol/l solution of H_2SO_4 at 10 mV/s.

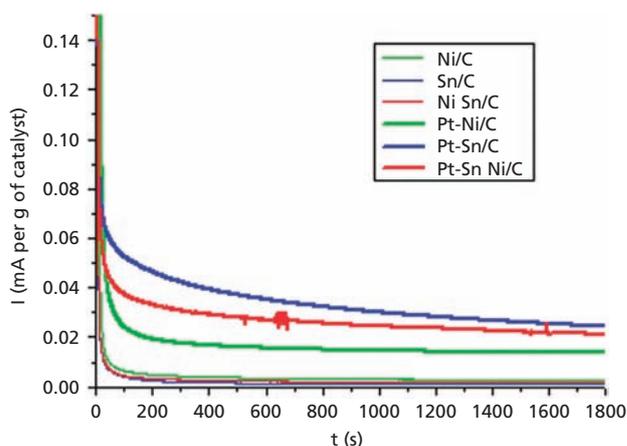


Figure 5. Current–time curves at 0.5 V in a 0.5 mol/l H_2SO_4 solution containing 1.0 mol/l of ethanol for Ni/C, Sn/C, SnNi/C, and the corresponding Pt-based electrocatalysts.

The starting materials Ni/C, Sn/C, and NiSn/C practically showed no activity for ethanol electro-oxidation. After spontaneous deposition of Pt, an increase of activity was observed for all obtained materials.

4. Conclusions

Pt-based electrocatalysts could be prepared by spontaneous deposition of Pt on Ni/C, Sn/C, and SnNi/C under room temperature and open atmosphere. EDX analysis showed the presence of Pt in the obtained materials; however, XRD diffractograms did not show the presence of the crystalline phases of Pt. The obtained materials showed an increase of activity for ethanol electro-oxidation compared with the starting materials. Further work is now necessary to investigate the electrocatalysts surface by different techniques and to elucidate the mechanism of ethanol electro-oxidation.

Acknowledgments

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