Journal of Applied Electrochemistry **30**: 1151–1155, 2000.

Platinum–tin alloy electrodes for direct methanol fuel cells

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Received 27 August 1999; accepted in revised form 25 April 2000

Key words: direct methanol fuel cell, electrocatalysis, Pt–Sn alloy

Abstract

Pt electrodes, modified by partial electrodeposited tin, were used as anodes for the catalytic electrooxidation of methanol in acid medium. Sn was electrodeposited galvanostatically and potentiostatically. Cyclic voltammetry was used to study the methanol electrooxidation. Pt modified with Sn proved superior to pure platinum as shown from the methanol peak current densities. Sn also improved the performance regarding the stability of the anode over repeated cycles. It was found that electrodeposited Sn facilitates the oxidation of intermediate poison products through a mixed homogeneous–heterogeneous catalytic mechanism.

1. Introduction

Considerable interest has been directed to the use of fuel cells in electric vehicle technology. One promising system is the direct methanol fuel cell (DMFC), since the fuel is best transported and converted into energy from the liquid state [1]. Unfortunately, efficient electrocatalysts for electrochemical reactions of the fuel are still far from satisfactory. To improve both the oxidation rate and electrode stability, considerable efforts have been directed towards the study of binary metallic electrodes for the direct electrochemical oxidation of methanol. Recent advances have shown that Pt-based bimetallic or multimetallic catalysts exhibit enhanced efficiency for methanol oxidation [2–4]. Alloy electrodes such as Pt–Ru, Pt–Rh, Pt–Rb, Pt–Re and Pt–Sn have been studied [5]. However, Pt–Ru and Pt–Sn are the most active of the binary alloys [6]. On the other hand, purely surface-adsorbed tin metal was found by Campbell and Parsons [7] to inhibit methanol oxidation.

The exact role of the alloying metal with Pt as promoters in the methanol electrooxidation is still not well understood. Contradictory assumptions about its role were found in the literature. One of these is that the alloying metal facilitates the adsorption of oxygen containing species such as OH_{ads} [8, 9]. Subsequently, the adsorbed Pt–OH reacts with organic poison. Another is that the enhancement occurs by preventing the formation of a strongly adsorbed poisoning species such as CO either by blocking the sites necessary for its adsorption [6], or by completely oxidizing CO in solution to CO_2 [10]. It was also assumed that a hybrid homogenous–heterogeneous mechanism accounts for the enhancement [11]. Sn spontaneously adsorbed on Pt as Sn(II) might catalyze the methanol oxidation in acid medium [12]. A pronounced enhancement of the catalytic activity towards methanol electrooxidation on Pt–Sn oxide was observed [13].

The aim of this work is to investigate the effect of Sn, electrodeposited using different methods, on Pt, on the methanol electrooxidation in acid medium.

2. Experimental details

The electrochemical measurements were performed using an Amel 5000 system (supplied by Amel instrument, Italy) driven by an IBM PC for data processing. The PC was interfaced with the instrument through a serial RS-232C card. Amel Easyscan software was used in connection with the PC to control the Amel 5000 system.

Details of the experimental cell can be found elsewhere [14]. The electrochemical measurements were performed on a Pt-sheet working electrode (area 1 cm^2) and on Pt electrodes modified by electrodeposited tin. The reference electrode to which all potentials are referred was Hg/Hg_2SO_4 /1 M H_2SO_4 (MMS). The Pt working electrode was treated in the usual way to remove any impurities adsorbed on the surface. The Sn-modified Pt electrodes were prepared by partial electrodeposition of tin at a constant current density of 1 mA cm^{-2} from a solution of 0.3 M $SnCl_2$ in 0.5 M H_2SO_4. The electrodeposition of Sn was performed on arbitrary chosen small areas on the Pt electrode surface. Another method of Sn deposition was conducted potentiostatically at a constant potential of −850 mV vs MMS. Methanol at the desired concentration was added and the cyclic voltammograms were measured between −0.2 to +0.4 V vs MMS. After Sn deposition (either galvanostatically or potentiostatically) the electrode was strongly heated on an O_2/natural gas (with temperatures about 1000 °C). To activate the surface, the electrode was polarized in a cyclic mode from the H_2 evolution potential (−0.8 V) to the O_2 evolution potential (1.4 V) at a scan rate of 100 mV s^{-1} for 50 cycles before each experiment.

