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Electrocatalytic activity of nanosized Pt alloys in the methanol oxidation reaction

I. Ávila-García, C. Ramírez, J.M. Hallen López, E.M. Arce Estrada*

IPN-ESIQIE, Departamento de Metalurgia y Materiales, UPALM Ed. 7, 07837 México, DF, Mexico

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ABSTRACT

The electrocatalysis of the methanol oxidation reaction on carbon supported nanosized Pt and Pt–M (M: Ru, Pd, Rh and Sn) electrocatalysts was investigated in 0.5 M H_2SO_4 + 0.1 M CH_3OH at room temperature by cyclic voltammetry and electrochemical impedance spectroscopy. The onset potential for methanol oxidation at GC/Pt–Ru/V was shifted to lower potentials and showed improved specific activity towards the methanol oxidation compared with platinum and the others Pt–M electrocatalysts studied. Accordingly, GC/Pt–Ru/V electrocatalysts showed an improved performance as anode materials in methanol oxidation reaction.

1. Introduction

Methanol is one of the most promising fuels for fuel cells, especially if it can be directly and completely oxidized to carbon dioxide. However, this direct electro-oxidation is difficult to proceed in a range of electrode potential suitable for its application in a direct methanol fuel cell (DMFC). The challenge is to enhance the kinetic of the electrocatalytic oxidation of methanol at lower electrode potential, and to avoid or limit the poisoning phenomena observed with pure platinum electrodes. Such enhancement can only be obtained by modification of the structure and the nature of the electrode. Improvements on the rates of methanol oxidation can be achieved by alloying Pt with other metals [1], like Ru [2,3], Ir [4], Au [5] and Sn [6]. Some mechanisms have been proposed to explain this enhancement: (i) modification of the electronic properties of the base metal, (ii) bifunctional mechanism, where the second metal facilitates the oxidation of the strongly adsorbed residue and (iii) the third body effect [7].

The aim of this work is to investigate the performance of platinum based binary catalysts (Pt–Ru, Pt–Rh, Pt–Sn and Pt–Pd) and to compare their electrochemical activity with that of the Pt electrode. The electrochemical activity on the methanol oxidation was evaluated by cyclic voltammetry and electrochemical impedance spectroscopy.

2. Experimental

2.1. Electrode preparation

Glassy carbon (GC) was used as substrate. Prior to electrode preparation this substrate was polished using 600, 1000, and 1200 SiC emery papers, ultrasonically cleaned for 20 min in acetone bath and for 5 min in isopropanol bath, and dried with high purity N_2.

The Pt/Vulcan XC-72 E-TEK (Pt/V; Pt: 10 wt.%, particle size 2.0 nm) and Pt–M/Vulcan XC-72 E-TEK (Pt–M/V; Pt:M = 1:1; M = Ru, Pd, Rh or Sn; particle size 2.0 nm) specimens were dispersed in a mix of deionized water and Nafion (1:1), then, ultrasonically blended for 30 min. After this procedure, the obtained catalyst suspension was applied as a homogeneous dispersion onto the GC electrode surface with a micropipette, in order to obtain GC/Pt/V and GC/Pt–M/V electrodes (3 mm diameter). The resulting electrodes were drying at room temperature in a nitrogen atmosphere for 24 h.

2.2. Electrochemical measurements

Electrochemical measurements were carried out at room temperature in a glass cell containing 0.5 M H_2SO_4 + 0.1 M CH_3OH. The solutions were prepared with high purity water (Millipore, 18 MΩ cm resistivity). Prior to start the electrochemical experiments, a stream of highly purified nitrogen gas was bubbled into the solutions to eliminate oxygen. The counter and reference electrodes were a platinum wire and $Hg/HgSO_4$, respectively. In this work all the potentials are quoted with respect to the reversible hydrogen electrode RHE. The controlled potential experiments were performed using a potentiostat–galvanostat Autolab PGSTAT 30. The impedance spectra were recorded by a frequency response analyzer module, FRA2. The frequency ranges from 10 kHz to 0.05 Hz were digitally recorded with 50 points per decade. Each spectrum was measured four times over the entire frequency range to ensure the stability of the electrode during the process and to assess the reproducibility of the data. Before to the methanol oxidation study, the surface of the working electrodes, GC/Pt/V and GC/Pt–M/V, were cleaned electrochemically by cycling the potential between −0.01 and 1.2 V in 0.5 M H_2SO_4 at a sweep rate of 500 mV s^{-1}, until the CV profiles showed no longer changes.

