

Short communication

## Oxygen reduction on a Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst prepared by the borohydride method in H<sub>2</sub>SO<sub>4</sub>/CH<sub>3</sub>OH solutions

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### Abstract

The activity for the oxygen reduction reaction (ORR) on carbon supported Pt–Ni electrocatalysts prepared by reduction of Pt and Ni precursors with NaHB<sub>4</sub> was investigated in sulphuric acid both in the absence and in the presence of methanol and compared with that of a commercial Pt/C electrocatalyst. In methanol-free sulphuric acid solution the Pt<sub>70</sub>Ni<sub>30</sub>/C alloy electrocatalyst showed a lower specific activity towards oxygen reduction compared to Pt/C. In O<sub>2</sub>-free H<sub>2</sub>SO<sub>4</sub> the onset potential for methanol oxidation on Pt<sub>70</sub>Ni<sub>30</sub>/C was shifted to more positive potentials, which indicates a lower activity for methanol oxidation than platinum. In the methanol containing electrolyte the higher methanol tolerance of the Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst for the ORR was ascribed to the lower activity of the binary electrocatalyst for methanol oxidation, arising from a composition effect.

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### 1. Introduction

Direct methanol fuel cells (DMFCs) are promising electrochemical energy converters for a variety of applications because of the system simplicity. The use of methanol as fuel has several advantages in comparison to hydrogen; it is a cheap liquid fuel, easily handled, transported, and stored, and with a high theoretical energy density [1–3]. Another advantage of the DMFC is the fact that it does not require complex humidification and heat management modules as in the hydrogen fed proton exchange membrane fuel cell (PEMFC) system. The dilute methanol/water mixture circulating around the DMFC provides the necessary humidification and heat management.

One of the major problems, which decreases the efficiency of conversion of the chemical energy of the methanol fuel

to electrical energy in a DMFC, is the methanol crossover through the polymer electrolyte. The problem of methanol crossover in DMFCs has been extensively studied [4–8]: methanol adsorbs on Pt sites in the cathode for the direct reaction between methanol and oxygen. The mixed potential, which results from the oxygen reduction reaction and the methanol oxidation occurring simultaneously, reduces the cell voltage, generates additional water and increases the required oxygen stoichiometric ratio. This problem could be solved either by using electrolyte membranes with lower methanol permeability or by developing new cathode electrocatalysts with both higher methanol tolerance and higher activity for the oxygen reduction reaction (ORR) than Pt. A higher methanol tolerance is reported in the literature for non-noble metal electrocatalysts based on chalcogenides [9–12] and macrocycles of transition metals [13,14]. These electrocatalysts have shown nearly the same activity for the ORR in the absence as well as in the presence of methanol. However, in methanol free electrolytes, these materials did not reach the catalytic activity of supported platinum. Developing a sufficiently selective and active electrocatalyst for the DMFC

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cathode remains one of the key tasks for further progress in this technology.

The current direction is to test the activity for the ORR of some alloys of the first-row transition metals, which present a higher activity for the ORR than platinum in low temperature fuel cells operated on hydrogen [15–19]. The improvement in the ORR electrocatalysis of these materials has been ascribed to different factors, such as changes in the Pt–Pt interatomic distance [20], the surface area [21] and the d-orbital vacancy [22].

Drillet et al. [23] studied the oxygen reduction reaction on Pt and Pt alloyed with 30 at.% Ni in  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and in  $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4/0.5 \text{ mol L}^{-1} \text{ CH}_3\text{OH}$  by means of a rotating disc electrode. An unsupported  $\text{Pt}_{70}\text{Ni}_{30}$  electrocatalyst was prepared by melting together Pt and Ni pellets in a vacuum arc. They found that in sulphuric acid solution, the overpotential for the ORR at  $1 \text{ mA cm}^{-2}$  is about 80 mV lower on  $\text{Pt}_{70}\text{Ni}_{30}$  than on pure Pt. On the other hand, it was found that in sulphuric acid solution containing methanol the onset potential for oxygen reduction on Pt–Ni is shifted to more positive potentials and the alloy electrocatalyst has a limiting current density for the ORR which is 11 times higher than on Pt.

Considering that in the DMFC carbon supported electrocatalysts are generally used to increase the active surface area of the materials, this work investigates the activity of carbon supported  $\text{Pt}_{70}\text{Ni}_{30}$  for the ORR in  $\text{H}_2\text{SO}_4$  solutions and in the same solutions with the addition of methanol.

