

Electrooxidation of Methanol on upd-Ru and upd-Sn Modified Pt Electrodes

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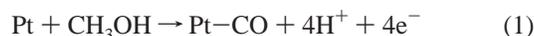
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The electrochemical oxidation of methanol has been investigated on underpotentially deposited-ruthenium-modified platinum electrode (upd-Ru/Pt) and on underpotentially deposited-tin-modified platinum electrode (upd-Sn/Pt). The submonolayers of upd-Ru and upd-Sn on a Pt electrode increased the rate of methanol electrooxidation several times as large as that on a pure Pt electrode. The best performance for methanol electrooxidation was obtained on a ternary platinum based catalyst modified by upd-Ru and upd-Sn simultaneously. The influence of the submonolayers of upd-Ru adatoms and upd-Sn adatoms on the oxidation of methanol in acid has been investigated. The effect of Ru on methanol electrooxidation lies on the distribution of Ru adatoms on a Pt surface. It has been shown that as long as the amount of upd-Ru deposits were controlled in a proper range, upd-Ru deposits would enhance the methanol oxidation obtained on a Pt electrode at whichever deposition potential the upd-Ru deposits were obtained. The effects of tin are sensible to the potential range. The enhancement effect of upd-Sn adatoms for the oxidation of methanol will disappear as the electrode potential is beyond a certain value. It is speculated that there exists a synergetic effect on the Pt electrode as adatoms Ru and Sn participate simultaneously in the methanol oxidation.

1. Introduction

The direct methanol fuel cell (DMFC) is a variant of the proton exchange membrane (PEM) fuel cell, which uses aqueous methanol directly without prior reforming. Operating fuel cells with liquid fuel is essential for transport applications. In addition, since DMFC can operate at temperature below 100 °C without a fuel processor, the complexity and cost of the system is considerably reduced. These advantages allow DMFC to be suitable for use in portable electronic devices. However, the performance of DMFC is obviously deteriorated by poor electrochemical activity and the kinetic loss of methanol oxidation at the anode, which account for a reduction in cell voltage of more than 0.3 V at 500 mA/cm² (at 90 °C). To increase the anode and cathode activities, the electrocatalysts employed in DMFC are usually unsupported and the platinum loading is typically as high as 5–10 mg/cm² in contrast with carbon-supported electrocatalysts in H₂-fueled PEM fuel cell, loaded with 0.2–0.5 mg/cm² of platinum. This platinum loading is too high to be practical for commercial exploitation of DMFC. Additionally, Pt is easily subject to CO poison, an intermediate of methanol oxidation although platinum is the most active catalyst of all metallic catalysts for methanol oxidation. So, it is necessary to remove CO from the surface of platinum, especially at a relatively negative potential. Adding ruthenium

into Pt catalysts has been known to be significantly effective for CO removal at a relatively negative potential.^{1–4} The catalytic action of PtRu proceeds mainly by the so-called “bifunctional mechanism”, that is, Ru sites adsorb oxygen-containing species at a potential of 0.2–0.3 V lower than the pure Pt sites, and the adsorbed carbonaceous species are preferentially oxidized by the oxygen-containing species.⁵ The whole mechanism can be shown as follows:



The electrocatalytic activity of PtRu depends on several factors, among which the composition and electronic state density get principal attention.^{6,7} According to the so-called bifunctional mechanism, Pt and the second atoms, that is, Ru, independently play their own roles in the catalysis of methanol oxidation. This suggests that it would not be critical whether Pt–Ru is present in forms of alloy, bimetallic compound, adatoms on substrate, or just simple mixture. The most important is in the geometric distribution and composition of the PtRu. Wasmus and Kuger discussed this in a review paper.⁵ Two optimum atomic percentages, 50 atom % and 10 atom %, of ruthenium in PtRu were suggested on the basis of Pt–CO_{ads} and 3Pt–CH₃OH, respectively.

PtSn is another catalyst system which has been widely discussed for enhancing methanol oxidation on Pt. The catalytic activity of Sn atoms in PtSn catalysts on methanol oxidation is usually interpreted in terms of a bifunctional mechanism.⁸