Chemicals were obtained from BDH (AR H_2SO_4, $SnCl_2$ analytical reagent and AR methanol). They were used without further purification and solutions were prepared using triply distilled water. All experiments were carried out at room temperature of 30 ± 2 °C.

3. Results and discussion

Cyclic voltammograms for the clean Pt electrodes were traced repeatedly in pure 0.5 M H_2SO_4 between H_2 and O_2 evolution potentials to ensure the surface cleanliness. The voltammogram was then repeated in presence of 0.5 M methanol at a scan rate of 50 mV s^{-1}. Figure 1 shows those results for Platinum. The anodic oxidation of methanol is clearly represented by two peaks, one in the anodic direction and one with slightly lower current density in the cathodic direction. Both the peak current densities decrease as a result of repeated cyclic polarization. Figure 1 shows the second cycle and fiftieth cycle. The first cycle was not recorded because it was not stable. The peak current density for methanol oxidation for the 50th cycle is only 38% of the 2nd cycle. It is well established that the loss of methanol oxidation efficiency is due to surface poisoning either by some intermediate products of the methanol oxidation process [15] or by the formation of platinum oxide [7]. The strong adsorption of –CHO type intermediates can lead to the formation of CO which blocks the surface to the methanol oxidation.

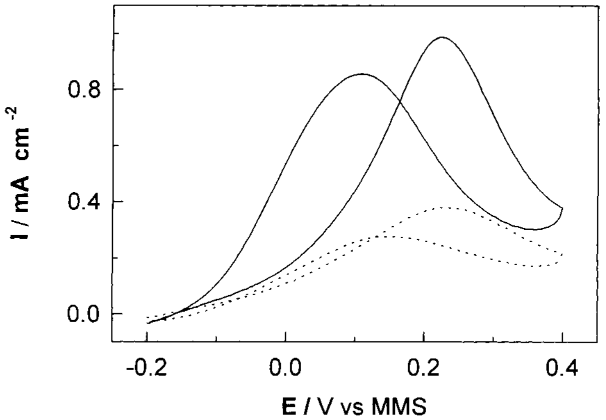

Fig. 1. Electrooxidation of 0.5 M methanol on pure Pt electrode in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. Cycle: (——) 2 and (........) 50.

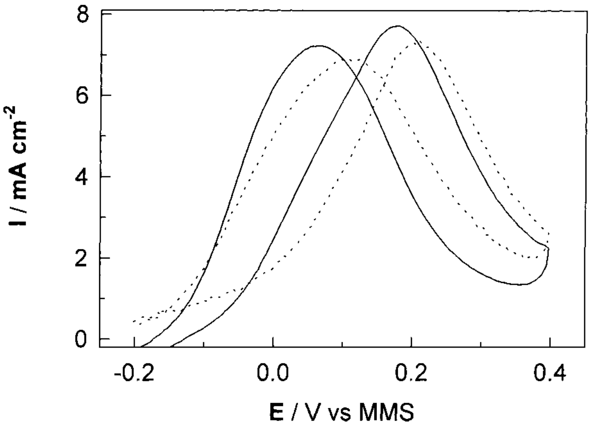

Fig. 2. Electrooxidation of 0.5 M methanol on Sn-modified Pt electrode in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. (Sn was deposited galvanostatically at 1 mA cm^{-2} for 7 min). Cycle: (——) 2 and (........) 50.