## 2. Experimental

Carbon supported Pt–Ni electrocatalysts with a nominal Pt:Ni atomic ratio 70:30 were prepared by a low temperature method, using sodium borohydride as the reducing agent. High surface area carbon (Vulcan XC-72, Cabot,  $240 \text{ m}^2 \text{ g}^{-1}$ ) was impregnated with a solution of chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , Johnson Matthey) and nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , Aldrich). The metals were then reduced at room temperature with a sodium borohydride solution, which was slowly added to the precursors solution under sonication. The final material was 20 wt.% metal on carbon.

The atomic ratios in the Pt–Ni/C electrocatalyst were determined by the EDX technique coupled to a scanning electron microscopy LEO Mod. 440 with a silicon detector with Be window and applying 20 keV.

X-ray diffractograms of the electrocatalysts were obtained in a universal diffractometer Carl Zeiss-Jena, URD-6, operating with Cu  $\text{K}\alpha$  radiation ( $\lambda = 0.15406 \text{ nm}$ ) generated at 40 kV and 20 mA. Scans were done at  $3^\circ \text{ min}^{-1}$  for  $2\theta$  values between  $20^\circ$  and  $100^\circ$ . The particle size of the catalysts was evaluated using Scherrer's equation with the parameters of the (2 2 0) peak of the Pt fcc structure, around  $2\theta = 70^\circ$ , and the recordings were done for  $2\theta$  values from  $60^\circ$  to  $80^\circ$  at the slow speed of  $0.02^\circ \text{ min}^{-1}$ .

In order to test the electrochemical behaviour in sulphuric acid solution (with and without methanol), the electrocatalysts were used to make gas diffusion electrodes (GDE). A diffusion layer was made with carbon powder (Vulcan XC-72) and 15 wt.% polytetrafluoroethylene (PTFE) and applied over a carbon cloth (PWB-3, Stackpole). On top of this layer, the electrocatalyst was applied in the form of a homogeneous dispersion of  $\text{Pt}_{70}\text{Ni}_{30}/\text{C}$ , or Pt/C, Nafion<sup>®</sup> solution (5 wt.%, Aldrich) and isopropanol (Merck) [39]. All electrodes were made to contain  $1 \text{ mg Pt cm}^{-2}$ .

Cyclic voltammograms (CV's) were recorded in  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  solution in a half cell built in PTFE with a volume of about 70 mL. Argon (White Martins) was passed for 30 min to eliminate oxygen. Gas diffusion electrodes containing  $\text{Pt}_{70}\text{Ni}_{30}/\text{C}$  and Pt/C electrocatalysts were used as working electrodes. A hydrogen electrode was used as reference and a platinum foil electrode as auxiliary. The CV's were recorded in the range 0.075–0.800 V versus a reversible hydrogen electrode (RHE) at a scan rate of  $20 \text{ mV s}^{-1}$ .

After the voltammetric study, oxygen was passed for 30 min to saturate the solution. The current–potential curves for the ORR were then registered in the absence and in the presence of different amounts of methanol. Linear sweep voltammetry curves were recorded in the range 0.1–1.0 V versus a RHE. The oxidation of methanol on  $\text{Pt}_{70}\text{Ni}_{30}/\text{C}$  and Pt/C was tested in 0.5 and  $3 \text{ mol L}^{-1}$  methanol solutions. The experiments were done at room temperature with a 1285A Solartron Potentiostat connected to a personal computer and using the software CorrWare for Windows (Scribner).

## 3. Results and discussion

The EDX composition of the carbon supported Pt–Ni electrocatalyst prepared here was 71:29, which is very near the nominal composition (Pt:Ni atomic ratio = 70:30).

Fig. 1 shows the XRD pattern of the carbon supported  $\text{Pt}_{70}\text{Ni}_{30}/\text{C}$  alloy electrocatalyst with a metal loading of

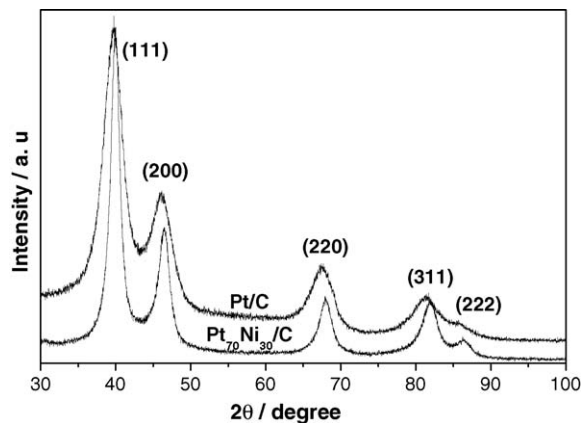


Fig. 1. XRD diffractograms of the as-prepared  $\text{Pt}_{70}\text{Ni}_{30}/\text{C}$  and of the commercial Pt/C electrocatalysts.