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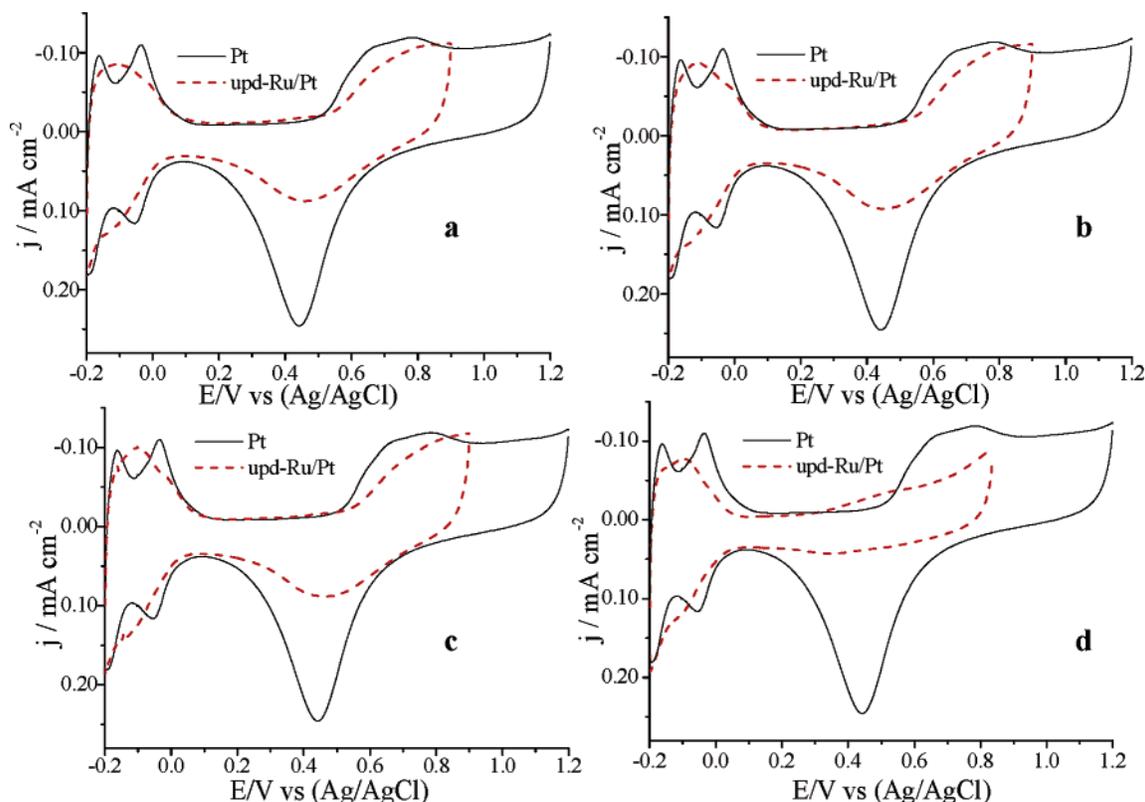


Figure 1. CV in 0.5 M H₂SO₄ at a sweep rate of 50 mV s⁻¹ on a Pt electrode (solid line) and upd-Ru/Pt electrodes (dashed line) formed in 0.5 M H₂SO₄ containing 5 mM RuCl₃ at $E_{\text{upd}} = 0.58$ V, $Q_{\text{upd}} = 10$ mC cm⁻² (a); $E_{\text{upd}} = 0.68$ V, $Q_{\text{upd}} = 15$ mC cm⁻² (b); $E_{\text{upd}} = 0.78$ V, $Q_{\text{upd}} = 15$ mC cm⁻² (c); and $E_{\text{upd}} = 0.78$ V, $Q_{\text{upd}} = 25$ mC cm⁻² (d).

Contrary to this general belief, Tillmann et al.⁹ hold that Sn mainly has an electronic influence on neighboring Pt atoms and thus changes the binding energy of CO to Pt.

The underpotential deposition (upd) of foreign atoms on a substrate metal has received much attention in electrocatalysis. It seems that the submonolayer characteristic of upd-Ru and upd-Sn deposits on Pt electrode would be very favorable to the methanol oxidation according to the so-called bifunctional mechanism. Although PtRu and PtSn catalysts have been extensively used for methanol electrooxidation, comparably little work on upd-Ru on Pt electrode for methanol oxidation can be found in the literature.¹⁰ In this communication, we present a upd-Ru and a upd-Sn on Pt surface to get upd-Ru and upd-Sn modified Pt electrodes for methanol oxidation. The effects and role of upd-Ru and upd-Sn on methanol oxidation are examined using electrochemical methods.

2. Experimental

2.1. Preparation of upd-Ru/Pt and upd-Sn/Pt Electrodes.

Pt disk electrode was polished on a polishing cloth with a suspension of 0.05 μm alumina and water and then was cleaned by ultrapure water from Mill-Q water treatment system. Then, the electrode was immersed in nitrogen-purged 0.5 M H₂SO₄ and was voltammetrically scanned from 0 to 1.8 V (vs Ag/AgCl) at a rate of 100 mV s⁻¹ to clean the surface. The cleanliness of the surface was checked by cyclic voltammetry from -0.2 to 1.2 V (vs Ag/AgCl). The geometric surface area of the Pt disk electrode is 0.071 cm² (diameter 3 mm).

The underpotential deposition was performed using CHI 660b electrochemical station (CH Instrument, Inc) in the cell consisting of a Pt disk electrode with a roughness factor of 1.57, a Pt sheet counter electrode, and a saturated-potassium-chloride silver chloride electrode (SSCE) reference electrode. All potentials

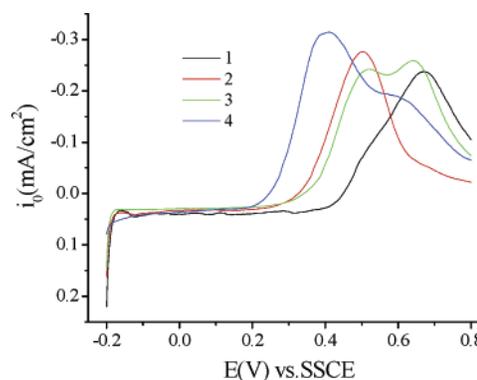
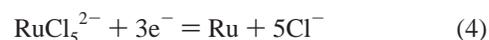


Figure 2. Methanol electrooxidation in 0.5 mol/L H₂SO₄ and 2 mol/L CH₃OH at a sweep rate of 1 mV s⁻¹ on a Pt electrode (line 1), on a upd-Ru/Pt made in 0.5 M H₂SO₄ containing 5 mM RuCl₃ at potential of 0.08 (line 2), and on a upd-Ru/Pt at 0.48 (line 3) and 0.58 V (line 4). For all Ru-modified Pt electrodes, the deposition maintains 5 min at the particular potential for all Ru.

