Journal of Alloys and Compounds 434–435 (2007) 764–767

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Electrochemical study of Pt–Pd, Pt–Ru, Pt–Rh and Pt–Sn/C in acid media for hydrogen adsorption–desorption reaction

I. Ávila-García, M. Plata-Torres, M.A. Domínguez-Crespo,
C. Ramírez-Rodríguez, E.M. Arce-Estrada *

Instituto Politécnico Nacional, Departamento de Metalurgia y Materiales, A.P. 75-874, 07300 México, D.F., Mexico

Available online 6 October 2006

Abstract

Four platinum-based binary catalysts (Pt–Ru, Pt–Rh, Pt–Sn, Pt–Pd/C) used for hydrogen adsorption–desorption reaction were investigated by cyclic voltammetry in 0.5 M H_2SO_4 at room temperature. For all the metallic alloys the difference between the total anodic and cathodic charges (1 and 50 cycles) is related to the amount of second metal dissolution. Changes in surface composition during continuous potential cycling are also due to the preferential dissolution of a second metal component. Comparison of the changes in electrosorption properties with the amount of metal dissolved leads to the conclusion that the surface involved in chemisorption reactions consisted of no more than a few atomic layers. The good electrocatalytic behavior for the Pt–Ru/C system is only attributed to the synergic effect of the second metal, which can cause a strong hydrogen adsorption (Q_H^c). The particle sizes were also determinate by conventional physical dispersion method. This method enabled us to observe the shape and size of the particles by transmission electron microscopy (TEM).

© 2006 Elsevier B.V. All rights reserved.

Keywords: Bimetallic electrodes; Hydrogen adsorption–desorption; Cyclic voltammetry

1. Introduction

Effects of the metal particle size on the catalytic properties of supported metal catalysts electrodes have not yet been revealed clearly [1,2]. The difficulty in such study must be caused mainly by the complexity of the structure of supported metal catalysts electrodes. In the search for improved catalysts, considerable attention has been directed towards understanding the properties of alloy systems (binary and ternary). Investigations have indicated that catalytic activity of an alloy can vary in a complex manner with the composition and can be greater than that of the individual components. Synergetic effects have been reported for heterogeneous catalysts of both gas phase reactions and electrode processes [3,4]. Although platinum, palladium, rhodium, tin and their alloys have been widely used as electrodes in the study of electrochemical process, little attention has been directed to the extend of dissolution of such metals. In general, the metals have been considered to be inert in non-complexing acids [5]. However, some reports have shown that both platinum and palladium dissolve under anodic conditions. It has been suggested that dissolution may play an important part in the electrochemical activation of platinum electrodes by anodic–cathodic treatments [6]. Since dissolution can seriously alter the surface composition of noble metal alloy systems and hence the electrocatalytic activity, an investigation of the hydrogen adsorption–desorption reaction of Pt–M alloy systems was considered important. In the present, paper four platinum-based binary electrodes (Pt–Ru, Pt–Rh, Pt–Sn, Pt–Pd/C) dispersed on glassy carbon were investigated in ultrapure conditions, in order to determinate the electrochemical behavior on hydrogen adsorption–desorption reaction (HAD) and the second metal stability in acid medium.

2. Experimental

The support of the electrode was a glassy carbon rod (5.0 mm in diameter). The base of the rod was polished with a cloth and alumina powder (ca. 0.3 μm). The working electrodes were prepared by attaching ultrasonically re-dispersed catalyst suspension containing 5 wt.% Pt + 5 wt.% M(Ru, Rh, Sn or Pd)/C powders in deionized water onto the glassy carbon. After drying in flowing high purity argon at room temperature, the deposited catalyst layer was then covered with ≈4 μl of a diluted aqueous Nafion solution and finally, the electrode was

---

* Corresponding author.
E-mail addresses: nanoparticula@yahoo.com (I. Ávila-García), mplatat@hotmail.com (M. Plata-Torres), adcrespo2000@yahoo.com (M.A. Domínguez-Crespo), claujenn@yahoo.com (C. Ramírez-Rodríguez), earce@ipn.mx (E.M. Arce-Estrada).