20 wt.%. For comparison, the XRD of a commercial Pt/C electrocatalyst with 20 wt.% metal loading is also shown in this figure. Only the reflexions corresponding to the planes (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2), characteristic of the face-centered cubic (fcc) structure of Pt were present in the pattern of Pt<sub>70</sub>Ni<sub>30</sub>/C, but the peaks are shifted to higher values of  $2\theta$  with respect to those of Pt/C, which is indicative of a contraction of the lattice. No characteristic peaks of metallic Ni or Ni oxides were detected, but their presence cannot be discarded because they may be present in a small amount or even in an amorphous form. The peaks of the as-prepared Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst were sharper than those of Pt/C E-TEK, indicating that they have larger particle sizes than the commercial supported platinum. The average size of the Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C nanoparticles was estimated using Sherrer's equation [24]. The values of the lattice parameter and the particle size were 0.3898 nm and 4.8 nm for Pt<sub>70</sub>Ni<sub>30</sub>/C and 0.3915 nm and 2.9 nm for Pt/C, respectively. The lattice parameters of the carbon supported Pt<sub>75</sub>Ni<sub>25</sub> and Pt<sub>67</sub>Ni<sub>33</sub> materials prepared by Yang et al. [25] were 0.3852 nm and 0.3824 nm, respectively, both remarkably lower than the lattice parameter of the Ni-containing electrocatalyst investigated in this work. The dependence of the lattice parameter of unsupported Pt–Ni alloys on Ni contents according to Vegard's law is reported in [26]. On the basis of the values of the lattice parameters for unsupported alloys, the amount of alloyed Ni in the Pt<sub>70</sub>Ni<sub>30</sub>/C catalyst was estimated to be about 6 at.% (poor degree of alloying). From these results, it can be inferred that in the Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst most of the nickel is in a non-alloyed form (as metal or as NiO species).

Fig. 2 shows cyclic voltammograms (CVs) obtained with gas diffusion electrodes containing Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C electrocatalysts. The active areas were calculated from the CVs using the charge associated to the hydrogen desorption from the electrode surface. With this method, the contribution of

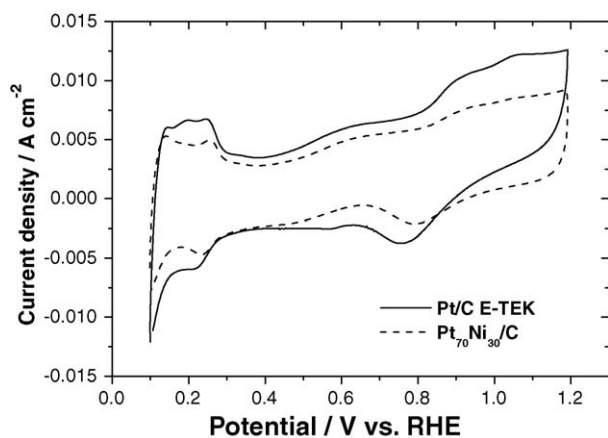


Fig. 2. Cyclic voltammograms for the commercial Pt/C and the as-prepared Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalysts at room temperature in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at a scan rate of 20 mV s<sup>-1</sup>.

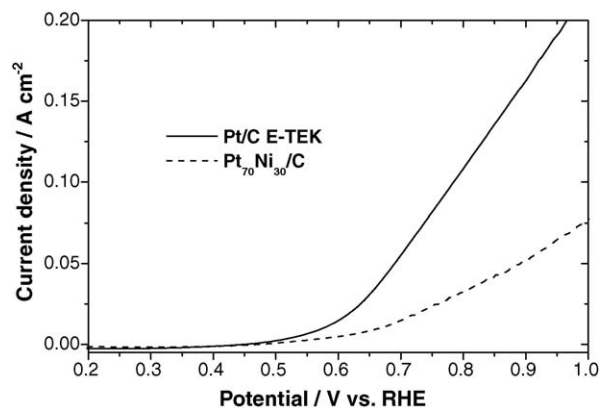


Fig. 3. Linear sweep voltammograms at room temperature for the methanol oxidation reaction on Pt/C and Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalysts in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> + 3.0 mol L<sup>-1</sup> methanol.

the alloying element to the roughness factor was difficult to discern and thus, following Mukerjee et al. [27], it will be assumed to be negligible. The electrochemical surface area of the binary electrocatalyst (50 m<sup>2</sup> g<sup>-1</sup>) was about one half that of Pt/C (95 m<sup>2</sup> g<sup>-1</sup>).