in this study were quoted with reference to SSCE (i.e., 0.20 V vs SHE) unless otherwise stated. As for preparation of upd-Ru/Pt, the cleaned Pt disk electrode was immersed in a solution of 0.5 M H₂SO₄ containing 5 mM RuCl₃. The upd-Ru deposition was performed by stepping the electrode potential to a potential E_{upd} , at which the Ru ad-atoms were underpotentially deposited. In this work, potentials, such as 0.48 V, 0.58 V, 0.68 V, and 0.78 V, were chosen to carry out the upd-Ru building on the Pt electrode. The deposition at the above potentials is an underpotential deposition for Ru in comparison with the equivalence potential, 0.40 V, of the reaction



The amount of deposited ruthenium was controlled by

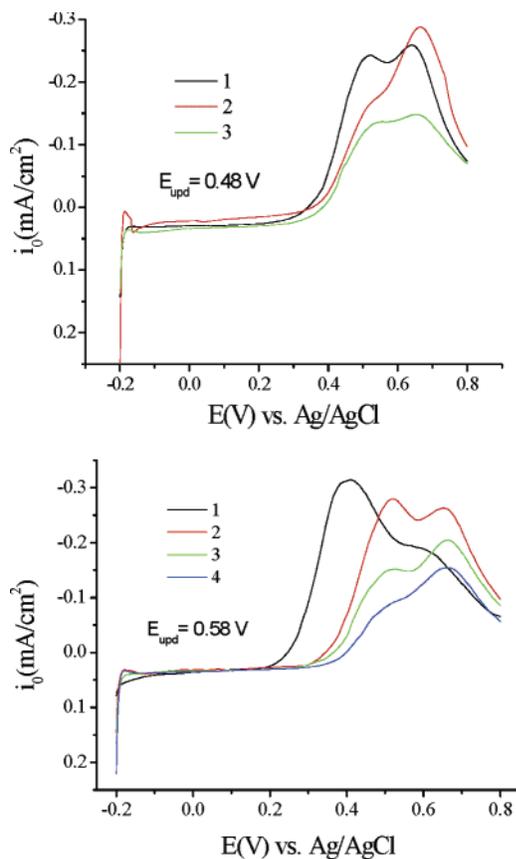


Figure 3. Methanol electrooxidation in 0.5 mol/L H_2SO_4 and 2 mol/L CH_3OH at a sweep rate of 1 mV s^{-1} on upd-Ru/Pt made in 0.5 M H_2SO_4 containing 5 mM RuCl_3 at potentials of 0.48 and 0.58 V with different deposition times. From lines 1 to 4, corresponding deposition time is 5, 10, 15, and 20 min, respectively.

deposition charge (Q_{upd}), for instance, 10, 15, 20, and 25 mC cm^{-2} and so forth.

For upd-Sn/Pt electrode, tin was underpotentially deposited according to a previous study¹¹ just at -0.17 V from freshly prepared deposition solution of 10^{-5} M SnSO_4 in 0.5 M H_2SO_4 with a deposition time of 10 s, 50 s, 100 s, and 300 s. The solution had to be freshly prepared to avoid the oxidation of Sn^{2+} to Sn^{4+} by dissolved oxygen.

The upd-RuSn/Pt electrode was prepared by construction of upd-Ru/Pt at 0.58 V first and then by construction of upd-Sn at -0.17 V sequentially.

2.2. Electrochemical Measurement. After deposition, upd-Ru and upd-Sn modified Pt electrodes were washed with ultrapure water and then were transferred to a cell containing 0.5 M H_2SO_4 with or sometimes without 0.5 M CH_3OH for electrochemical measurement.

3. Results

3.1. Methanol Oxidation on upd-Ru/Pt Electrode. The CV (i.e., cyclic voltammetry) of Pt disk electrode and upd-Ru modified Pt electrode (upd-Ru/Pt) were recorded in 0.5 M H_2SO_4 as shown in Figure 1. To avoid the oxidation of the ruthenium to a state that either dissolves in the aqueous phase and is lost or produces a form of oxidized ruthenium that is in a state that cannot be electrochemically reduced,¹² the vertex potential in the CV of upd-Ru/Pt electrode was kept below 0.9 V. The suppressed area of hydrogen desorption in a potential range from -0.20 to 0.15 V and the Pt–O electrochemical reduction from 0.60 to 0.20 V in the CV of upd-Ru/Pt electrode

