

Electrooxidation of methanol on platinum bonded to the solid polymer electrolyte, Nafion

AKIKO ARAMATA, TAKURO KODERA, MAKIHIKO MASUDA

Research Institute for Catalysis, Hokkaido University, Sapporo 060, Japan

Received 21 September 1987; revised 10 February 1988

The electrooxidation of methanol was enhanced on PtSn-SPE, PtRu-SPE and PtIr-SPE in sulfuric acid solution, when compared with the activity of Pt-SPE, which has already been shown to have a higher activity than a Pt electrode. SPE is an abbreviation for Nafion, a solid polymer electrolyte. It is suggested that this dual enhancement of the oxidation rate for PtSn-SPE and PtRu-SPE catalysts is due to the modification of the oxidation state of Pt by Sn and Ru and to the presence of H₂O and CH₃OH, both modified by the SPE matrix. This modification appears to weaken their hydrogen bonds in solution. Both Pt and Ir have catalytic properties for methanol oxidation, but a PtIr-SPE catalyst showed a more enhanced catalytic activity than either of them. This will be discussed in terms of Ir, oxidized at relatively low positive potentials, assisting the redox process of Pt⁰/Pt²⁺ or Pt²⁺/Pt⁴⁺ in the SPE matrix, where CH₃OH and H₂O are present in modified forms. For comparison, IrPd-SPE was also used as an electrode and showed a higher activity than Ir alone, although Pd did not have any activity toward methanol oxidation in sulfuric acid solution. Irrespective of the kind of Pt-SPEs, the Tafel slope was approximately 120 mV; the CH₃OH concentration dependence was of the order of 0.2-0.6. The pH dependence was nearly 0.5 against NHE. The activation energy of the Pt-SPEs for the reaction ranged between 20 and 33 kJ mol⁻¹.

1. Introduction

The ion-conducting solid polymer electrolyte membrane (SPE) is used as a separator in electrolysis chambers [1], for separation of ionic species [2, 3], for coating of electrodes [4-6] and for electrolysis without a liquid solvent [7].

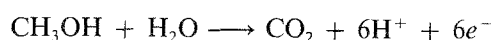
The physico-chemical nature of an SPE has been investigated from various standpoints. Nafion, a cation-conductive perfluorinated polymer, used as an SPE in the present work, was suggested to have void cages [8, 9] of ~ 40 Å with channels of 10 Å [10] between the cages inside its membrane, where H₂O is present and plays an important role in the conductive nature of Nafion. IR spectra have shown a change in OH and SO₃⁻ stretchings with a change in water content [11, 12]. Some of the water in Nafion SPE only interacts with -CF₂- and remains in an isolated state, being free of a hydrogen bond. Thus, the structure of water is modified by the SPE field.

By the addition of water, the SPE swells, increasing the size of its void cages from 40 to 50 Å [9]. In a mixture of water and alcohol [13], the degree of SPE swelling is increased when compared to that using water or alcohol alone. The additive effect of the water-alcohol mixture increases the size of the void cages and provides additional interaction between SPE and the mixture.

In such SPE cages, the chemical features of water and alcohol are expected to be different from those in the bulk solution. Electrode metals entering the cages can be prepared by the Torikai-Takenaka method [14] and may also have a different behaviour from the

metals exposed to the bulk solution. The metals that enter the SPE cages are schematically shown by Pts in Fig. 1. Such Pts bonded on the SPE membrane, which are denoted as Pt-SPE, are expected to play a specific role in some electrode processes.

The methanol electrooxidation reaction



involves the activation of CH₃OH and H₂O with the liberation of CO₂ and H⁺. Water, free of a hydrogen bond in SPE, may take part in the activation of the methanol oxidation process, where methanol may also be activated by the SPE. On the other hand, methanol oxidation with Pt group metals has been extensively studied [15-17]. Pt, the most active metal in this group, is the electrode mainly used. However, its electrocatalytic activity is not high enough for practical use as a methanol fuel cell anode. Therefore, binary electrodes such as PtSn, PtPb, PtIr, PtRu, etc. have been investigated; these show higher catalytic activity than Pt itself [18-22].

In the present report, various Pt-SPEs were examined for use as electrodes for methanol oxidation since they are expected to show an enhanced catalytic activity.

