Short communication

Hydrogen oxidation on ordered intermetallic electrodes covered with CO

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Abstract

This describes an experimental evaluation of the electrocatalytic activity of the hydrogen oxidation reaction on electrodes of platinum and the ordered intermetallic phases PtSb and PtSn, on which CO has previously been deposited. The experiments were carried out in perchloric acid solution and the analysis based on steady-state polarization curves and Tafel plots derived from chronoamperometric data. Both intermetallics, PtSb and PtSn, performed better than Pt towards the HOR, when their surface was deliberately covered with CO. It is suggested that the intermetallic surfaces have a lower affinity for CO molecules, causing a lower CO coverage on these surfaces, and/or a weaker surface–CO interaction, compared to Pt under the same conditions.
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1. Introduction

There is considerable interest in the potential application of proton exchange membrane fuel cells (PEMFC), which use hydrogen as fuel, in stationary power generation plants and automotive vehicles, in view of the high-energy conversion efficiency, low pollutant emission and low operating temperatures (about 80 °C) of these devices [1–3]. The hydrogen oxidation reaction (HOR) at the PEMFC anode is one of the best studied reactions, and it proceeds very rapidly in the presence of platinum-based catalysts [4–6]. One of the greatest problems facing PEMFC development is the deactivation of the Pt anode by small amounts of carbon monoxide (10–100 ppm) [7,8]; this is present in the fuel as an impurity, as the hydrogen is produced from the catalytic reforming of biomass-derived compounds.

Hence, it is crucial that alternative electrocatalysts, featuring both tolerance to CO contamination and good performance for hydrogen oxidation, are developed. Recently a kinetic and mechanistic study of the hydrogen oxidation reaction (HOR) was carried out on Pt–M (M = Mn, Pb, Sb and Sn) ordered intermetallic phases in acidic media, employing the rotating-disk electrode (RDE) technique and Tafel diagrams obtained by chronoamperometry [9]. It was found that the intermetallic phases PtSb and PtSn performed better than Pt under the same experimental conditions, suggesting that the formation of the intermetallic phase had favorably modified the electron density at the adsorption surface sites and thus favored the adsorption step (Tafel or Heyrovsky) in the HOR mechanism [9].

In many studies of this reaction, a mixture of H_2/CO has been used as a means of probing the HOR activity of electrode surfaces composed of Pt and some Pt alloys (PtRu, $Pt_{70}Mo_{30}$, Pt_3Sn, PtRe) [7,8,10]. Gasteiger et al. [10] have used the RDE technique to study the kinetics of the oxidation of CO/H_2 (0.1 and 2% CO) mixtures on Pt, Ru and two PtRu alloys, in $0.5\,mol\,L^{-1}\,H_2SO_4$ at 62 °C. They observed that pure Ru was inactive for oxidation of the CO/H_2 mixtures; however, on PtRu alloys, CO/H_2 electroxidation was characterized by two activity states: a low but finite activity state and a high activity state. The transition potential related to those states depends on the compositions of the gas mixture and the alloy: the surface with the highest Ru content had the lowest transition potential, after which came $Pt_{50}Ru_{50}$ and, last of all, Pt, with the highest potential. The electrochemical oxidation of H_2/CO (500 ppm–2%) mixtures on the $Pt_{70}Mo_{30}$ alloy, in $0.5\,mol\,L^{-1}\,H_2SO_4$ at 333 K, was studied by Grgur et

al., employing the RDE technique [8]. They obtained polarization curves for this oxidation reaction that were qualitatively similar to those of the $Pt_{50}Ru_{50}$ alloy [10]. In conclusion, these studies have shown that the presence of another metal, except Re, alloyed with the Pt, reduces the steady-state CO_{ads} coverage by oxidative stripping, freeing Pt sites for H_2 oxidation. All the studies cited above were carried out with a H_2/CO mixture; however, to find out whether any electrocatalytic activity for hydrogen oxidation remains on a surface deliberately poisoned by CO, it is necessary to deposit the CO first and then carry out the measurements in a CO-free solution.

