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State and Action of the Tin Atoms in Platinum–Tin Catalysts for Methanol Fuel Cells

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The behavior of platinum–tin electrodes in cyclic voltammetry in pure acid and the kinetics of methanol oxidation on these electrodes have been studied. By using the cyclic voltammetry technique it was possible to demonstrate that the tin atoms are present in the zero-valent state and hence are not acting as a cocatalyst via a redox couple between their oxidic forms. It is furthermore shown that the zero-valent tin atoms influence the adsorption properties of the platinum atoms. The enhancement in methanol oxidation rate on platinum–tin electrodes is explained in terms of a "ligand" effect.

I. INTRODUCTION

Platinum–tin catalysts have been found to exhibit considerably higher methanol electro-oxidation rates than pure platinum (*1–3*). In the literature this enhancement has been attributed to a redox mechanism (*1*), with the tin being assumed to be present in an oxidic form.

In this mechanism the adsorbed residue $C_sH_pO_q$ [see Eq. (1) below], supposedly impeding the reaction on pure Pt, is thought to be oxidized by an adsorbed and immobilized redox-active compound, the reversible potential of which should be close to the hypothetical equilibrium potential of the methanol oxidation reaction [Eq. (4) below]. This so-called surface-redox concept was first suggested for electrolyte-dissolved sodium molybdate (*4*). In the case of tin, the action of the cocatalyst, assumed to be SnO_2, could be expressed as follows:

$$sCH_3OH + (q-s)H_2O \rightarrow C_sH_pO_q + (2s-p+2q)H^+ + (2s-p+2q)e, \quad (1)$$

$$C_sH_pO_q + (2s-q)SnO_2 \rightarrow sCO_2 + pH^+ + pe + (2s-q)SnO, \quad (2)$$

$$2s-q\{SnO + H_2O \rightarrow SnO_2 + 2H^+ + 2e\}, \quad (3)$$

$$s\{CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e\}. \quad (4)$$

The equations are written in accordance with Breiter's (*5*) formalism for adsorbed residues. For reaction (3) an equilibrium potential of approx +100 mV vs NHE (normal hydrogen electrode) has been quoted (*2*), which is indeed close to the hypothetical potential of Eq. (4), viz, +20 mV vs NHE.

Cathro (*1*) based his conclusion in favor of this mechanism on (a) the observation by chronopotentiometry that a relatively large charge is required to oxidize Pt–Sn electrodes below 0.6 V as compared to pure Pt electrodes, and (b) on the fact that he found a reaction order of unity in methanol. However, the former observation can be

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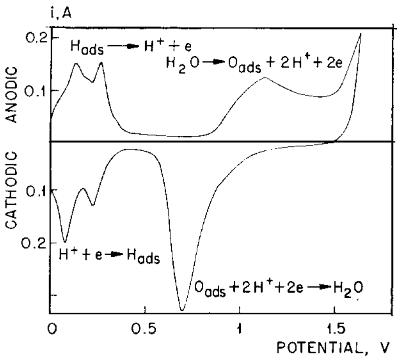

FIG. 1. Voltammogram of electrodeposited platinum in 4 *M* H_2SO_4 at 23°C. Electrode area 4.16 cm^2, loading 62.5 mg Pt, sweep speed 16.4 mV s^{-1}.

explained not only by a transition from Sn^{2+} to Sn^{4+} but also by, e.g., the Pt–Sn electrode having a larger specific surface area than the Pt black, as was shown previously (*3*). The latter finding would indicate that the oxidation of the residue is no longer rate determining, but is not consistent with other observations since it also implies that the methanol oxidation rate would equal the methanol adsorption rate, which, as was shown by Cathro (*1*), must not be the case.