The linear scan voltammograms for the oxidation of methanol on the carbon supported Pt and Pt–Ni catalysts in nitrogen saturated 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>/3 mol L<sup>-1</sup> CH<sub>3</sub>OH are shown in Fig. 3. The methanol-containing electrolyte was previously purged with nitrogen in order to avoid oxygen contamination. It can be seen that the current densities for the methanol oxidation reaction on the Pt<sub>70</sub>Ni<sub>30</sub>/C alloy electrocatalysts are lower than that on the Pt/C electrocatalyst and that the onset potential for the methanol oxidation on Pt<sub>70</sub>Ni<sub>30</sub>/C (440 mV) is more positive in comparison to that on Pt/C (375 mV), indicating that the alloy electrocatalyst is less active for the oxidation of methanol than the Pt/C electrocatalyst.

The experimental results regarding the ORR in H<sub>2</sub>SO<sub>4</sub> solution are shown in Fig. 4a. Here, the current density is expressed in terms of the mass activity (MA, in A mg<sup>-1</sup>Pt) which, being the Pt loading 1 mg cm<sup>-2</sup> for all the electrodes, is numerically equivalent to the current density in terms of the geometric surface area (A cm<sup>-2</sup>). In Fig. 4b the current density is expressed in terms of the real surface area of platinum calculated from the hydrogen desorption regions of the CV, i.e. in terms of the specific activity (SA). The onset potential for the ORR is about the same for Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C electrocatalysts, at about 850 mV. The slope of the current density–potential plot ( $dj/dE$ ), for Pt<sub>70</sub>Ni<sub>30</sub>/C is remarkably lower, in terms of mass activity, and slightly higher, in terms of specific activity, than that of the Pt/C electrocatalyst. This means that the activity for the ORR of the Pt<sub>70</sub>Ni<sub>30</sub>/C catalyst is lower than that of the Pt/C electrocatalyst. The overpotentials of Pt<sub>70</sub>Ni<sub>30</sub>/C at a current density of 0.1 A mg<sup>-1</sup> Pt (MA) and 0.1 mA cm<sup>-2</sup> (SA) are about 150 and 20 mV higher, respectively, than those for Pt/C. This behaviour can be explained by the low degree of alloying of Pt–Ni/C. The

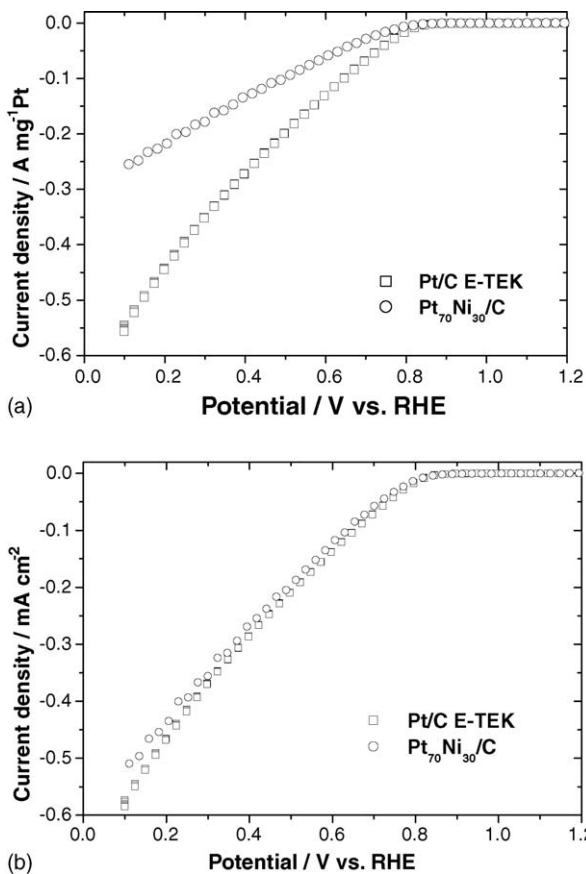


Fig. 4. Oxygen reduction at room temperature in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> on Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C electrocatalysts. (a) Current densities normalized with respect to the mass activity (MA); (b) current densities normalized with respect to the Pt surface area (SA).