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* Corresponding author. Tel.: +52 5553552508; fax: +52 5557296000.
E-mail address: earce@ipn.mx (E.M. Arce Estrada).

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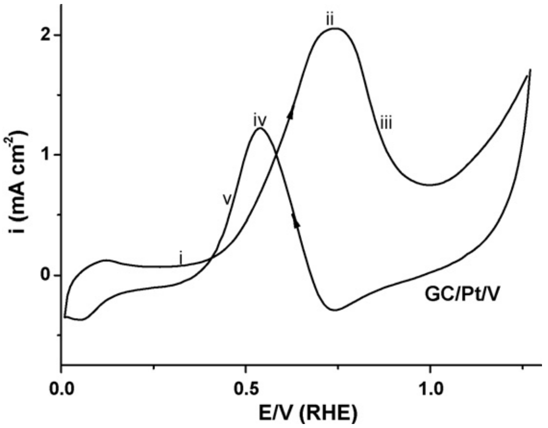

Fig. 1. Cyclic voltammogram of GC/Pt/V electrode in 0.5 M H_2SO_4 + 0.1 M CH_3OH; room temperature, sweep rate, 35 mV s^{-1}.

3. Results and discussion

Fig. 1 shows the stationary cyclic voltammogram recorded at 0.03 V s^{-1} for the GC/Pt/V catalysts in 0.5 M H_2SO_4 + 0.1 M CH_3OH solution for the methanol oxidation reaction. In the positive scan, the adsorption and dehydrogenation of methanol result in the formation of CO–Pt at low overpotential (region i). It is observed an anodic current peak around *ca.* +0.778 V (region ii), where surface water might react with adsorbed CO on the GC/Pt/V electrode and produce CO_2, proton (H^+), electron (e^-), a vacant site and the formation of different species on the Pt surface such as HCHO [8,9], HCOOH [8,10], and $HCOOCH_3$ [11,12]. At higher potential (region iii), the current decreases due to the formation of hydroxide on the GC/Pt/V surface [13]. On the negative scan, it can be seen an anodic peak (region iv) associated with the oxidation of species formed due to the oxidation of CH_3OH. Finally, the current decreases due to surface blocking by CO (region v) [14].

Table 1
E_{p1}, i_{p1}, Q_1, and E_{onset} values for the GC/Pt/V and GC/Pt–M/V electrodes.

Electrode	E_{p1} (V)	I_{p1} (mA cm^{-2})	Q_1 (μC cm^{-2})	E_{onset} (V)
GC/Pt/V	0.778	2.05	1187	0.48
GC/Pt–Pd/V	0.769	3.25	1863	0.45
GC/Pt–Ru/V	0.766	2.62	2583	0.40
GC/Pt–Rh/V	0.783	4.00	1791	0.50
GC/Pt–Sn/V	0.867	3.24	923	0.46

The complete electro-oxidation of methanol is expressed as

$$CH_3OH + H_2O = CO_2 + 6H^+ + 6e^- \qquad (1)$$

In general, conventional elementary processes are considered to be

$$Pt + CH_3OH = Pt\text{–}CO + 4H^+ + 4e^- \qquad (2)$$

$$Pt + H_2O = Pt\text{–}OH + H^+ + e^- \qquad (3)$$

$$Pt\text{–}CO + Pt\text{–}OH = 2Pt + CO_2 + H^+ + e^- \qquad (4)$$

Fig. 2 shows cyclic voltammograms recorded at 0.03 V s^{-1} for the GC/Pt–M/V electrodes in 0.5 M H_2SO_4 + 0.1 M CH_3OH, for the methanol electro-oxidation reaction in the potential range from 0.05 to 1.2 V. Table 1 presents E_{p1}, i_{p1}, Q_1, and E_{onset} values for