A radical increase in the peak current density for the methanol oxidation was observed on Sn-modified Pt electrodes (Figure 2). Sn was galvanostatically deposited on the Pt surface for 7 min at a cathodic current density of 1 mA cm^{-2}. It must be noted that the deposition of Sn was only partial on the electrode surface. The working electrode was dipped into molten paraffin wax in order to cover its surface. It was then removed and the wax was left to solidify. Small parts of wax were removed from the surface. Each part was in the form of circle of about 1 mm diameter. In this way most of the surface was covered with wax leaving only about 1.5–2% of the surface uncovered. After the deposition of Sn, the wax was removed by heating, which proved to be an essential part of the procedure to insure alloying of Sn with Pt. Surface layers of Sn tend to dissolve in H_2SO_4. Table 1 shows a comparison between the performance of pure Pt and Sn-modified Pt electrodes for the electrooxidation of methanol. It is obvious from the data in Table 1 that the Sn-modified electrodes are superior to those of pure Pt from the following essential points:

(i) The peak current density for the oxidation of methanol is much higher in presence of Sn compared to the pure Pt surface.

(ii) The Sn-modified Pt electrodes show a slight loss of efficiency after many repeated cycles (93% of the peak current density was retained after 50 cycles) compared to the pure Pt electrode,

Table 1. Values of peak potentials and peak current densities for the electrooxidation of 0.5 M methanol in 0.5 M H_2SO_4 on pure Pt and on Pt + Sn alloy

Peaks*	Pure Pt		Pt + Sn[†]	
	2nd cycle	50th cycle	2nd cycle	50th cycle
E_{p1}/mV	108	152	64	103
E_{p2}/mV	223	232	169	210
I_{p1}/mA cm^{-2}	0.856	0.277	7.23	6.91
I_{p2}/mA cm^{-2}	0.988	0.380	7.688	7.35

* p1 and p2 are refer to the anodic peaks in the reverse and forward scan, respectively

[†] Sn was deposited on Pt galvanostatically at 1 mA cm^{-2} for 7 min

(iii) The Sn-modified Pt electrodes show a slight decrease of overpotential for methanol oxidation compared to pure Pt. In both cases repeated cycling shows a slight increase in overpotential. Repeated cyclic polarization might increase the amount of adsorbed species, intermediates, that are responsible for increasing the overpotential (compare the peak current density of cycle 2 to that of cycle 50).

The results revealed that Sn has to be alloyed with Pt for the electrocatalysis of methanol oxidation in acid solution. Electrooxidation of methanol was not observed on pure Sn surfaces. The treatment carried out after the deposition of Sn (removing wax by heating after the electrochemical deposition of Sn, see above) suggests that Sn dissolves to an appreciable extent in Pt in the solid state. Some of the deposited Sn leaches out in acid solution though functioning as a homogeneous catalyst for methanol [2]. Sn is known also to form active oxygen compounds that help the fast oxidation of intermediates (i.e., –CHO type compounds and CO) to CO_2 [6] thus facilitating the methanol oxidation. Polarization of Pt electrodes in the O_2 evolution potential region has the same effect on adsorbed poisons (see below). Figure 3 shows the effect of the amount of Sn deposited on the methanol oxidation peak current density (forward scan). It is observed that in both the galvanostatic (Figure 3(a)) and potentiostatic (Figure 3(b)) methods of deposition, a certain ratio of Pt:Sn shows the maximum electrocatalytic effect, otherwise the current density falls again. Table 2 represents the variation of the weight of Sn as a function of the deposition time (galvanostatically and potentiostatically). The data in this table in connection with Figure 3 show that weight of about 9.22×10^{-3} mg (galvanostatic deposition) and 2.66×10^{-2} mg (potentiostatic deposition) of Sn alloyed with Pt and dispersed over a surface area of 1 cm^2 along the Pt surface show the highest catalytic activity. It seems that the platinum active centers are blocked if this ratio is exceeded in both cases. The results of Wrighton et al. [5], at electrodes modified with polyaniline and Pt/Sn particles, showed a variation of the catalytic methanol oxidation as a function of Pt to Sn ratio. It was found that the most active catalysts show surface ratios of Pt:Sn between 8:1 to 2:1.