The purpose of the work presented here was to find more conclusive evidence to elucidate the mechanism of enhanced methanol oxidation on Pt–Sn electrodes. In doing so, extensive use was made of the cyclic voltammetry technique. This technique provides information on the electrosorption characteristics of the electrode surface and thus on its condition and composition. It will be shown that, in contrast to earlier work on Pt–Sn electrocodeposits (*1*), this technique proved very elucidative for immersion-type electrodes (*3*). For the redox mechanism to be valid the observation by this technique of both anodic and cathodic peaks near the redox potential of Eq. (3) is a prerequisite. Other workers, who studied the oxidation of organic compounds at redoxactive nickel electrodes in alkali (*6*), indeed found cyclic voltammetry to be a very useful tool in this respect.

A second mechanism which was proposed in the literature for some other binary systems, viz, the so-called adsorption mechanism, will be included in our considerations. Unlike the redox mechanism, where the properties of the surface Pt atoms are unaffected even though one of their functions is taken over by the cocatalyst, the adsorption mechanism involves a modification of the surface Pt atoms via electronic interaction with the second element. This interaction, known as the so-called ligand effect (*7*) in heterogeneous catalysis, may result in a weaker bonding of the methanol residue and moreover facilitate the coadsorption of water molecules [Eq. (4)]. Such a mechanism can only be envisaged to take place on very intimately mixed systems such as alloys. Indeed, this mechanism has been postulated for Pt–Ru alloys (*8*, *9*), although recently a redox function has also been proposed for Ru surface atoms in such catalysts (*10*).

II. METHODS

Three types of Pt–Sn electrodes were used: first, immersion-type electrodes in which tin was deposited onto a pure Pt surface via immersion of a hydrogen-covered Pt electrode (in this case a Pt

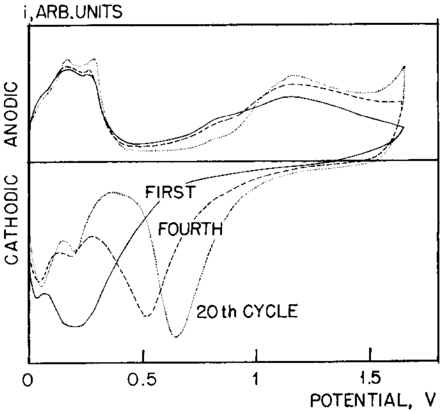

FIG. 2. Voltammograms of platinum–tin electrode prepared by immersion of electrodeposited platinum in $SnCl_4$ solution; 4 *M* H_2SO_4, 23°C.

electrodeposit) in an aqueous tin solution (*3*); further, conventional electrocodeposits in which Pt and Sn were electrodeposited simultaneously from an aqueous solution containing both species and, finally, true alloys prepared by melting.

The electrode preparation methods as well as the electrochemical testing techniques employed have been described in detail elsewhere (*3*). Unless stated otherwise, all potentials are given in this paper as they were measured, i.e., relative to a reversible hydrogen reference electrode in the same solution.

III. RESULTS AND DISCUSSION

1. Cyclic Voltammetry of Pt–Sn Electrodes

Figure 1 shows the cyclic voltammogram of pure Pt in 4 *M* sulfuric acid. The voltammograms obtained immediately after tin adsorption via immersion (Figs. 2 and 3) differ widely from that of pure Pt. However, they show no signs of redox activity of the adsorbed tin species. On the contrary, in the low potential region where such behavior should be observed [+100 mV, Eq. (3)], the areas of the anodic hydrogen peak have become smaller; obviously, adsorbed tin reduces hydrogen adsorption. If the adsorbed tin had indeed been redox active these peak areas would have become larger since two electrons are involved in the oxidation of a tin atom [Eq. (3)] instead of one electron for a hydrogen atom. The shape of the hydrogen oxidation peaks has not changed for low tin coverages (Fig. 3). [Elsewhere (*3*) it has been shown that with adsorbed tungstate or molybdate enlarged peaks at low potentials are indeed found.]