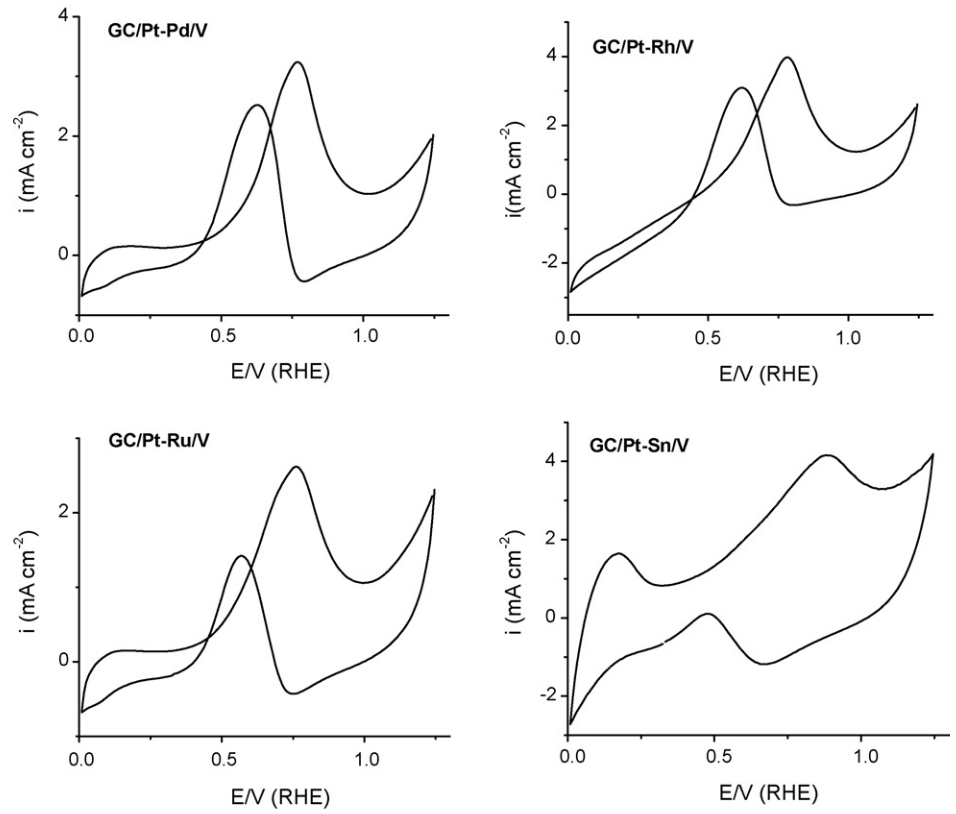

Fig. 2. Cyclic voltammogram of GC/Pt–M/V electrode in 0.5 M H_2SO_4 + 0.1 M CH_3OH; room temperature, sweep rate, 35 mV s^{-1}.