2. Experimental details

2.1. Pt-SPE preparation by the Torikai-Takenaka method [14]

Nafion 315 membrane was used as the SPE. Although this material is in a laminated form of different ion

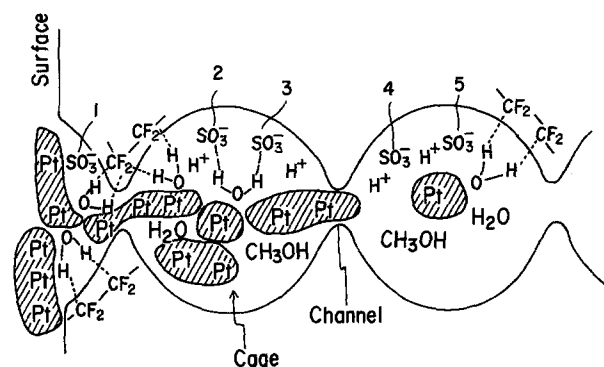


Fig. 1. Schematic of Pt-SPE on the SPE structure proposed by Gierke and Hsu [9].

equivalent weights (1500 and 1100), the present results were independent of which face of the membrane was used for bonding of the Pt. The details of the preparation are described elsewhere [23, 24]. The penetration of reducing agent (NaBH_4 or N_2H_4) from one face of the membrane to the other face, which is in contact with PtCl_6^{2-} ions, takes place and Pt^0 is deposited at the latter face.

The amount of surface Pt on the Pt-SPE was determined from the amount of adsorbed hydrogen observed by cyclic voltammetry, where the hydrogen is adsorbed in the atomic ratio of 1:1 for Pt:H with a roughness factor as listed in Table 1. Table 1 shows that the reducing agent, NaBH_4 , apparently gives a higher roughness factor than N_2H_4 . The utility of platinum as surface Pt is 5% when using NaBH_4 as the reducing agent but only 2.5% with N_2H_4 . The average size of platinum was estimated to be 200 Å, which is in conformity with the size of a Pt cluster in Nafion observed by electron microscopy [7].

2.2. PtIr-SPE preparation

From the mixture of Ir and Pt chloride solutions in the atomic ratio of 1:1 for Ir:Pt, PtIr-SPE was prepared on Pt-SPE by using the identical method for the Pt-SPE preparation, where Ir ion reduction was catalyzed by Pt to give PtIr-SPE.

2.3. PtSn-SPE and PtRu-SPE by electrodeposition of Sn and Ru on Pt-SPE

PtSn or PtRu by Sn or Ru deposition on Pt metal has been shown to give enhanced catalytic activity toward methanol oxidation [19–22]. Accordingly, electrodeposition of Sn or Ru on Pt-SPE was carried out in

a solution of 0.02 M H_2PtCl_6 + 0.02 M SnCl_4 (or RuCl_4) at 0.24 V vs NHE to give PtSn-SPE or PtRu-SPE, respectively, after the method of Janssen and Moolhuysen [20], where a Pt ion can be reduced with Sn (or Ru) occlusion. The charge passed almost corresponded to the formation of a monolayer of Pt. The amount of Sn was evaluated from the amount of hydrogen on the Pt, on the assumption that Sn does not adsorb hydrogen in the potential region where Pt adsorbs hydrogen. Since Ru adsorbs hydrogen [25], the value of the anodic current at $E = 0.3\text{V}$ was used for the evaluation of the surface Pt. After electrodeposition, PtSn-SPE and PtRu-SPE were put into boiling water for an hour, during which the tin (or ruthenium) was expected to be converted into an oxide or hydroxide. Without such boiling water treatment, tin was dissolved during the CV. We report the case where the coverage of Sn and Ru was $\theta_{\text{Sn}} = 0.74$ and $\theta_{\text{Ru}} = 0.3$.

2.4. Electrochemical measurement

The Pyrex glass cell used in these experiments has been described elsewhere [23, 24]. Current-potential-time characteristics were observed under potentiostatic conditions. He and H_2 gases were bubbled into the test electrode compartment and the reference electrode compartment, respectively. The electrode potential of the latter electrode was taken as the reversible hydrogen electrode potential (RHE) in the respective solutions. For the following results, we will only report the case of Pt-SPEs prepared by the reducing agent, NaBH_4 . The electrochemical measurements were carried out using a Toho Type 2000 potentiostat, mainly at 23°C in an air bath. Current density, i , was evaluated from the true area of Pt on the Pt-SPE, PtSn-SPE and PtRu-SPE, and of Pt and Ir on the PtIr-SPE. Apparent current density is expressed by I and electrode potential, E , is expressed with respect to RHE in the following sections.