Given the good performance shown by the intermetallics PtSb and PtSn in previous studies of the HOR, in this paper electrocatalytic activity of these materials for the HOR is evaluated when CO is deliberately deposited on the electrode surface. The analysis is based on steady-state polarization curves, obtained by the chronoamperometric technique. The performance of these intermetallics will be compared with that of polycrystalline Pt under the same experimental conditions, to make a better assessment of the CO poisoning effect on the electrode material.

2. Experimental

The intermetallic phases PtSb and PtSn were prepared from the respective pure metals – platinum (Alfa Aeasar, sheet, 99.9% pure), antimony (Aldrich, pieces, 99.9999%) and tin (Berzog, powder, 99.9%) – which were weighed in 1:1 stoichiometric proportions and melted together in an electric-arc furnace, in an argon atmosphere, as previously reported elsewhere [9,11]. The melting conditions were selected from the corresponding phase diagrams [12]. Each melt was homogenized and transferred to a thermal induction furnace (Inductoheat) with a prefixed thermal gradient, in which the direction and rate of solidification could be controlled. This furnace was held for 24 h at the temperature at which the desired phase was stable (taken from the appropriate phase diagram), with an atmosphere of argon, after which the material was quenched rapidly, so as to maintain this phase unchanged. The cylindrical ingot thus produced was sectioned with a diamond-impregnated rotary saw into disk-shaped test-pieces, which were used both for the characterization of each material and for the construction of the rotating-disk electrodes (RDEs) for the electrochemical experiments.

The materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS) [11]. The results obtained by these respective techniques provided evidence of the crystalline nature and elemental composition of the PtSb and PtSn ordered 1:1 intermetallic phases, at the surface, and the formation of the intermetallic phases with a modification of the electron density at the surface platinum sites [9,11].

The system used for electrochemical measurements was set up as previously described [9]. Thus, electrochemical experiments were performed by using a EG&G PAR Model 263A Galvnostat Potentiostal controlled by M270 electrochemical software. RDE technique was applied through a Pine Instru-

ments Analytical Rotator. A high surface area platinum wire was used as counter electrode and the reversible hydrogen electrode (RHE) as reference.

Firstly, CO was deposited on the electrode surface by electrode polarization at a pre-determined potential (0.05 V vs. RHE[1] for Pt and 0.15 V vs. RHE for PtSb and PtSn) for a period of 10 min in the electrolytic solution of $0.15 \, mol \, L^{-1}$ $HClO_4$ (Merck, AR), which was initially purged by bubbling N_2 (White Martins, 5.0) for 15 min, to remove all traces of O_2, and then saturated with CO (AGA, 2.5) by bubbling for 10 min. After deposition, the CO remaining in the solution was completely removed by bubbling N_2 for 10 min. Finally, the solution was bubbled with H_2 (AGA, 4.0) for 15 min to perform the studies of the HOR. This method has proved reliable, giving reproducible results on the influence of the CO-covered surfaces on the HOR. This CO poisoning procedure was adopted to investigate to what extent a deliberately poisoned surface would still be able to catalyze the hydrogen oxidation reaction. From a scientific point of view, such information should allow inferences to be drawn on the tolerance of the surfaces to CO poisoning.

Steady-state measurements were performed chronoamperometrically over different potential intervals, depending on the electrode material condition, always before the mass-transfer control region [9]. A previously determined pulse potential was then applied to the working electrode and the resulting steady-state current recorded after 10 s. The HOR is widely known to be a fast reaction and 10 s has proved sufficient to reach a steady-state current. During the data acquisition, the electrode was rotated at 3500 rpm to ensure, as far as possible, a constant flow of reactant to the electrode surface.