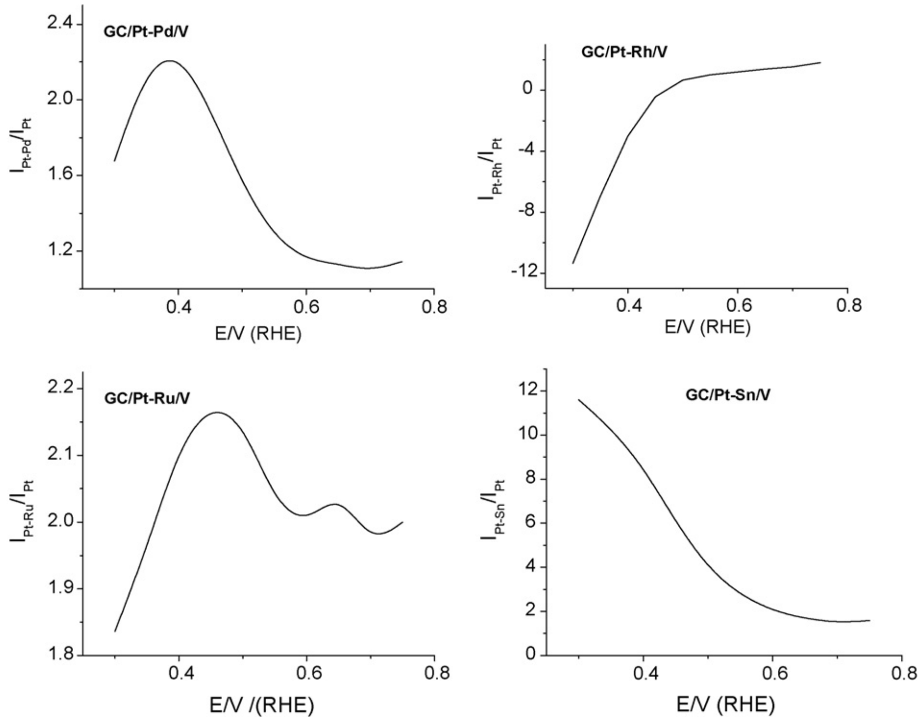

Fig. 3. Ratios I_{Pt-M}/I_{Pt} for methanol oxidation in 0.5 M H_2SO_4 + 0.1 M CH_3OH for GC/Pt–M/V electrode, from Fig. 2.

the GC/Pt/V and GC/Pt–M/V electrodes. These values show that the onset of the methanol oxidation reaction occurs at lower potentials for the electrode containing Ru followed for Pd, Sn and Rh electrodes and that the global current density and the charge are higher for GC/Pt–Ru/V than for the others electrodes. These results are in good agreement with those of Watanabe and Motoo [15] that achieved the highest current densities at potentials around 0.45 V for Pt electrodes modified by Ru deposits with Ru ratios between 36 and 60 wt.% in 0.5 M H_2SO_4 + 1.0 M CH_3OH solutions at 40 °C. Jusys et al. [16] and Guo et al. [17] showed the same tendency regarding the E_{onset} to lower values for Pt–Ru electrodes.

This enhancement of the methanol oxidation rate on GC/Pt–Pd, GC/Pt–Ru/V and GC/Pt–Sn/V electrodes in comparison to GC/Pt/V catalysts is attributed to the ability of the second metal, M (Pd, Ru and Sn) to adsorb OH radicals at less positive potentials than Pt [18]. The mechanism at bifunctional alloys composed of Pt and a second metal (M) capable of activating H_2O molecule at lower potentials is showed below [19–21]:

$$M + H_2O \rightarrow M\text{–}H_2O_{ads} \tag{6}$$

$$M\text{–}H_2O_{ads} \rightarrow M\text{–}OH_{ads} + H^+ + e^- \tag{7}$$

$$Pt\text{–}CO_{ads} + M\text{–}OH_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^- \tag{8}$$

where M could be any metal being adsorbed on or alloyed with platinum, which is oxidized at potentials between 0 and 0.6 V versus RHE.

In Fig. 3, the ratios between the current obtained in the electro-oxidation of methanol with each GC/Pt–M/V electrode and with GC/Pt/V, in the range of electrode potential from 0.3 to 0.45 V are presented. The relation of the current of methanol oxidation on GC/Pt–Pd/V electrode and current on GC/Pt/V is greater than 1 (about 2.2 at the maximum in the potential between 0.3 and 0.45 V). However, at more positive potentials, a decrease in the catalytic activity is observer indicating inhibition. The GC/Pt–Rh/V electrode shows a poisoning effect in the whole range of potential. The relation of the current of methanol oxidation on GC/Pt–Ru/V and the current on GC/Pt/V is greater than 2, indicating that the GC/Pt–Ru/V electrode has an enhancement effect on the catalytic activity. However, this current ratio decreases when potential increases. GC/Pt–Sn/V electrode appears to be the best electrode at low potential with a current ratio of 11. However, this factor decreases when potential increases due to inhibition effect of methanol oxidation products.