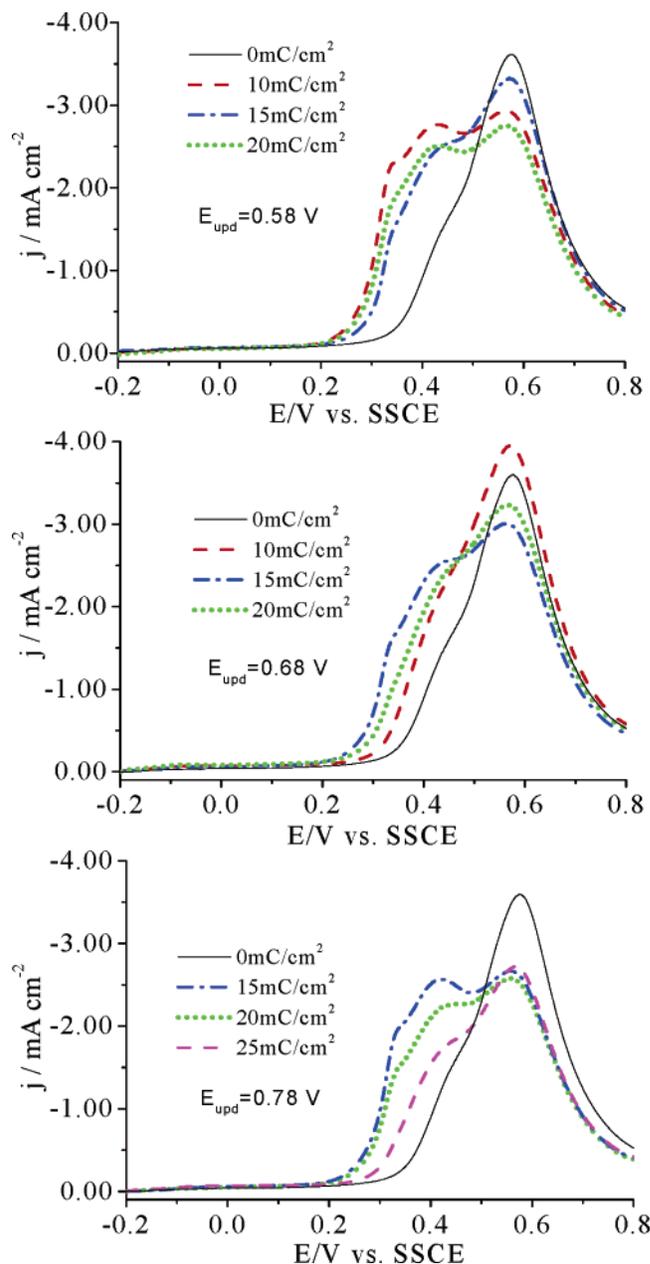
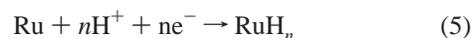


Figure 4. Methanol electrooxidation in 0.5 M CH_3OH + 0.5 M H_2SO_4 at a sweep rate of 5 mV s^{-1} on upd-Ru/Pt electrodes obtained at different underpotentials with different deposition charges compared with pure Pt electrode.

testify to the presence of Ru adatoms on the Pt electrode as shown in Figure 1. Although widely used,^{13,14} it has been proved not to be good to estimate the coverage of Ru adatoms according to the difference in area of the hydrogen desorption in the CV from -0.20 to 0.15 V before and after upd-Ru in Figure 1 because of the overlap of the hydrogen desorption and ruthenium oxidation currents, with the latter commencing at around 0.05 V. In addition, seemingly more than one monolayer of hydrogen can be established at a ruthenium surface because of absorption into the oxide lattice as a result of the formation of ruthenium bronzes and also dissolution of atomic hydrogen into the metallic ruthenium.^{12,15}



The coverage of Ru adatoms was controlled by the length of the deposition time at a certain deposition potential, in other

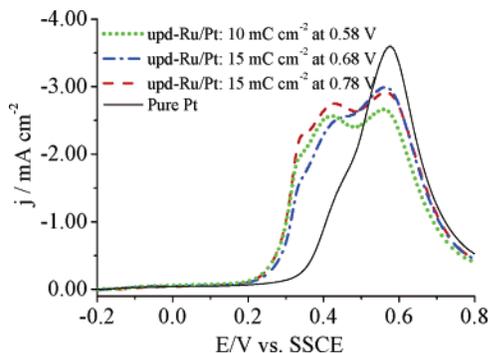


Figure 5. Methanol oxidation in 0.5 M CH₃OH + 0.5 M H₂SO₄ at a sweep rate of 5 mV s⁻¹ on upd-Ru/Pt electrodes made in 0.5 M H₂SO₄ containing 5 mM RuCl₃ at different potentials for different deposition charges.

TABLE 1: Performance of upd-Ru/Pt Electrode Prepared in Different Potentials

	Pt	upd-Ru/Pt	upd-Ru/Pt	upd-Ru/Pt
E_{upd}/V		0.58	0.68	0.78
$Q_{\text{upd}}/\text{mC cm}^{-2}$		10	15	15
$E @ 0.5 \text{ mA cm}^{-2}/\text{V}$	0.37	0.27	0.29	0.27
$j @ 0.3 \text{ V}/\text{mA cm}^{-2}$	0.13	0.97	0.69	1.02

words, by the deposition charge, Q_{upd} , as illustrated in Figure 1. Because of the presence of other reactions in a potential range of upd-Ru deposition, such as formation of surface Pt–O, partial reduction of RuCl₅²⁻, and so forth, the deposition charge Q_{upd} is certainly not totally consumed in upd-Ru deposition. Consequently, the coverage of Ru adatoms cannot be estimated according to Q_{upd} . In effect, only a small portion of Q_{upd} was used for a submonolayer of upd-Ru deposits, but most Q_{upd} was consumed in side reactions such as eq 5 in the potential range of underpotential deposit in consideration of that the roughness factor of the Pt disk working electrode is about 1.57. The influence of the potential held in Ru deposition on methanol oxidation is shown in Figure 2. Either upd-Ru (curves 3 and 4) or overpotentially deposited Ru, i.e., opd-Ru (curve 2) shows a good enhancement for methanol oxidation on Pt electrode in 0.5 M CH₃OH + 0.5 M H₂SO₄. As far as the deposition conditions illustrated in Figure 2 are concerned, upd-Ru made at 0.58 V exhibits the best enhancement for methanol oxidation. Figure 3 shows the influence of Ru deposition time at potentials of 0.48 and 0.58 V on methanol oxidation in 0.5 mol/L H₂SO₄ and 2 mol/L CH₃OH. Figure 3 tells us that too much Ru deposits on a Pt electrode are not so good for

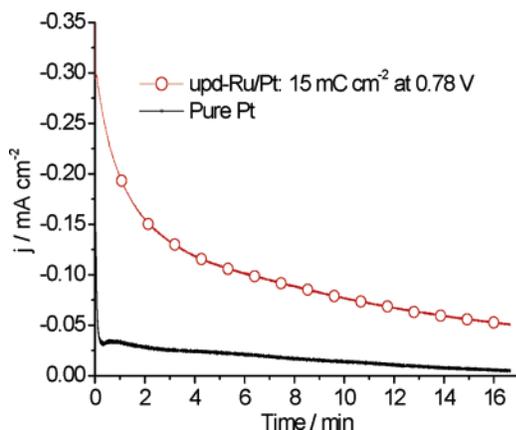


Figure 6. Current vs time as potential is kept at 0.28 V in 0.5 M H₂SO₄ + 0.5 M CH₃OH on a pure Pt electrode and a upd-Ru/Pt electrode.