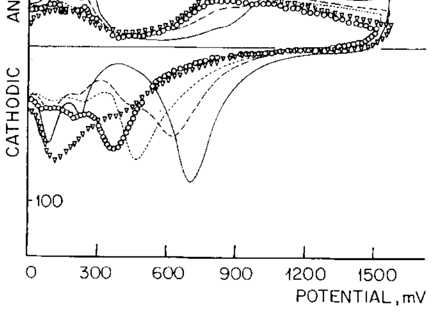

FIG. 3. First cycles of Pt–Sn catalysts as a function of concentration of immersion solution. Loadings approx equal, 5.0 mg Pt; sweep speed 64 mV s^{-1}; 4 *M* H_2SO_4, 23°C.

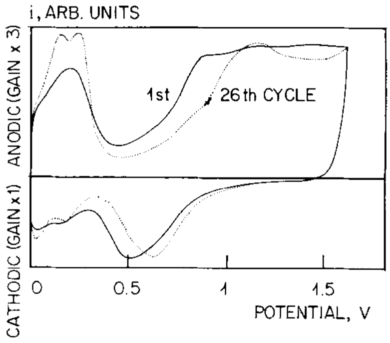

FIG. 4. Voltammograms of platinum–tin electrode prepared by electrocodeposition; 4 *M* H_2SO_4, 23°C.

At higher potentials, the original oxygen adsorption region has also become smaller and moreover a new peak or shoulder has appeared at about 830 mV; the latter phenomenon is explained in Sect. III.2. In the cathodic current region the oxygen reduction peak has shifted to lower values and at high surface tin contents it even merged with the hydrogen adsorption peaks. These observations are explained in Sect. III.3. The magnitude of the decrease in adsorption area and the shift of the oxygen reduction peak depend on the tin content of the immersion solution and thus on the surface tin content, as can be seen in Fig. 3. In contrast, the additional anodic peak at 830 mV does not change position. The effects do not depend on the type of immersion solution. By using a $Na_2Sn(OH)_6$

solution we found that only a relatively small coverage can be obtained but that the effect is similar to that of employing a $SnCl_4$ solution.

Cycling of a freshly immersed catalyst causes the oxygen reduction peak to shift gradually to its original position (Fig. 2). In other experiments it was observed that this shift may proceed via an intermediate double peak, indicating that the surface can also be inhomogeneous, exhibiting both pure Pt and Pt–Sn characteristics. The shoulder or separate peak in the oxygen adsorption region decreases to very low levels. Especially the anodic hydrogen peaks clearly show increases in the area available for chemisorption. The increases of the peak areas and the oxygen reduction peak shift are accompanied by increases in passivation current and decreases in the surface tin content to stable levels (*3*).

When measuring a freshly immersed electrode at elevated temperature (85°C) the shoulder in the oxygen adsorption region appears as a separate peak at 720 mV. This peak virtually disappears after the first cycle, indicating rapid dissolution of the tin.

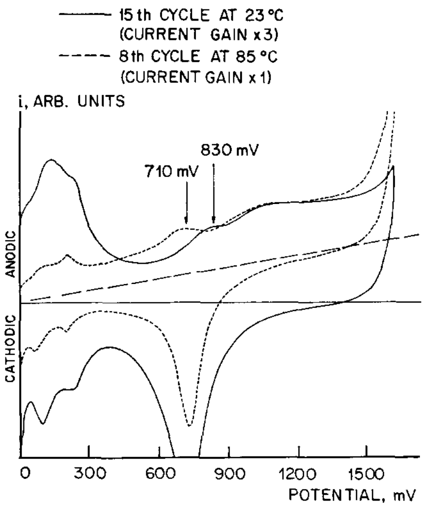

FIG. 5. Voltammograms of PtSn alloy samples in 4 *M* H_2SO_4 at 23 and 85°C. Sample areas approx equal.

The cyclic voltammogram of an electrocodeposited Pt–Sn catalyst (Fig. 4) shows that the oxygen reduction peak of this catalyst is generally less displaced than that of an immersed catalyst. On cycling, the features of the peak shift and the increase in hydrogen desorption peak area are seen as well.