Figure 4 shows the effect of changing the methanol concentration on the peak current density (forward scan) (Figure 4(a)) and peak potential (Figure 4(b)) for Pt and Sn-modified Pt electrodes. Generally, the peak current density increases with increasing methanol concentration (Figure 4(a)). Again the peak current densities are higher, as expected for the modified electrodes. A potential shift towards positive values is observed for the methanol oxidation peaks as the methanol concentration increases. The shift is more pronounced in the case of the Sn-modified electrodes (Figure 4(b)). It was found that increasing the methanol concentration increases the rate of poisoning and causes a shift of the oxidative removal of the strongly adsorbed intermediates to a more positive potential [16]. Figure 5 presents the variation of the peak current density and the peak potential of methanol electrooxidation as a function of the square root of the scan rate. The peak current density increases linearly with the square root of

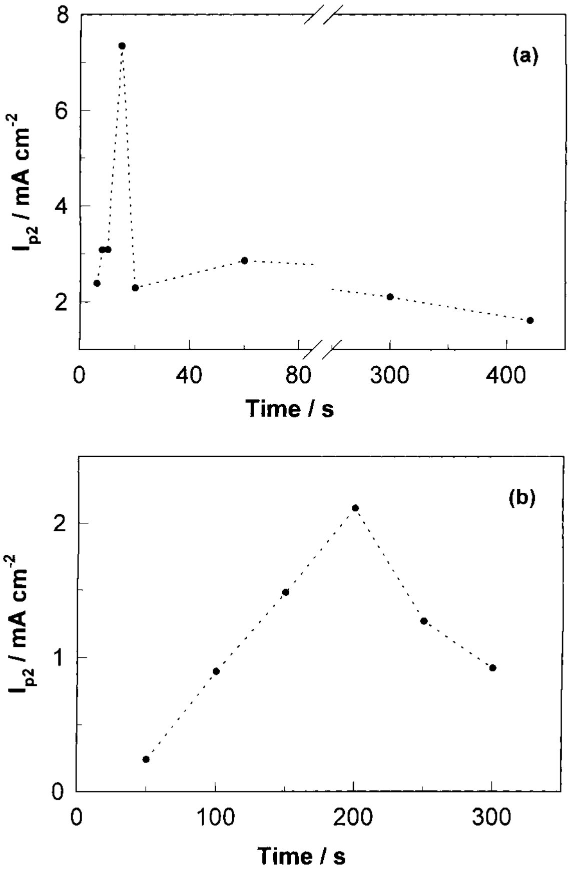

Fig. 3. Variation of the peak current density (forward scan) I_{p2} of methanol electrooxidation with the time of Sn deposition on Pt. (a) Galvanostatic deposition at 1 mA cm^{-2}. (b) Potentiostatic deposition at −800 mV vs MMS.

Table 2. Variation of the weight of Sn with time of deposition (galvanostatically and potentiostatically)

Time/s	Wt/mg × 10^{-3}
Galvanostatic deposition	
6	3.6900
8	4.9200
10	6.1500
15	9.2250
20	12.3
60	36.9
300	184
420	258
Potentiostatic deposition	
50	0.37605
100	6.9197
150	12.3
200	26.6
250	35.0
300	44.6