3. Results and discussion

In order to verify the effectiveness of the potential selected for CO deposition on the Pt and intermetallic surfaces, potentiodynamic experiments were performed after CO deposition and also after the hydrogen oxidation reaction on the CO-covered surfaces. The resulting voltammograms are shown in Fig. 1(a and b), where peaks arising from CO oxidation can be observed at 0.78 and 0.80 V for Pt and PtSb, respectively, showing that CO had been effectively deposited. No CO oxidation peak was clearly observed on PtSn (Fig. 1(c)); however, as will be seen later, the HOR experiments afforded evidence of effective CO deposition on the PtSn surface. The voltammetric curve obtained for the CO-covered Pt surface shows indubitably that, even after the HOR, the Pt surface is still poisoned by CO. In Fig. 1(b), there is a broad peak at 0.80 V associated with the oxidation of CO adsorbed on the PtSb surface. In subsequent cycles, this peak is no longer recorded. In the same figure, the voltammetric curve recorded after performing HOR experiments on the CO-covered PtSb surface is also displayed. From these results it is suggested that the HOR might cause the removal of CO from the surface, since no evidence of its removal was observed in voltammograms recorded in the absence of the HOR over
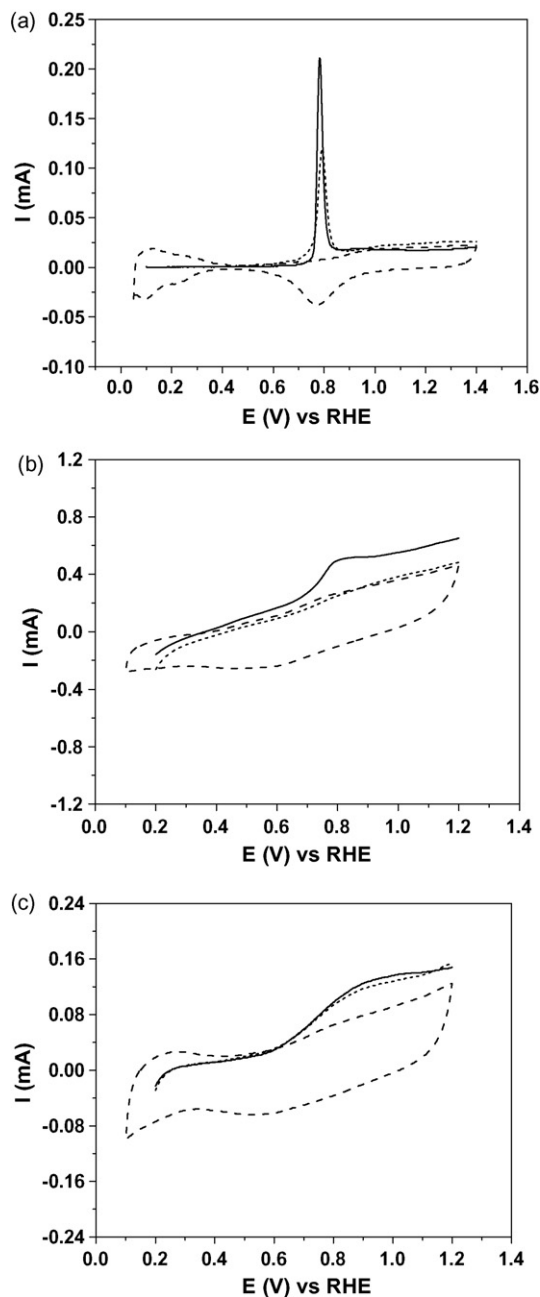
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[1] Reversible hydrogen electrode.

Fig. 1. Potentiodynamic profiles for (a) Pt, (b) PtSb and (c) PtSn; (–) stripping of deposited CO in the first positive-going sweep before HOR experiments, (- -) subsequent voltammetric cycle after the CO stripping; (· · ·) stripping of deposited CO in the first positive-going sweep after HOR experiments. In $0.15\,mol\,L^{-1}$ $HClO_4$ solution ($v = 50\,mV\,s^{-1}$) at room temperature.