small amount of alloyed nickel in Pt<sub>70</sub>Ni<sub>30</sub>/C gives results in a small change in the Pt–Pt bond distance and in the Pt d-band vacancy, which are insufficient to improve the ORR activity. Indeed, Yang et al. [25] found a maximum activity for the ORR on Pt–Ni/C electrocatalysts for 30–40 at.% of alloyed Ni. In the same way, the unsupported Pt<sub>70</sub>Ni<sub>30</sub> electrocatalyst investigated by Drillet et al. [23], which showed an enhanced activity for the ORR with respect to Pt, was prepared at high temperature and as a consequence had a high degree of alloying.

Fig. 5 shows the activity for the ORR of the commercial Pt/C electrocatalyst (Fig. 5a) and the prepared Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst (Fig. 5b), in terms of MA, in the presence of various concentrations of methanol, from 0 to 3 mol L<sup>-1</sup>. A comparison with the ORR results in methanol-free H<sub>2</sub>SO<sub>4</sub> solution (Fig. 4), shows that both the Pt<sub>70</sub>Ni<sub>30</sub>/C and the Pt/C electrocatalysts present an increase in overpotential for the ORR, under the same current density, in the presence of methanol.

Fig. 6 shows the dependence of the potential on the concentration of methanol at 0.05 and 0.1 mA cm<sup>-2</sup> (specific activity). A polynomial regression for the Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C data gives the result:

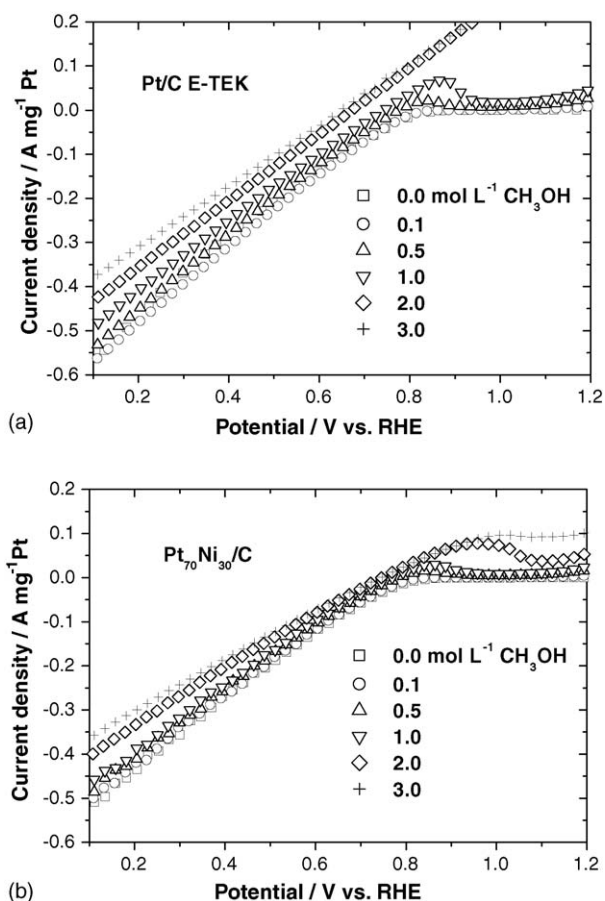


Fig. 5. Oxygen reduction at room temperature in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> containing different amounts of methanol. Pt/C by E-TEK (a); Pt<sub>70</sub>Ni<sub>30</sub>/C (b). Current densities normalized with respect to the mass activity (MA).

Pt<sub>70</sub>Ni<sub>30</sub>/C:

$$E(V) = E_0(V) - 44V \times (\text{mol L}^{-1})C_{\text{CH}_3\text{OH}} + 6.6V \times (\text{mol L}^{-1})^{-2}C_{(\text{CH}_3\text{OH})_2} \quad (1)$$

Pt/C:

$$E(V) = E_0(V) - 73V(\text{mol L}^{-1})C_{\text{CH}_3\text{OH}} + 6.8V \times (\text{mol L}^{-1})^{-2}C_{(\text{CH}_3\text{OH})_2} \quad (2)$$

where the concentration of methanol ( $C_{\text{CH}_3\text{OH}}$ ) is expressed in mol L<sup>-1</sup>.