In order to investigate the catalytic activity for the methanol electro-oxidation reaction on GC/Pt–Ru/V electrodes, the electrochemical impedance spectroscopy method was used. Impedance spectra of the supported catalyst electrode were carried out in 0.5 M H_2SO_4 + 0.1 M CH_3OH solution at room temperature at potentials of 0.4, 0.6 and 0.7 V in. Fig. 4 shows Nyquist plots of the GC/Pt–Ru/V electrode working at the abovementioned potentials. A semicircle is observed in the complex plane impedance plot. The diameter of this semicircle decreases as the applied potential increases. The impedance spectra show small potential's independence impedances in the high frequency region, which is followed by a lower frequency arc that has a magnitude dependent on potential. A loop reflecting an inductive behavior appears at the low frequency end for 0.7 V. This inductive effect has been attributed to the kinetics of the electro-oxidation of methanol, in particular, to slow reaction rate adsorption/dehydrogenation/oxidation of methanol [22]. Large amount of intermediate CO is strongly adsorbed on the surface blocking sites for the adsorption of the hydrogen and dehydrogenation of methanol [22,23]. The time constant at high frequencies corresponds to the occurrence of a fast reaction step and are related to the dehydrogenation of methanol, similar results was observed on GC/Pt/V. Melnick and Palmore [24] observed a similar behavior on the polycrystalline platinum electrode and Wagner and Schulze on Pt–Ru/C anode [25].

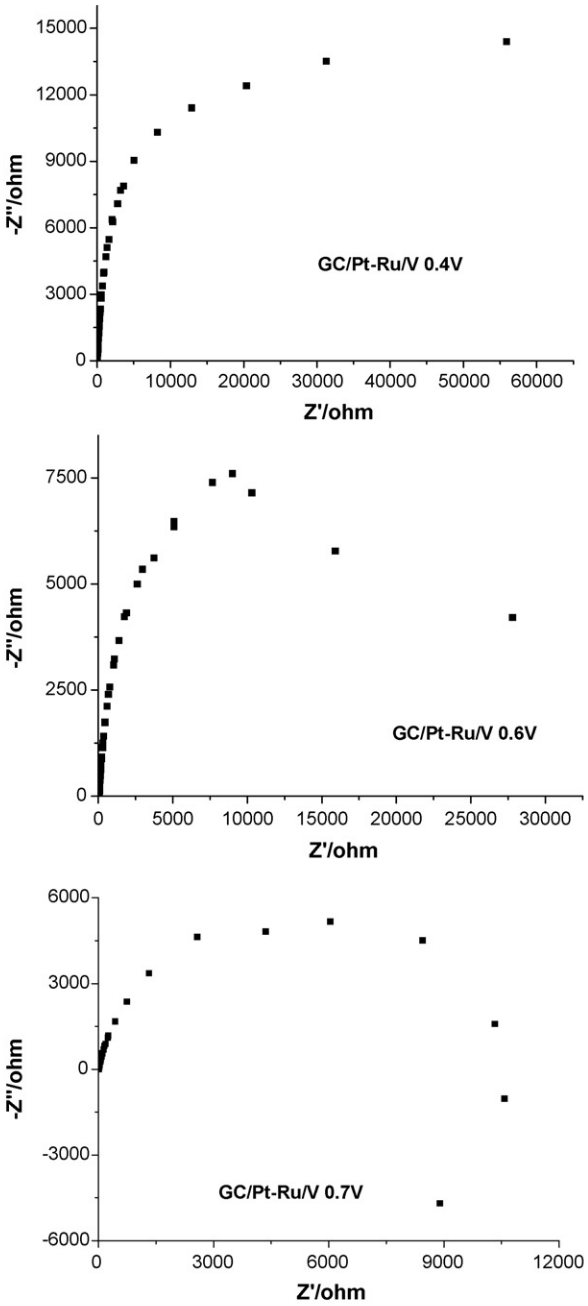

Fig. 4. Complex plane impedance plots in 0.5 M H_2SO_4 + 0.1 M CH_3OH at various electrode potentials for GC/Pt–Ru/V.

4. Conclusions

Nanoparticles Pt–Ru, Pt–Pd and Pt–Sn enhanced methanol oxidation reaction compared to Pt nanoparticles. GC/Pt–Ru/V is more active than the GC/Pt/V and present a lower onset potential for the methanol oxidation. GC/Pt–Rh/V shows susceptibility to strong poisoning by the methanol oxidation products and GC/Pt–Pd/V and GC/Pt–Sn/V present an inhibition effect at higher potentials. The enhancement of the methanol oxidation rate on GC/Pt–Ru/V electrode is attributed to the ability of Ru to adsorb OH radicals at less positive potentials.

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