the same potential sweep. Regarding the PtSn surface, a quite different result was obtained, a slight decrease in the current density assigned to CO_{ads} oxidation (at 0.85 V) being observed when the voltammetric curve recorded after the HOR was compared with the pre-HOR curve. CO coverage was estimated for all electrode materials by integrating the stripping voltammetric curves in Fig. 1 over the potential range related to CO oxidation; the values $\theta_{CO} = 0.81$, 0.46 and 0.50 were calculated, respectively, for the Pt/CO, PtSb/CO and PtSn/CO surfaces, by considering the electroactive surface areas calculated as reported

in Ref. [9]. It must be pointed out that a similar value of θ_{CO} has been reported elsewhere for Pt [13,14], in excellent agreement with the value calculated in the present study. On the other hand, no θ_{CO} values for intermetallic surfaces have been published until now. However, it has been reported for Pt–Sn alloys that CO molecules are preferentially adsorbed at Pt sites alone and even then in a weaker interaction than that observed for polycrystalline Pt [15–17]. Here we suggest that on the PtSb intermetallic surface a similar phenomenon takes place, considering the similarity between the two intermetallics and the corresponding calculated coverage values. Values of θ_{CO} as low as those calculated in this study must be interpreted in terms of two major material characteristics: the low affinity of CO for the intermetallic surfaces and the composition of the surfaces, where it is proposed that CO is preferentially deposited at the Pt sites. θ_{CO} was also calculated after performing the HOR on the same electrode surfaces and the values 0.68 and 0.30 were found for Pt/CO and PtSn/CO, respectively. As previously mentioned, potentiodynamic experiments suggested that θ_{CO} for the PtSb/CO surface after the HOR was close to zero. It is evident that there is a stronger and more stable CO–surface interaction on the Pt surface than on the intermetallic surfaces, considering the higher θ_{CO} values determined before and after the HOR. The data show a decrease in θ_{CO} of about 16 and 40% for the Pt/CO and PtSn/CO surfaces, respectively, provoked by the occurrence of the HOR. This result suggests that the CO-blocked surface sites on PtSn were not totally freed by the HOR, indicating that CO may interact more strongly with PtSn than with PtSb. It is also possible that a surface-site freeing process may take place during the HOR on PtSb/CO, owing to the weaker CO–PtSb interaction. It has been suggested that the surface of PtRu interacts weakly with CO and shows better tolerance of CO poisoning than polycrystalline Pt, on both theoretical (density functional theory) and experimental (UHV) grounds [18–21]. These studies pointed to a decrease in the adsorption energy of CO on Pt in bimetallic surfaces caused by an alteration in the electron density of Pt atoms due to the influence of neighboring Ru atoms. As a consequence, CO coverage was decreased, favoring the HOR.

The steady-state polarization curves extracted from chronoamperometric data for the HOR on Pt, PtSb and PtSn surfaces, bare or CO-covered, are shown in Fig. 2. It can be observed that, for the HOR on non-poisoned Pt and intermetallic surfaces, the current density increased in proportion to the applied potential, up to a potential where it increased more slowly. The intermetallic materials performed better than Pt in the whole potential interval explored in these experiments. The polarization curve (Fig. 2(a)) obtained for the HOR on PtSb/CO exhibited considerably poorer performance than that on the non-poisoned surfaces; nevertheless, this system showed current densities a great deal higher than any other surface-blocked material. The HOR polarization curve on PtSb/CO shows a continuous increase in the current density as the applied potential is increased. In light of these results, it is reasonable to propose that on the PtSb/CO surface, an adsorption-site freeing process takes place during the HOR, as suggested earlier from the potentiodynamic experiments.
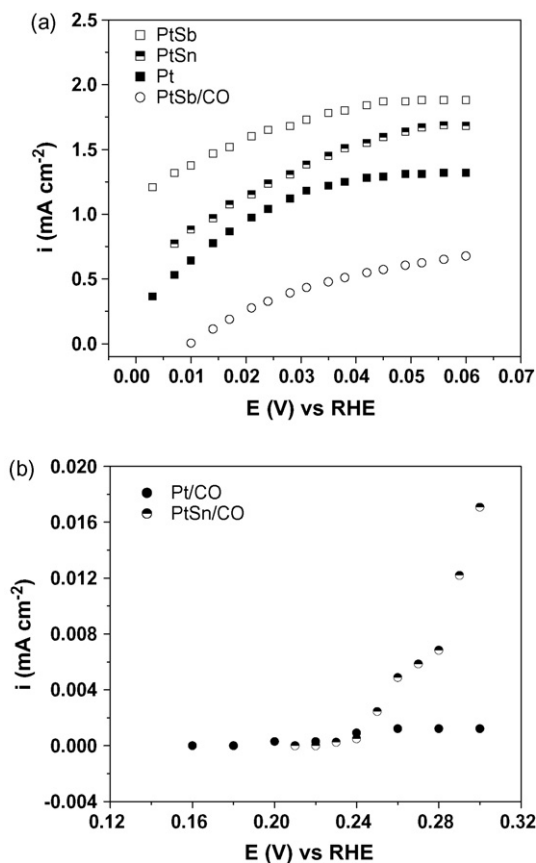
Fig. 2. Steady-state polarization curves for H_2 oxidation on (a) Pt, PtSb, PtSn and PtSb/CO and (b) Pt/CO, and PtSn/CO in 0.15 mol L^{-1} HClO$_4$ solution, at room temperature.