During the first cycle of a Pt–Sn alloy (Fig. 5, only data for PtSn are presented) large corrosion currents are recorded. The characteristic shoulders in the oxygen adsorption region already emerge in the second cycle; they decrease gradually on cycling, as was found for the other types of catalyst. As a result of corrosion the baseline in the voltammograms shows a distinct slope, especially at 85°C.

It is finally worth mentioning that considerable readsorption of tin is observed when Pt–Sn electrodes, after potential cycling in acid between 0 and 1.6 V to remove tin from the surface, are not immediately taken out of the solution but are kept for some time at 0 V potential (hydrogen adsorption level). This behavior can be expected from the analogy of this treatment with the immersion preparation procedure (*3*). However, in the present case we are dealing with minute amounts of dissolved tin that were previously desorbed from the same electrode.

In conclusion, it can be said that the three types of Pt–Sn catalyst, viz, immersed, electrocodeposited and alloyed, show the same features in the cyclic voltammograms, indicating that their surfaces are very much the same. A similar conclusion was reached on the basis of their activities (*3*). No evidence of an electrochemical redox behavior at low potential was found.

2. The State of the Tin Atoms on the Surface of Pt–Sn Electrocatalysts

As remarked above, besides the decreases in available Pt area, there are two noticeable features due to the presence of tin on the platinum surface, namely, an additional anodic peak near 830 mV and a shift of the oxygen reduction peak to lower potentials. These features cannot be explained in terms of redox behavior of the adsorbed tin.

The anodic peak (or shoulder at low tin coverage) at 830 mV can be explained most easily by the dissolution of tin from the surface. This explanation is supported by the absence of a cathodic counterpart and by the fact that the areas of the hydrogen and oxygen adsorption peaks increase as the 830 mV peak decreases. The high potential of the peak with respect to the standard potentials of bulk tin ($Sn = Sn^{2+} + 2e$, $E^0 = -136$ mV vs NHE) or bulk tin oxides means that the tin is very strongly adsorbed (or "adsorption stabilized"). This can be explained by assuming that tin forms an intermetallic bond with platinum in a two-dimensional surface alloy, which strongly suggests that tin is in the zero-valent state. From the shift of the oxidation potential with respect to the bulk value, ΔE, of 966 mV, a value for the stabilization free energy ($\Delta G = -nF\Delta E$) of almost 2 eV (or ≈165 kJ/mol) is calculated for the tin atoms adsorbed on Pt. The observation of the adsorption stabilization phenomenon also means that the tin atoms are present in submonolayer coverage at the Pt surface, because otherwise bulk tin behavior would have been observed. This is in good agreement with the results of our radioactive tracer study (*3*) in which adsorbed tin coverages were actually measured.

The phenomenon of adsorption stabilization manifests itself also in deposition of the first monolayer on a foreign solid at potentials above the reversible oxidation potential, for which the term "underpotential deposition" is used. As such it has been the subject of numerous specific and a few general studies (*11–13*). It has furthermore been shown (*14*) that the partial monolayers formed do have catalytic effects such as those we are dealing with in the present study.

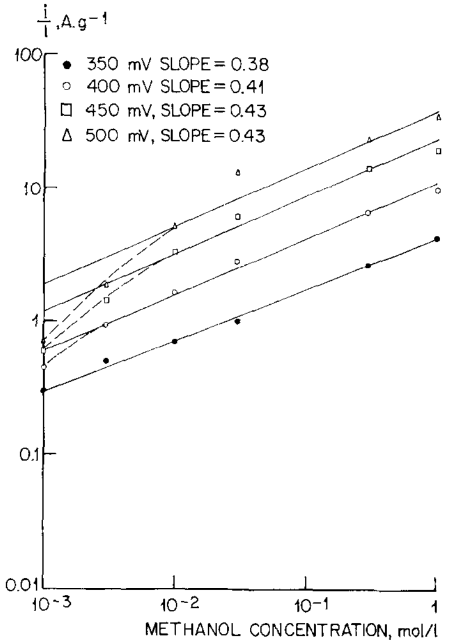

FIG. 6. Dependence of reaction rate on methanol concentration for immersion-type Pt–Sn electrode at 85°C in 0.5 *M* H_2SO_4 solutions.