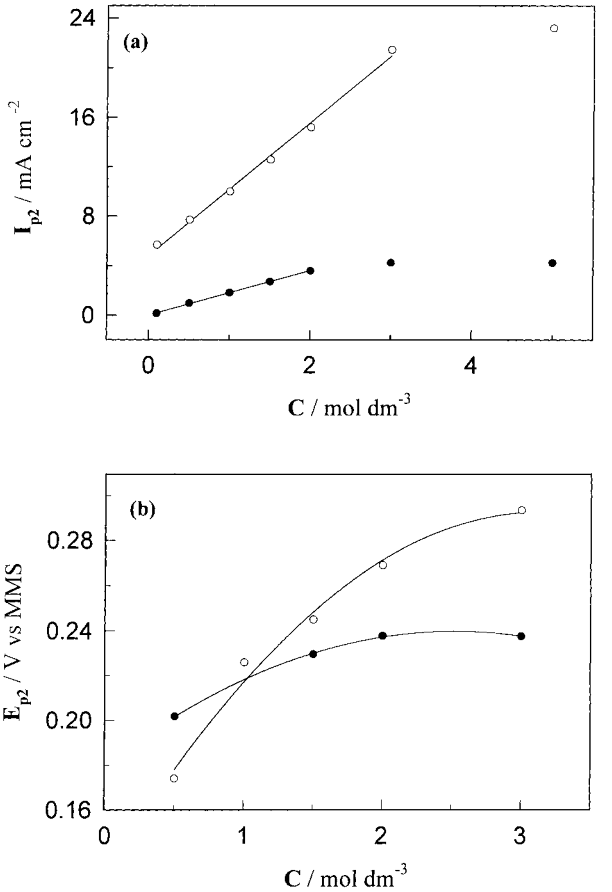

Fig. 4. Variation of the peak current density I_{p2} (a) and the peak potential E_{p2} (b) of methanol oxidation with its concentration. (●) Pure Pt, (○) Pt + Sn. (Sn deposited by the galvanostatic method at 1 mA cm^{-2} for 7 min).

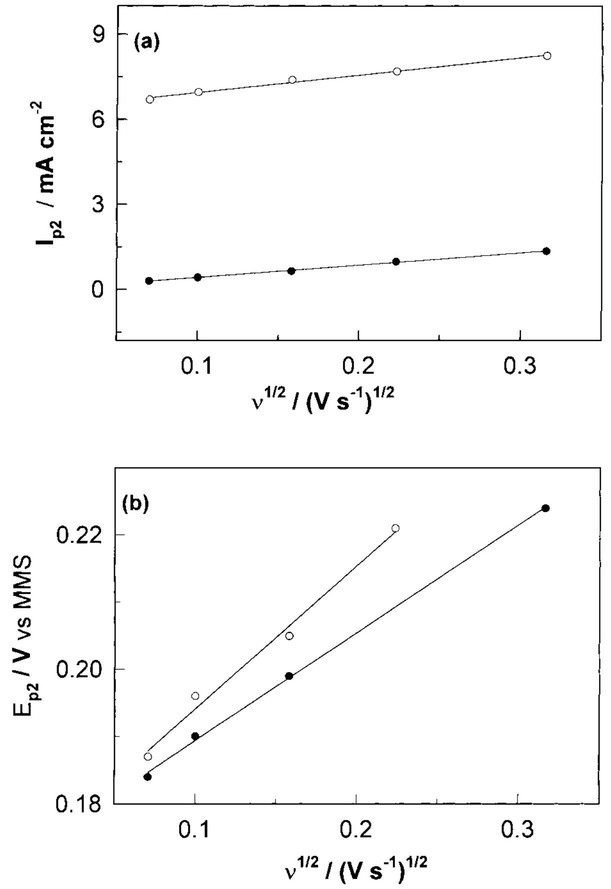

Fig. 5. Variation of the peak current density I_{p2} (a), and the peak potential E_{p2} (b) of methanol oxidation with the square root of scan rate. (●) Pure Pt, (○) Pt + Sn. (Sn deposited by the galvanostatic method at 1 mA cm^{-2} for 7 min).

the scan rate. Surface diffusion of methanol, or one of the intermediates, on the electrode surface may be the limiting factor in this case. Generally the explanation given above for the positive potential shift of the peak potential also applies here for the scan rate effect. Increase in the scan rate might be accompanied by a corresponding increase in the adsorbed intermediates, which in turn requires a high positive potential for their oxidative removal. On the other hand, the simple explanation of the possibility of increasing *iR* drop as a result of the increase in scan rate cannot be ruled out. Extending the potential range of the cyclic voltammogram in the direction of either O_2 evolution or H_2 evolution leads to an increase in the anodic peak current density for methanol oxidation. Figure 6 shows some of these results. Polarization within the O_2 evolution potential range enhances the electrochemical oxidation of poisoning intermediates and accordingly leads to an activated surface that shows a higher oxidation peak current density for methanol (Figure 6(a)). Hydrogen evolution also activates the surface, probably via another mechanism, leading similarly to an activated Pt–Sn surface and higher current densities for methanol oxidation (Figure 6(b)).