As a first approximation, up to 2 mol L<sup>-1</sup> CH<sub>3</sub>OH the dependence of  $E$  on  $C_{\text{CH}_3\text{OH}}$  is linear for both Pt<sub>70</sub>Ni<sub>30</sub>/C and Pt/C, and  $dE/dC_{\text{CH}_3\text{OH}}$  for Pt<sub>70</sub>Ni<sub>30</sub>/C ( $-31 \text{ mV mol}_{\text{CH}_3\text{OH}}^{-1} \text{ L}$ ) is about one half the value for Pt/C ( $-60 \text{ mV mol}_{\text{CH}_3\text{OH}}^{-1} \text{ L}$ ) both at 0.05 and 0.1 mA cm<sup>-2</sup> (SA). Then, it may be concluded that Pt<sub>70</sub>Ni<sub>30</sub>/C is more tolerant to methanol (i.e. less active) than Pt/C.

Maillard et al. [28] found that electrocatalysts for the ORR with small metal particle size have enhanced methanol tolerance. In this work, the higher methanol-tolerance

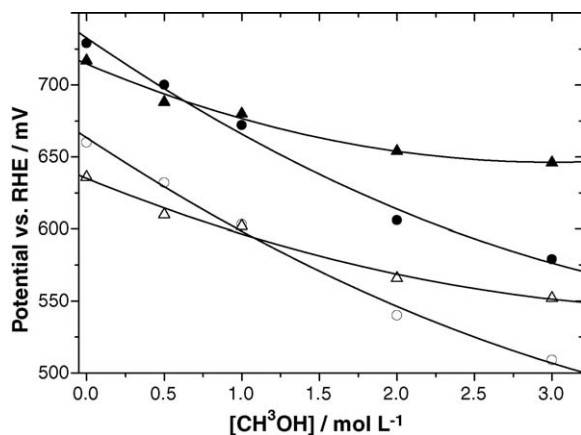


Fig. 6. Cell potential vs. methanol concentration at 0.05 and 0.1 mA cm<sup>-2</sup> (SA). Triangles: Pt<sub>70</sub>Ni<sub>30</sub>/C; circles: Pt/C. Solid symbols:  $j = 0.05$  mA cm<sup>-2</sup>; open symbols:  $j = 0.1$  mA cm<sup>-2</sup>. Base electrolyte 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>.

the binary electrocatalysts cannot be ascribed to a particle size effect, being the particle sizes of Pt/C smaller than those of the Pt<sub>70</sub>Ni<sub>30</sub>/C material. It is believed that methanol adsorption and oxygen adsorption are competing with each other for the surface sites. Also, it is well established that for methanol oxidation at least three adjacent Pt sites in the proper crystallographic arrangement are necessary to activate the chemisorption of methanol [29–31]. For the Pt<sub>70</sub>Ni<sub>30</sub>/C alloy electrocatalyst, the probability of finding three neighbouring Pt atoms on the surface is lower, if no Pt enrichment of the surface takes place. Since the dissociative chemisorption of methanol requires several adjacent Pt ensembles, the presence of methanol-tolerant Ni around the Pt active sites could hinder methanol adsorption on Pt sites due to the dilution effect. On the other hand, oxygen adsorption, which usually can be regarded as dissociative chemisorption and requires only two adjacent Pt sites, is not influenced by the presence of Ni atoms. Then, the small amount of Ni in the alloyed form is enough to hinder the adsorption of methanol, and to improve in this way the methanol tolerance of the electrocatalyst during the oxygen reduction.

#### 4. Conclusions

The experimental findings in this investigation can be summarized as follows:

- (1) The activity of the Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst for the methanol oxidation reaction in oxygen-free H<sub>2</sub>SO<sub>4</sub> is lower than that of Pt/C.
- (2) The activity of the Pt<sub>70</sub>Ni<sub>30</sub>/C electrocatalyst for the oxygen reduction reaction in methanol-free H<sub>2</sub>SO<sub>4</sub> is lower than that of Pt/C.
- (3) Considering the ORR in the presence of methanol, the potential loss per mol of CH<sub>3</sub>OH present on Pt<sub>70</sub>Ni<sub>30</sub>/C is only one half that observed on Pt/C.

The low content of alloyed Ni in the Pt<sub>70</sub>Ni<sub>30</sub>/C alloy (ca 6 at.%) is enough to hinder the MOR (ensemble effect), but it is not enough to increase the rate of the ORR in pure H<sub>2</sub>SO<sub>4</sub> (too small geometrical and electronic effects).

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