0925-8388/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2006.08.161

immersed in nitrogen purged electrolyte to record the cyclic voltametry. 10 wt.% Pt/C was also prepared as reference during the electrochemical measurements. The electrodes were carefully prepared in order to obtain reproducible electrode surfaces and comparable electrocatalytic results. All electrochemical measurements were conducted in conventional glass cells. The base electrolyte used for these experiments was 0.5 M H_2SO_4 and room temperature. The counter electrode was a graphite bar and the reference electrode a Hg/Hg_2SO_4 (0.6415 V *versus* RHE) connected to the working electrode compartment via Luggin capillary. The cycles were run between −0.01 and +1.29 V *versus* RHE for hydrogen adsorption–desorption at a scan rate of 500 mV s^{-1} [7]. All the specimens were analyzed up to 50 cyclic potential scans. The nanomorphology of the supported catalysts was observed by transmission electron microscopy (TEM), using a JOEL JEM-20000 FXII microscope. The samples for the TEM analysis were prepared by ultrasonically treating the catalyst powders in ethanol. A drop of the suspension was applied onto clean holey copper grids and dried in air.

3. Results and discussion

Voltamperometric curves for hydrogen adsorption-desorption reaction on Pt–M/C (M: Ru, Rh, Sn, Pd) alloy systems and Pt/C electrode as a reference after 50 potential sweeps are shown in Fig. 1. These curves are similar to the shape of voltammograms of Pt metal, well characterized in the literature [8,9] and they are also similar to the shapes of curves published for some Pt–M/C alloys [10–12]. Two anodic (desorption) and cathodic (adsorption) peaks H_1^a, H_2^a, H_1^c and H_2^c, respectively, can be distinguished, except Pt–Sn/C. The peaks H_1^a, H_2^a, H_1^c and H_2^c have been interpreted in the literature as weakly and strongly bonded hydrogen adatoms [10–12]. In the hydrogen desorption region, the peak present at more negative potentials H_2^a is considered to be due to hydrogen desorption from the bulk of the metal together with the desorption of hydrogen adsorbed on the surface [11,12]. The peak obtained at more positive potentials (H_1^a) is attributed exclusively to adsorbed hydrogen [13]. Changes in the amount of hydrogen desorbed manifested by the peaks H_1^a and H_2^a are proportional to the changes of the real surface area of the Pt–M/C alloys [14]. Pt/C and Pt–Ru/C showed the highest real surface area for this reaction. Pt–Sn/C electrode only showed one hydrogen adsorption (H_2^c)–desorption H_2^a peak. After this peak, the hydrogen desorption continues over the double layer region with an increase in the capacitance. In all the specimens, metal oxide formation between 0.67 and 0.93 V *versus* RHE and its corresponding reduction from 0.67 to 0.60 V *versus* RHE was detected and has been attributed to the second metal addition. The reduction peaks shifted and the current density increased depending of the second metal characteristics.

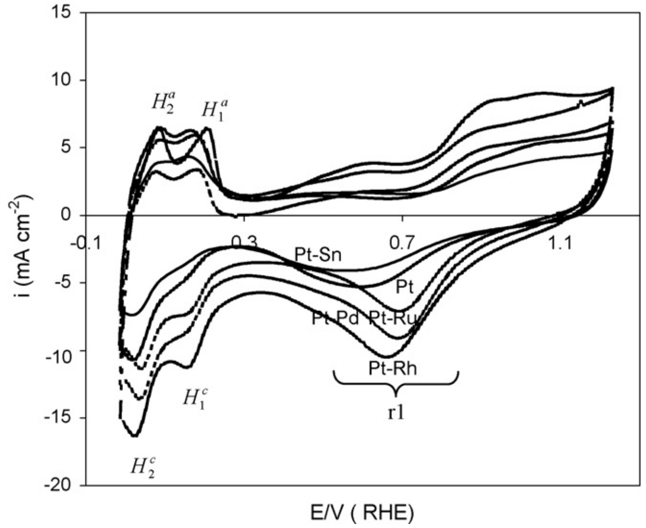

Fig. 1. CV curves after 50 potential sweeps in 0.5 M H_2SO_4 at room temperature with a sweep rate of 500 mV s^{-1} in positive direction.