The results show that modified platinum electrodes are superior to pure platinum regarding the electooxidation of methanol. Not only are the peak current densities higher, but the stability of the electrocatalysts over repeated cycles is also much higher (Table 1). It was found that Sn dissolves to a large extent in Pt forming Pt_3Sn [2]. The surface composition of the Pt–Sn alloys is almost independent of the bulk concentration and only a very small bulk concentration (e.g., 1–5%) will produce about 33% Sn on the alloy surface. Here, the function of Sn is twofold. First, it improves the rate of methanol oxidation via a homogeneous–heterogeneous catalytic mechanism. Second, it improves the stability over a relatively large number of repeated cycles. The second feature is related to the ease with which intermediate adsorbed poisons (e.g., CO) are oxidized via oxygen active species on Sn [6]. Mehandru et al. [17] found, using thermal desorption spectra (TDS), that CO dissociates on Pt–Ti alloys much easier than on pure Pt. They found that clean Ti surfaces dissociate CO at room temperature and expected that the behavior of Pt–Sn alloys would be qualitatively similar to that of Pt–Ti alloys.

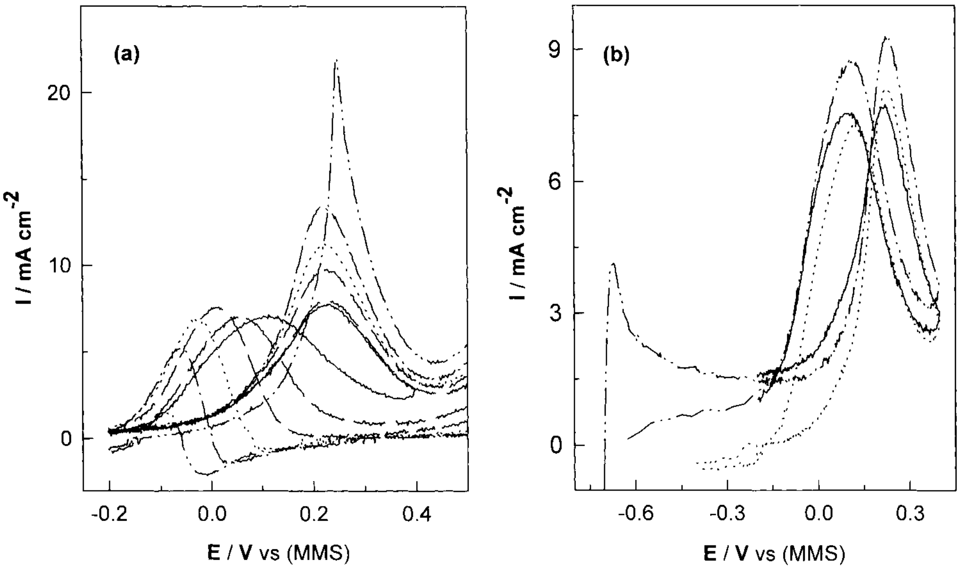

Fig. 6. Effect of extending the potential region on the electrooxidation of methanol. (**a**) To the O_2 evolution region: (——) to 0.4 V, (– – – –) to 0.6 V, (- - - - -) to 0.8 V, (·········) to 1.0 V, (–·–·–·–·) to 1.2 V and (–··–··–··) to 1.4 V. (**b**) To the H_2 evolution region: (——) to −0.2 V, (··········) to −0.4 V and (–·–·–·–·) to −0.8 V.

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