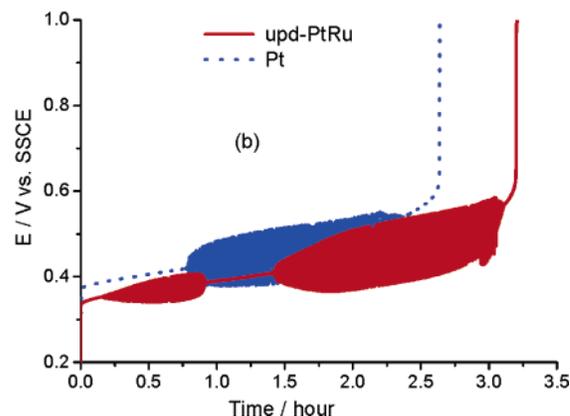
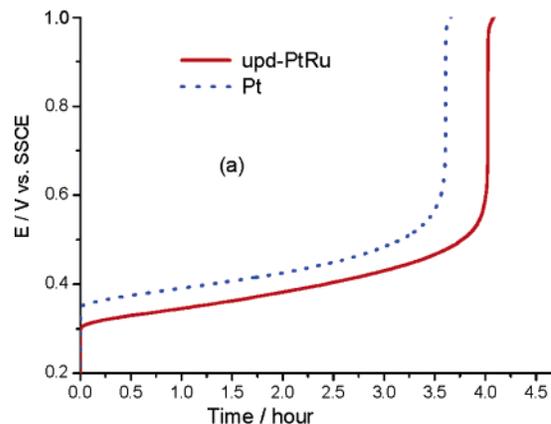


Figure 7. Potential vs time on Pt and upd-Ru/Pt at 5 mA cm⁻² (a) and 10 mA cm⁻² (b) in 0.5 M H₂SO₄ + 0.5 M CH₃OH.

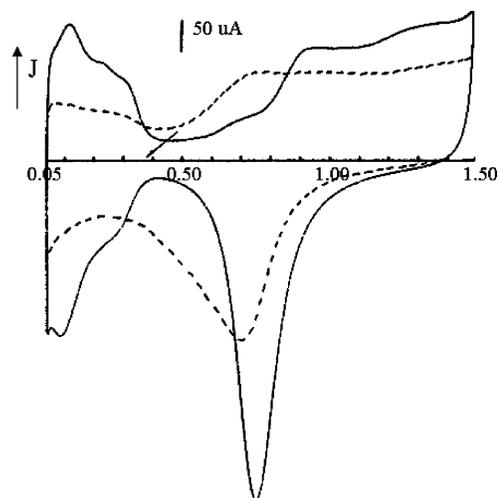


Figure 8. CV of a pure Pt in 0.1 M HClO₄ (solid line) and in 0.1 M HClO₄ with 10⁻⁶ M Sn²⁺ (dashed line) at 50 mV s⁻¹.

methanol oxidation. This is in good agreement with the bifunctional mechanism of methanol oxidation. The number of exposed Pt sites is necessary for the initial dehydrogenation of methanol molecules.¹⁶ Figure 4 shows methanol oxidation on upd-Ru/Pt electrodes obtained at three different underpotentials with different deposition charges in comparison with a pure Pt electrode in 0.5 M CH₃OH + 0.5 M H₂SO₄. The best results obtained at potentials 0.58, 0.68, and 0.78 V, respectively, were overlapped together in Figure 5. It gives a sign that as long as the amount of upd-Ru deposits were controlled in a proper range, upd-Ru deposits would enhance the methanol oxidation obtained on a Pt electrode at whichever deposition