Fig. 3. Tafel plots, corrected for mass transfer, for HOR on PtSb and PtSb/CO in 0.15 mol L^{-1} HClO$_4$ solution, at room temperature.

Moreover, considering the θ_{CO} estimated for this surface, its catalytic performance towards the HOR should only be possible if a weak CO–PtSb interaction is assumed.

The HOR polarization curves for Pt/CO and PtSn/CO surfaces are displayed in Fig. 2(b). It is noticeable that the current densities for the HOR on these surfaces are much lower than those recorded for the other systems studied here. Furthermore, a substantial shift of the HOR onset potential to more positive values was observed on these surfaces, indicating that the alteration of the surface/electrolyte interface by CO deposition effectively inhibited the HOR. Moreover, it is also observed that over the whole experimental potential range, the current density for the HOR on Pt/CO remains quite constant and close to zero, while for the same reaction on PtSn/CO, a slight increase in the current density is noted as the applied potential becomes more positive (>0.24 V). It should be recalled that the partial elimination of CO from the PtSn/CO surface by the HOR was observed in potentiodynamic experiments. This partial freeing process on the PtSn/CO surface was significantly more effective than on the Pt/CO surface, but less so than on PtSb/CO.

It is suggested that the enhanced activity of the intermetallic phases, relative to Pt, for hydrogen oxidation on the surfaces covered with CO, has two main causes: lower θ_{CO} on the intermetallic surfaces than on Pt and/or the easier removal of CO from
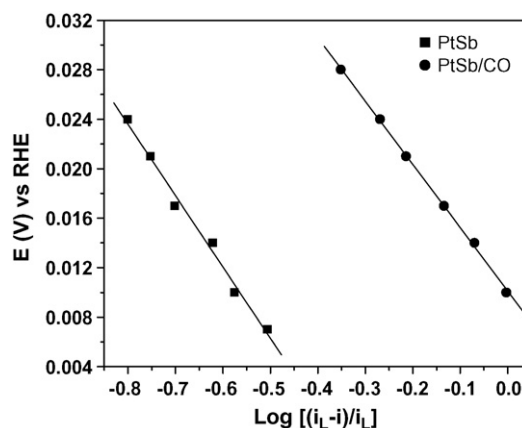
the intermetallic surfaces, both of which may be due to the low affinity between CO molecules and the intermetallic surfaces. It is known that CO has two preferred modes of adsorption on the Pt surface: on-top (or linear) and bridged [7,22]. A linear adsorption configuration would use only one platinum site, making it easy to eliminate the deposited CO. A bridge-like configuration uses two platinum sites, giving a more stable configuration. The structure of the ordered intermetallics increases the distance between the Pt sites [9], inhibiting CO adsorption in the bridge configuration. Therefore, on the basis of previous experiments, it is proposed that the interactions between the CO and the surface of the PtSb and PtSn intermetallic phases occur mainly in the on-top configuration [23]. Such a configuration may even provoke "holes" in the deposited layer of CO, causing a low θ_{CO} value relative to Pt, as observed above. In the above-mentioned work of Grgur et al. [8] and Gasteiger et al. [10], this explanation is given for the HOR activity in the presence of CO on alloys such as PtMo and PtRu. According to those authors, a modification in the configuration of the CO adsorbed at the Pt sites must take place, causing "holes" in the CO$_{ads}$ monolayer, where H_2 can be oxidized.