A single peak (r_1) during cathodic sweep was also observed. This peak is normally assigned to the oxide reduction profile of both metals (Pt–M/C), rather than the sum of the individual contributions, which indicates the existence of an alloy phase. As can be observed in the figure, the potential of this peak is characteristic of the particular metal or alloy being investigated.

These observations indicate that second metal additions influence the hydrogen adsorption–desorption potential and affect the oxide reduction potential and the charge passed due to hydrogen adsorption, increasing the active sites, as have been reported by some researchers [8]. Some factors that could explain this electrocatalytic performance are: (a) the ratio of low coordinated surface atoms which is increased inversely with the particle size, (b) the electronic state of small metal particles, (c) the strong metal–support interaction and (d) the synergistic effect.

As is well known, the problem of defining surface atoms becomes more serious when one considers higher order planes likely to be present on a polycrystalline surface. Moreover some investigations have shown that the surface atoms may reside in structures which need not correspond to those calculated from bulk unit cell. In view of the nature of the assumptions involved, the choice of a particular value for Q_H^a real must be arbitrary. Nevertheless, it is convenient to refer results to some standard of real area, particularly with rough electrodes, and generally, it has been considered that the charge associate with hydrogen monolayer is 210 μC cm^{-2} [10–12]. Table 1 summarizes the charge passed due to hydrogen desorption (Q_H^a); real area (A_r); active sites number (N_A); and mass deposited on the surface (W). These values were obtained by linear extrapolation of the double-layer region and integration to the current minimum just after molecular hydrogen evolution, as shown in Fig. 1. This table shows that there is a marked influence of the surface composition on the hydrogen adsorption capacity of the alloys. Comparing Pt–M/C electrodes, it is observed that Pt–Ru/C presented the highest active sites for the HAD. This suggested that ruthenium metal is easily and reversibly oxidized when the anodic potential is too positive (1.15 V *versus* RHE). Pt–Ru/C electrodes are not stable in acid medium due to a rapid preferential dissolution of ruthenium and there is therefore an evolution of electrode towards

Table 1
Electrochemical parameters 10 wt.% Pt/C and its alloy

Sample	Q_H (μC)	A_r (cm^{-2})	N_A ($\times 10^{-15}$)	W ($\times 10^7$ g)
Pt/C	243	1.45	1.89	6.15
Pt–Pd/C	154	0.91	1.20	3.89
Pt–Ru/C	206	1.23	1.61	5.21
Pt–Rh/C	152	0.90	1.19	3.84
Pt–Sn/C	110	0.85	0.65	1.12