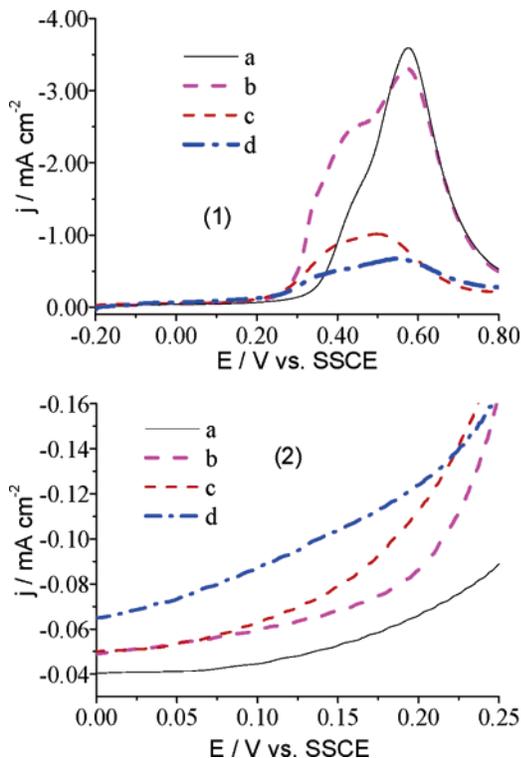


Figure 9. Methanol electrooxidation in 0.5 M H₂SO₄ + 0.5 M CH₃OH at a sweep rate of 5 mV s⁻¹ on a pure Pt electrode (a), a upd-Ru/Pt electrode formed in 0.5 M H₂SO₄ containing 5 mM RuCl₃ at $E_{\text{upd}} = 0.58$ V with $Q_{\text{upd}} = 10$ mC cm⁻² (b), and upd-Sn/Pt electrodes formed in 0.5 M H₂SO₄ containing 10⁻⁵ M SnSO₄ at $E_{\text{upd}} = 0.172$ V hold for 10 s (c) and for 100 s (d). (2) The potential window of 1 from 0 to 0.25 V.

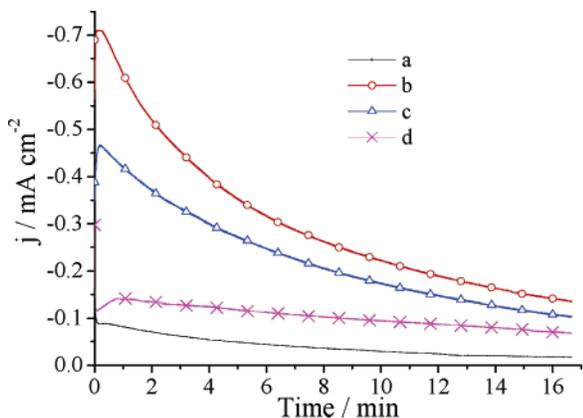


Figure 10. Current vs time as potential is kept at 0.38 V in 0.5 M H₂SO₄ + 0.5 M CH₃OH on a pure Pt electrode (a) and upd-Sn/Pt electrodes formed in 0.5 M H₂SO₄ containing 10⁻⁵ M SnSO₄ at $E_{\text{upd}} = 0.172$ V hold for 10 s (b), 50 s (c), and 100 s (d).

potential the upd-Ru deposits were obtained. The reason why more deposition charge is consumed for upd-Ru deposition at a more positive deposition potential is because the more positive the deposition potential is, the lower the current efficiency is for Ru deposition.

On a upd-Ru/Pt electrode, there are two methanol oxidation peaks. One at a relatively positive potential corresponds to the oxidation of methanol on the pure Pt island, and one at a relatively negative potential corresponds to on the upd-Ru/Pt island. By contrast, there is only one methanol oxidation peak either on an opd-Ru/Pt electrode or on a pure Pt electrode as shown in Figure 2. Obviously, it is because there is only one type of electrode surface in the case of either an opd-Ru/Pt

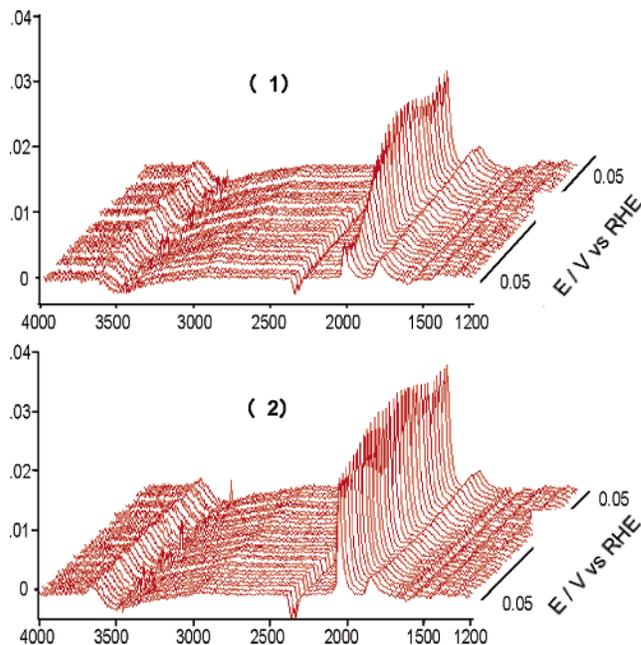


Figure 11. 3-D plot of IR spectra corresponding to the first (1) and the fourth (2) continuous cyclic voltammograms of methanol oxidation on a Pt electrode with modulation of a potential sweeping at a rate of 50 mV s⁻¹ in 1 M CH₃OH and 0.1 M HClO₄.