From the data plotted in the PtSb/CO polarization curves in Fig. 2(a), it was possible to construct Tafel plots, shown in Fig. 3, together with the plot for CO-free PtSb as a means of comparison. The plots have been corrected for mass transfer by supposing reversible kinetics for the HOR[2]. Tafel plots could not be produced for the HOR on the Pt/CO and PtSn/CO surfaces because the current densities reached quite constant and very low values. From the data in Fig. 3, it can be seen that the mechanism of the HOR does not change as a consequence of the partial blocking of the PtSb surface by CO. The calculated Tafel slopes were 57 and 52 mV dec^{-1}, respectively, for the HOR taking place at PtSb and PtSb/CO surfaces. A 60 mV dec^{-1} Tafel slope cannot be definitely ascribed to a unique mechanistic situation [24,25]. Such a slope is usually associated with a Tafel/Heyrovsky–Volmer mechanism when the intermediate

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[2] In the absence of a limiting current density value, the maximum current reached in the experiment was used.

surface coverage (θ_{Hads}) changes with the potential (condition reached at low overpotentials) in a non-Langmuir isotherm condition. Thus, either the Tafel or Heyrovsky steps might be considered as rate-determining. In either case, it is clearly indicated that a different condition of intermediate adsorption coverage is achieved as the electrode surface is changed from polycrystalline Pt to the intermediate. As proposed earlier, this modification of the intermediate adsorption condition on ordered intermetallic surfaces could be a consequence of a suitable electron density of the surface sites, as suggested by analysis of the XPS data [9]. In summary, it was found that relative to the pure platinum sample, a shift of 6 eV to lower binding energy values was observed for the Pt $3d_{3/2}$ and $3d_{5/2}$ orbitals of PtSb. PtSn showed no shift in the Pt orbital peaks; however, in this material, a shift of 10 eV to higher binding energies was seen in the Sn $3d_{3/2}$ orbital peak [9,11]. It was concluded that in general, as expected, the formation of intermetallic phases led to an effective alteration of the surface atom electron densities that, in its turn, should influence their adsorptive characteristics [9].

Nevertheless, a comparison between the current densities for the CO-free intermetallic PtSb and PtSb/CO shows that the current decreased when the CO was deposited, suggesting that, even though the interaction between CO and the intermetallic surface was weaker than that with the Pt surface, there still remained a partial blockage of the surface by CO molecules. Thus, only some of the active sites on the intermetallic were available for the HOR.

A comparison between the current densities recorded for the intermetallics PtSb and PtSn shows that the better activity is still observed on the PtSb surface, whether CO-covered or CO-free. It is suggested that the CO interaction with the PtSb surface is weaker than that with the PtSn, making CO removal easier and favoring the HOR; this phenomenon is believed to be related to modification of the electron-density structure at the intermetallic surface. Some theoretical work, utilizing *ab initio* methods *via* computer simulation and complementary experimental studies, is being carried out to gain a firmer understanding of the relationship between the electron-density changes and the catalytic activity of the intermetallics for the HOR, on both the free and CO-poisoned surfaces.

4. Conclusions

The evaluation of the performance of the intermetallic phases PtSb, PtSn, PtSb/CO and PtSn/CO in catalyzing the HOR showed that both the bare and CO-covered PtSb and PtSn surfaces achieved current densities higher than equivalent Pt surfaces, in perchloric acid medium. In the case of the CO-covered surfaces, the improved HOR activity of the PtSb and PtSn intermetallic phases, relative to Pt, was attributed to a weaker interaction of the CO molecule with the intermetallic surface, favoring the removal of part of the CO from the surface, or even the lower θ_{CO} estimated for these surfaces. It was also concluded that CO has a higher affinity for the Pt surface than for the intermetallic surfaces, due probably to the electron-density structure of the surface sites of the intermetallic phases.

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