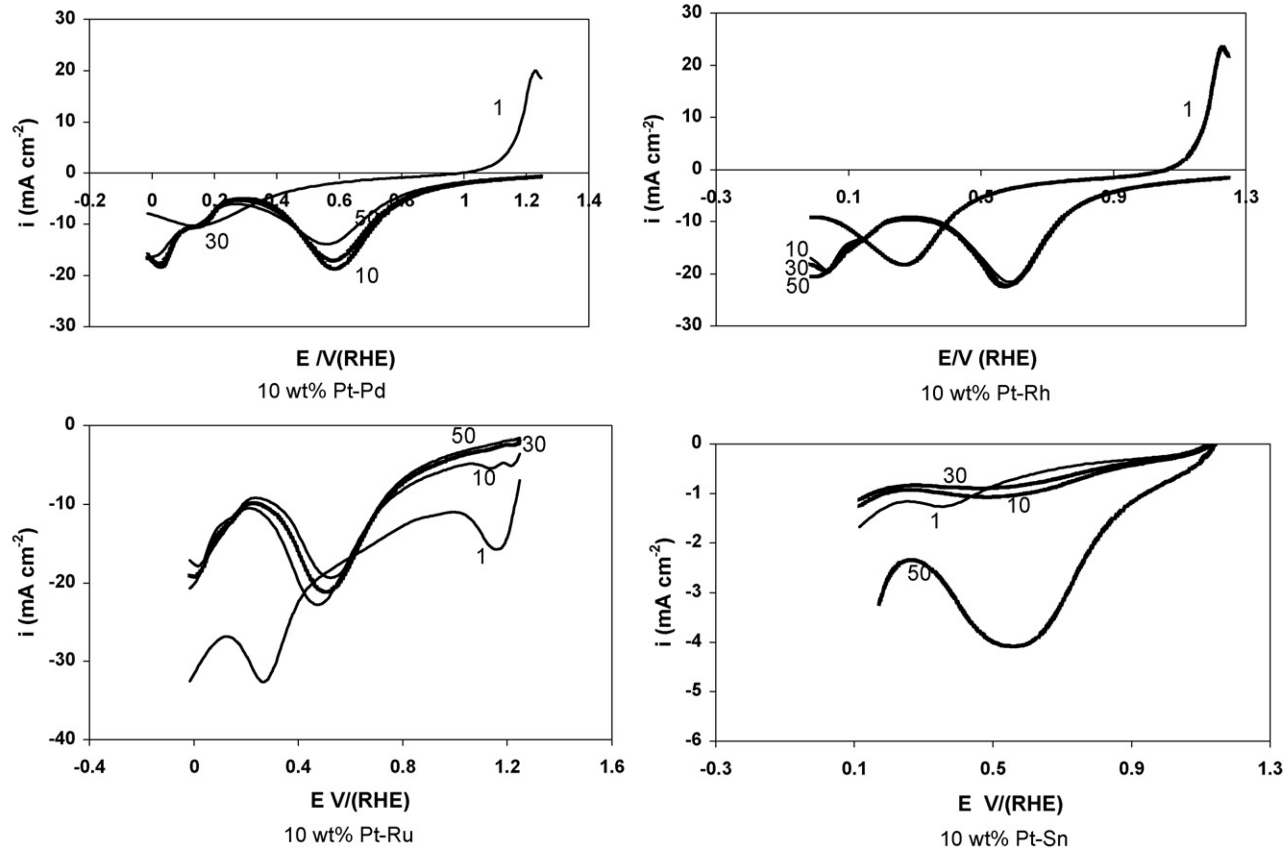

Fig. 2. Current *vs.* potential curves for cathodic zone at different potential sweeps (1, 10, 30, and 50 cycles).

pure platinum; the amount of Ru interacting with Pt metal and the support is enough to cause an increased in the catalytic activity.

In Fig. 2, voltammograms show changes in electrosorption properties on continuous potential cycling. Such changes are associated with the dissolution of the second metals from the surface; analysis of the curves after 1, 10, 30 and 50 cycles show that Ru dissolves at a greater rate. In general in all Pt–M/C electrodes, the surface concentration of platinum gradually increases with the result that oxygen reduction peak shifts to higher potentials with each succeeding cycle. Eventually, voltammograms become constant in shape and are almost identical to that for platinum in all the cases, except to Pt–Sn/C [9]. Pt–Sn/C shows a higher stability, and only can be dissolved after 300 potential cycles. This suggested that Sn metal causes blockage of Pt active sites which could affect the hydrogen adsorption–desorption properties. The dissolution of metal on potential cycling will involve charge transfer and the resulting anodic current will lead to an inequality in the total anodic and cathodic charges passed. The difference between the two charges (1 and 50 cycles) for Pt–M/C alloys corresponds to the amount of dissolved metal. The preferential dissolution of second metal in the Pt–M/C electrodes and their catalytic activity was in the following order: Pt–Ru > Pt–Pd > Pt–Rh > Pt–Sn.