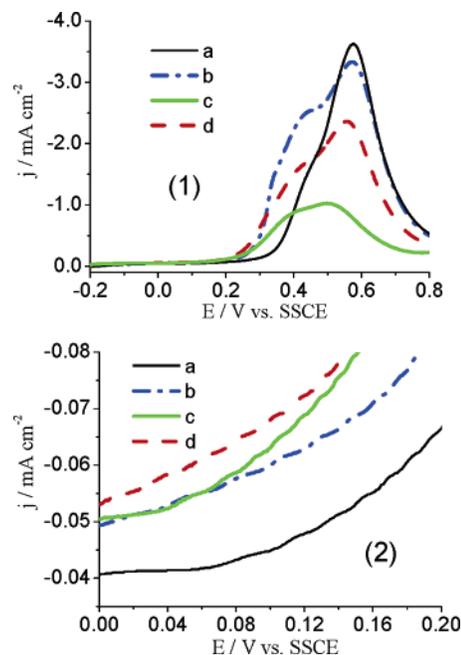


Figure 12. Methanol electrooxidation in 0.5 M H₂SO₄ + 0.5 M CH₃OH at a sweep rate of 5 mV s⁻¹ on a pure Pt electrode (a), a upd-Ru/Pt electrode formed at $E_{\text{upd}} = 0.58$ V with $Q_{\text{upd}} = 10$ mC cm⁻² (b), a upd-Sn/Pt electrode formed in 0.5 M H₂SO₄ containing 10⁻⁵ M SnSO₄ at $E_{\text{upd}} = 0.172$ V hold for 10 s (c), and a upd-RuSn/Pt electrode formed in 0.5 M H₂SO₄ containing 5 mM RuCl₃ at $E_{\text{upd}} = 0.58$ V with $Q_{\text{upd}} = 10$ mC cm⁻² and then in 0.5 M H₂SO₄ containing 10⁻⁵ M SnSO₄ at $E_{\text{upd}} = 0.172$ V hold for 10 s (d). (2) The potential window of 1 from 0 to 0.2 V.

electrode or a pure Pt electrode. The position of methanol oxidation peak corresponding to the Pt island at the potential scale stays at almost the same potential from the upd-Ru/Pt electrode to a pure Pt electrode. However, the position of methanol oxidation peak corresponding to upd-Ru/Pt island at the potential scale changes with difference in preparation of the upd-Ru/Pt electrode as shown in Figures 2–4. This suggests

TABLE 2: Comparison among Pt, upd-Ru/Pt, upd-Sn/Pt, and upd-RuSn/Pt

electrode	V_0/V^a	V_0^-/V^b	$j @ 0.20 \text{ V/mA cm}^{-2}$	$j @ 0.30 \text{ V/mA cm}^{-2}$	$j @ 0.32 \text{ V/mA cm}^{-2}$	$j @ 0.40 \text{ V/mA cm}^{-2}$
Pt	0.35		-0.067	-0.135	-0.172	-0.873
upd-Ru/Pt	0.20	0.15	-0.086	-0.503	-0.790	-2.214
upd-Sn/Pt	0.10	0.25	-0.115	-0.369	-0.476	-0.873
upd-RuSn/Pt	0.10	0.25	-0.124	-0.636	-0.790	-1.526

^a V_0 : onset potential of methanol oxidation. ^b V_0^- : potential of V_0 shift to negative direction relative to Pt.

that the electrochemical performance of the upd-Ru/Pt electrode with different Ru adatoms is different from one another. It may be ascribed to the difference in electronic state density of the upd-Ru/Pt electrode resulting from the difference in the amount of Ru adatoms.⁶

The data taken from Figure 5 are summarized in Table 1. It clearly demonstrates that the potential at methanol oxidation current of 0.5 mA cm^{-2} shifts toward the negative direction, and the methanol oxidation current at potential of 0.3 V increases several times with the modification of upd-Ru to the Pt electrode.

The long-run tests for methanol oxidation on a pure Pt electrode and on a upd-Ru/Pt electrode are illustrated in Figure 6 and Figure 7. The enhancement of upd-Ru deposits in electrocatalysis of methanol oxidation on a Pt electrode is apparent in every respect of the low oxidation potential at a certain oxidation current (see Figure 6) and the large oxidation current at a certain oxidation potential (see Figure 7). It is interesting why the methanol oxidation on a pure Pt electrode and on a upd-Ru/Pt electrode oscillates only at a large oxidation current, for example, 10 mA cm^{-2} , but not at a small oxidation current, for example, 5 mA cm^{-2} . It is beyond the scope of this communication to discuss this phenomenon thoroughly. The detailed investigation about this issue has been under way.

3.2. Methanol Oxidation on upd-Sn/Pt Electrode. The CV of a pure Pt electrode in absence (solid line) and presence (dashed line) of $10^{-6} \text{ M Sn}^{2+}$ are shown in Figure 8. The suppressed hydrogen desorption area in the CV indicates the deposits of Sn adatoms on the Pt surface.

The electrooxidation of methanol on the upd-Sn modified Pt electrodes is shown in Figure 9 together with that on a Pt electrode and a upd-Ru/Pt electrode for comparison. Methanol oxidation on the upd-Sn/Pt electrode shifts toward an even more negative potential than that on upd-Ru/Pt. In a potential range from 0 to 0.22 V, the current of methanol oxidation on upd-Sn/Pt with underpotential deposition of 100 s is larger than that on upd-Ru/Pt. It suggests that the upd-Sn adatoms are more favorable to enhance the methanol electrooxidation in the lower potential range than the upd-Ru adatoms. Figure 10 reveals that the current of methanol electrooxidation increases with coverage of upd-Sn deposits within the potential range of 0.22 V. It does not mean that the higher the coverage of the upd-Sn deposits, the better it will be for methanol oxidation. Over the potential of 0.22 V, Figure 9 shows that the low coverage of upd-Sn deposits on the Pt surface is favorable for methanol electrooxidation.

By using ellipsometric technique, Frelink et al.^{17,18} found that Sn-oxide is formed at a very lower potential than Pt-oxide and that the Sn-oxide disappeared when methanol is present in the solution because of the reaction between Sn-oxide and the poisoning intermediate formed from the oxidation of methanol. The mechanism of the effect of Sn on the oxidation of methanol is extraordinarily complex. The puzzlement is that the bifunctional mechanism cannot explain why electrosorbed or electrodeposited Sn on the Pt surface is a good catalyst for methanol oxidation, while PtSn alloys are not. Moreover, as Wasmus and Kuver discussed in a review paper,⁵ it is sometimes unclear

whether a binary system is an alloy or just a mixture of two metals, and Sn may leach out under acid conditions being in turn readsorbed electrolytically at Pt sites. Xia¹⁹ investigated the influence of upd-Sn on the electrooxidation of formic acid on platinum in an acidic solution and proposed that the electrooxidation is accelerated by formation of $\text{Sn}[(\text{OH})]_{\text{ad}}^+$. Bittins-Cattaneo and Iwasita reported that the species of upd-Sn adatoms on platinum surface in the potential range 0.2–0.45 V (vs RHE) exists as an adsorbed $\text{Sn}_{\text{ad}}^{2+}$.²⁰ However, the detailed mechanism of tin for methanol oxidation would still be a subject for debate.