In the earliest work on Pt–Sn electrodes (*1, 15*) it was not realized that the tin species might be zero-valent. However, Bowles and Cranshaw (*16*) have demonstrated by Mössbauer spectroscopy that tin adsorbed on Pt in an acidic medium is in the zero-valent state and Andrew *et al.* (*2*), applying the same technique to electrocodeposited Pt–Sn electrodes, showed that, though the majority of the tin is present as SnO_2, a minor portion of the tin is present as a dilute Pt–Sn alloy. X-Ray photoelectron spectroscopy as applied by Andrew *et al.* (*2*) showed tin to be mainly present in an oxidic form; in our work, too, only Sn^{4+} was detected by this technique. It should be realized, however, that these studies were hampered by the lack of a good zero-valent tin standard. Finally, underpotential deposition of tin on gold

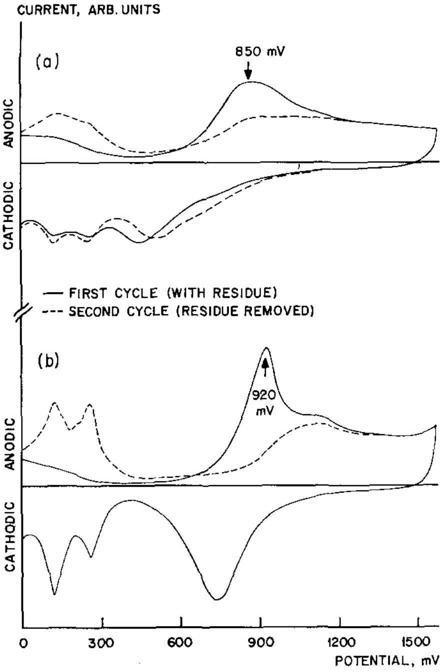

FIG. 7. Voltammograms of electrodes precovered with methanol residue at 400 mV. Sweep speed 64 mV s^{-1}; 4 *M* H_2SO_4, 23°C. (a) High surface tin content (shortly after Sn immersion); (b) very low surface tin content (same electrode after many cycles).

was observed by Vicente and Bruckenstein (*17*).

3. Kinetics and Mechanism of Methanol Oxidation

As shown in the preceding section there is evidence to indicate that the tin atoms in Pt–Sn catalysts are stable in their zero-valent state at potentials at which methanol oxidation will take place (generally below 450 mV). Consequently, it is difficult to envisage that tin atoms operate in a redox mode to enhance the oxidation rate of methanol. Instead, since the tin atoms are bound so strongly to the Pt surface, it is more likely that electronic or so-called ligand effects (*7*) will play a role resulting in a change in properties of the surface Pt atoms. Such an effect has indeed been observed. It shows up most clearly in the voltammograms of the immersion-type electrodes as a tin-coverage-dependent shift of the oxygen reduction peak to lower potentials: Figs. 2 and 3 indicate that oxygen adsorption has become stronger. The effect, although weaker, was also noted for Pt–Sn electrocodeposits by Cathro (*1*) and by Andrew *et al.* (*2*); these latter workers noted that the effect was caused by a degree of modification of the Pt surface by tin.

Further evidence in support of the adsorption mechanism could be provided by a kinetic study of methanol oxidation. Since on a pure Pt catalyst the oxidation of the fuel residue is supposed to be the rate-determining step, the reaction order in methanol should be zero. However, in the case of the redox mechanism [Eqs. (1)–(3)] we expect Eq. (1) to become rate determining, resulting in a reaction order of one in methanol. In the case of the adsorption mechanism we cannot clearly identify the various steps and so we may expect the order in methanol to have any value between zero and one. Kinetic studies at 23 and 85°C were carried out by potentiostatic polarization tests as described elsewhere (*3*); concentration and potential ranges are given in Fig. 6. The reaction rates were considered to be steady state values. For pure Pt at 85°C the order in methanol is indeed very close to zero. Only at low concentrations ($<10^{-2}$ *M*), where no Tafel behavior was found, does the order approach one because diffusion becomes rate determining. For pure Pt at 23°C an order greater than zero is also observed at higher concentrations (viz, in the Tafel region), a value of 0.24 being found on the average. The tendency towards higher order here starts already below 10^{-1} *M* because diffusion is much slower at this temperature. For Pt–Sn electrodes an average order of 0.40 is found at 85°C (Fig. 6) and of 0.58 at 23°C. Since the reaction rates are higher, the tendency of these orders towards one begins at higher concentrations than for pure Pt.