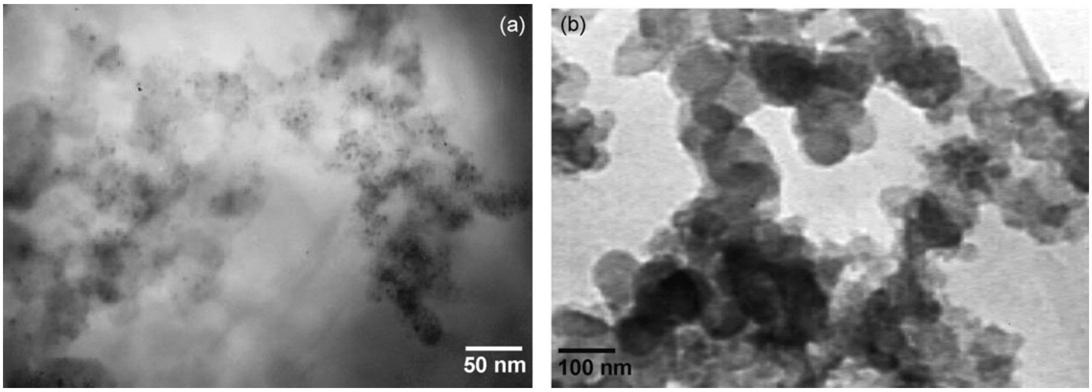

Fig. 3. TEM micrographs of: (a) Pt/C and (b) Pt–Ru/C electrodes.

Typical TEM image of the Pt–M/C (Ru as an example) and Pt/C prepared catalysts are shown in Fig. 3. The distribution of the particles is homogenous on the support and the catalysts are well dispersed, consisting of particles averaging from 2 to 4 nm. Although, the dispersion of the metallic particles was better for the Pt/C than Pt–Ru/C samples, the smallest particle detected has a size of about 1.8 nm whereas the largest one is about 6 nm. In this work, the catalytic performance of Pt–M/C do not depend strongly of metallic dispersion but rather the electronic properties (synergistic effect).

4. Conclusions

The results of this work show that there is a difference between the anodic and cathodic charges passed during a potential cycle. This difference is attributed mainly to the second metal dissolution. Ruthenium metal (Pt–Ru/C) is more easily and reversibly oxidized than the others Pt–M/C when the anodic potential is less negative. Yet Pt–Ru/C electrodes are not so stable in acid medium due to a rapid preferential dissolution of ruthenium and evolution of electrode towards pure platinum. It exhibited the best electrocatalytic performance. This behavior could be attributed to the miscibility of Ru–Pt, and nature of the Pt–Ru/C catalyst increasing its activity (synergistic effect). Although, Pt–Sn/C showed the best metal stability, it can block Pt active sites which affect the hydrogen adsorption–desorption properties.

Comparison of the change in electrosorption properties with the amount of metal dissolve and TEM observations leads to the conclusion that the surface involved in chemisortion reactions consisted of no more than a few atomic layers in all the specimens.

Acknowledgements

Authors wish to thanks the financial support from CGPI-IPN and CONACYT.

References

[1] B.D. McNicol, P. Attwood, R.T. Short, J. Chem. Soc., Faraday Trans. 77 (1981) 2017.
[2] K. Kinoshita, Modern Aspects of Electrochemistry, Coll., vol. XIV, Plenum Press, New York, 1982, p. 557.
[3] L.D. Burke, J.K. Casey, J. Appl. Phys. 23 (1993) 573.
[4] L. Geniès, R. Faure, R. Durand, Electrochim. Acta 44 (1998) 1317–1327.
[5] P.L. Cabot, E. Guezala, J.C. Calpe, J. Electrochem. Soc. 147 (2000) 43.
[6] D.A.J. Rand, R. Woods, J. Electroanal. Chem. 31 (1971) 29.
[7] R.E. Melnick, G.T.R. Palmore, J. Phys. Chem. B 105 (2001) 9449–9457.
[8] T. Feeling, W. Vischer, J.A.R. Van Veen, J. Electroanal. Chem. 382 (1995) 65.
[9] B. Beden, F. Kardigan, C. Lamy, J.M. Leger, J. Electroanal. Chem. 127 (1981) 75–85.
[10] R. Woods, in: A.J. Bard (Ed.), Chemisorption at Electrodes in Electroanalytical Chemistry, vol. 9, Marcel Dekker, New York, 1976.
[11] A. Czerwinski, R. Marassi, S. Zamponi, J. Electroanal. Chem. 316 (1991) 211.
[12] A. Czerwinski, J. Electroanal. Chem. 379 (1994) 487.
[13] A.N. Correia, L.H. Mascaro, S.A.S. Machado, L.A. Avaca, Electrochim. Acta 42 (1997) 493.
[14] A. Czerwinski, Pol. J. Chem. 69 (1995) 699.