To find something new about the mechanism of methanol oxidation, we investigated the surface states of the Pt electrode in methanol electrooxidation by use of surface-enhanced infrared absorption spectroscopy (SAIRAS). Figure 11 shows the 3-D plot of IR spectra corresponding to the first (1) and the fourth (2) continuous cyclic voltammograms of methanol oxidation on a Pt electrode with modulation of a potential sweeping at a rate of 50 mV s^{-1} in 1 M CH_3OH and 0.1 M HClO_4 . The bands at 2000–2100 and 1800–1900 cm^{-1} correspond to the absorbance of linear-CO (CO_l) and bridge-CO (CO_b), respectively. The band intensities of linear- and bridge-CO for the first CV cycle are small at low potentials below 0.35 V, but the band intensity of linear-CO increases remarkably after 0.35 V, at which the electrooxidation of CH_3OH starts to occur significantly. The intensity of linear-CO band stays nearly constant in the cathodic direction sweeping. It is supposed that the amount of CO generated by eq 1 is offset by the consumption of eq 2. In the successive potential sweeping, the intensities of linear-CO bands increase gradually, while the intensities of bridge-CO bands remain almost constant and are independent of potentials. The intensities of bridge-CO bands are smaller than that of linear-CO since the first cycle. This may imply that only a few sites on the Pt surface are suitable for the bridge-CO selective absorption. In addition, according to Zhou et al.,²¹ the bridge-CO is unstable and can transform to a linear-CO with the increase of potential. The increased potential decreases the electron density of Pt surface and thus blocks the electron flow from the Pt atoms to the σ - π bond of Pt-CO and finally weakens the Pt-CO_b bond. The fact that the significant increase in the intensities of linear-CO bands accompanying the obvious decrease in current of the CVs discloses that the poisons to the Pt electrode come from the linear-CO absorbance. The 3-D plot of IR spectra with potential sweeping on a upd-Sn/Pt electrode displays the similar behavior as on the Pt electrode shown in Figure 11. This suggests that CO poison to the upd-Sn/Pt electrode is still a key problem. The mechanism of methanol oxidation despite on the Pt electrode or on a upd-Sn/Pt electrode is no different in the light of CO poisons.

3.3. Methanol Oxidation on upd-RuSn/Pt Electrode. According to the foregoing discussion, ruthenium and tin adatoms on the Pt surface play an enhancement role in methanol oxidation in a different potential range. There may be a possibility to get an electrode with a good catalysis in a wide potential range if Ru and Sn adatoms present on platinum surfaces simultaneously. It is supposed that ruthenium and tin would not

compete but would complement each other, yielding an even higher synergetic electrocatalytic activity for methanol oxidation. With this belief, we prepared upd-RuSn/Pt electrode and examined its catalytic activity in 0.5 M CH₃OH + 0.5 M H₂-SO₄.

Figure 12 shows the methanol electrooxidation on a pure Pt electrode, a upd-Ru/Pt electrode, a upd-Sn/Pt electrode, and a upd-RuSn/Pt electrode. The key data have been summarized in Table 2. As listed in Table 2, the methanol electrooxidation on a upd-RuSn/Pt starts as early as that on a upd-Sn/Pt but starts much earlier than that on a upd-Ru/Pt and, needless to say, on a pure Pt electrode. Compared with a upd-Ru/Pt electrode, the introduction of upd Sn atoms into the upd-Ru/Pt electrode leads to a high current of methanol oxidation in a potential range lower than 0.32 V. Meanwhile, the current of methanol oxidation on a upd-RuSn/Pt electrode is even higher than that on a upd-Sn/Pt in a low potential range. It indicates that some synergetic effects work as adatoms Ru and Sn participate simultaneously in the methanol oxidation. Over a potential of 0.32 V, adatoms Sn would bring a detrimental effect on methanol oxidation on the upd-Ru/Pt electrode. It is not difficult to understand that at a quite higher potential it is possible for formation of oxygen-containing species, such as Ru-OH, which is a better CO remover than Sn-OH.

4. Conclusions

The influence of the submonolayers of upd ruthenium adatoms and upd tin adatoms on the oxidation of methanol in acid has been investigated.

On the basis of the facts, Ru and Sn adatoms on the Pt surface play an enhancement role in methanol oxidation in a different potential range. A ternary catalyst containing Ru, Sn, and Pt elements was prepared. It was shown that the Pt electrode modified by upd-Ru and upd-Sn adatoms exhibits the best catalysis for methanol electrooxidation in every respect of the onset oxidation potential and the oxidation current in a certain potential range. The larger current of methanol electrooxidation on the upd-RuSn/Pt electrode, that is, a upd-Ru/Pt electrode further modified by upd-Sn adatoms, than that on the upd-Ru/Pt electrode in a potential range, in which no enhancement effect

was observed on the upd-Ru/Pt electrode compared with a pure Pt electrode, indicates that some synergetic effects work as adatoms Ru and Sn participate simultaneously in the methanol oxidation.

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