From the fact that Pt and Pt–Sn give rise to different orders in methanol it must be concluded that methanol oxidation proceeds via different mechanisms on these catalysts; a similar conclusion was already indicated by the differences observed in the Tafel slopes (*3*). It is, however, impossible to give a clear indication of the actual mechanism on the basis of the reaction scheme involving Eqs. (1)–(3). Cathro's observation (*1*) that the methanol order equals one for Pt–Sn is probably erroneous.

In conclusion, these results again point to the adsorption mechanism being operative.

As mentioned in the Introduction, Binder *et al.* (*8*) postulated the adsorption mechanism for Pt–Ru alloys. They envisaged this mechanism to proceed because of a weaker bond strength between the methanol residue and the surface as a result of alloying, so that, at a given potential, more sites become available for adsorption of H_2O molecules. This was evidenced by cyclic voltammetry of residue-covered electrodes in acid in which they observed a 170 mV shift of the residue-oxidation peak to lower potentials for the alloy compared to pure Pt. We were able to reproduce this result qualitatively on immersion-type Pt–Ru electrodes. However, we would like to remark that this result can also be accounted for by an explanation suggested by Andrew *et al.* (*2*) for the case of Pt–Sn, in which stronger bonding of the second reactant of Eq. (4), viz, H_2O, presumably in the form of OH groups, is effected by alloying. In any case, the latter explanation supports the adsorption mechanism equally well. The experiments were carried out using two separate solutions (*8*). The electrode was preoxidized at 1.5 V in a 0.5 M H_2SO_4/1 M CH_3OH solution and then subjected to methanol adsorption at a potential of 400 mV for 15 min. Thereafter the electrode was transferred to a 4 M H_2SO_4 solution and the residue was oxidized by a fast anodic sweep. The characteristics of the residue formed were not dependent on the potential of the residue formation up to values as high as 0.6 V, in accordance with Biegler's work (*18*) on pure Pt. Some results are given in Fig. 7. It is seen that the potential of the residue oxidation peak of the high-tin-coverage electrode is approx 70 mV below that of the low-tin-coverage electrode. In addition, careful analysis of the results of a large number of experiments showed that in the oxidation of the residue on Pt–Sn electrodes 1.2–1.5 electrons are involved per Pt site made bare (one Pt site is defined as a site where one Pt–H complex is formed). On pure Pt this amount was found to be unity, in agreement with results from the literature (*19*).

Hence, these last results are also indicative of a difference in oxidation mechanism and/or reactant–solid bond strength between Pt–Sn and pure Pt electrodes.

CONCLUSIONS

1. From the similarity of the voltammograms of immersion-type, electrocodeposited and alloyed Pt–Sn electrodes it is evident that their surfaces are identical on an atomic scale.
2. It has been confirmed that the tin atoms are present in a zero-valent state at the platinum surface at potentials where methanol oxidation takes place. They influence the properties of the surface Pt atoms in such a way that oxygen is adsorbed more strongly.
3. On the basis of conclusion (2) as well as on the facts that no tin redox peaks are observed in the voltammograms and that on Pt–Sn methanol oxidation takes place with an order of less than one, we conclude that the enhancement in methanol oxida-

tion rate on Pt–Sn is brought about not by a redox but by an adsorption mechanism. A full explanation in terms of rate-determining steps has still to be given.

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