3. Results and discussion

3.1. Cyclic voltammograms (CV)

The CVs of various Pt-SPEs in 0.5 M H_2SO_4 are shown in Fig. 2. The CVs of the modified Pt-SPEs, shown in Fig. 2b–d exhibited features of Pt and the respective second metals Sn, Ru and Ir. The CV of PtIr-SPE showed the presence of Ir and Pt at the surface based on the hydrogen and oxygen adsorption

Table 1. Features of Pt-SPE observed by hydrogen adsorption

Reducing agent	Pt amount (mg cm^{-2})	Roughness factor	Area ($\text{m}^2 \text{g}^{-1}$)	Particle diameter (Å)	Atoms/true area (10^{16}cm^{-2})
NaBH_4	5.6	700	12.5	220	2.4
N_2H_4	4.2	230	5.5	510	5.5

Calculated number of platinum atoms on monolayer surface = $0.13 \times 10^{16} \text{atoms cm}^{-2}$.

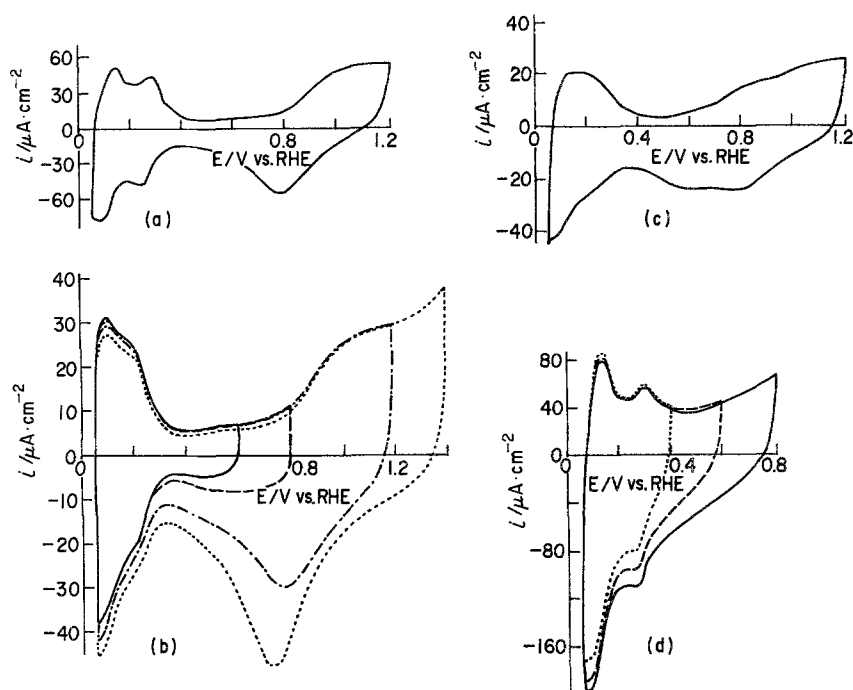


Fig. 2. Cyclic voltammograms on various Pt-SPEs in 0.5 M H_2SO_4 . (a) Pt-SPE at 50 mV s^{-1} , (b) PtIr-SPE at 20 mV s^{-1} , (c) PtSn-SPE at 20 mV s^{-1} and (d) PtRu-SPE at 50 mV s^{-1} .

characteristics, e.g. the strong negative peak at 0.8 V is associated with reduction of oxygen species on Pt while oxygen species formation at $E < 0.8 \text{ V}$ is associated with Ir. The peaks in the hydrogen adsorption region showed different features between Pt and Ir [26], both of which contributed to hydrogen adsorption at $E < 0.4 \text{ V}$, as in Fig. 2b. In the case of PtSn-SPE (Fig. 2c), the additional peak in the cathodic sweep appeared at 0.6 V, which is probably due to the interaction of Pt and Sn at the surface [22]. The PtRu-SPE gave the CV in Fig. 2d. The comparison between the CV features of Ru and Pt can be found in the work of Woods [25].

3.2. CVs with methanol present in a solution

With methanol present in a solution, the peaks of adsorbed hydrogen on Pt are known to be depressed due to the adsorbed species from methanol. The

degree of the depression is shown for Pt-SPEs in Fig. 3. It has been suggested [23] that the depression of the peaks for Pt-SPE and Pt is slightly different and the former is not as depressed as the latter. Figure 3 also shows that for all Pt-SPEs the depression of the hydrogen adsorption peaks was due to the addition of methanol, where the degree of the depression was evaluated from the amount of adsorbed hydrogen, Q^{H} and Q_0^{H} , which are evaluated with and without methanol from cathodic hydrogen adsorption CVs, respectively. The value of $Q^{\text{H}}/Q_0^{\text{H}}$ equal to 0.3 for Pt-SPE in H_2SO_4 conforms with that in HClO_4 [23]. For PtSn-SPE and PtRu-SPE, $Q^{\text{H}}/Q_0^{\text{H}}$ is approximately 0.6, which is larger than that for Pt-SPE.

3.3. Durability of the polarization activity at constant potentials

For Pt itself, neither its initial high activity after anodic

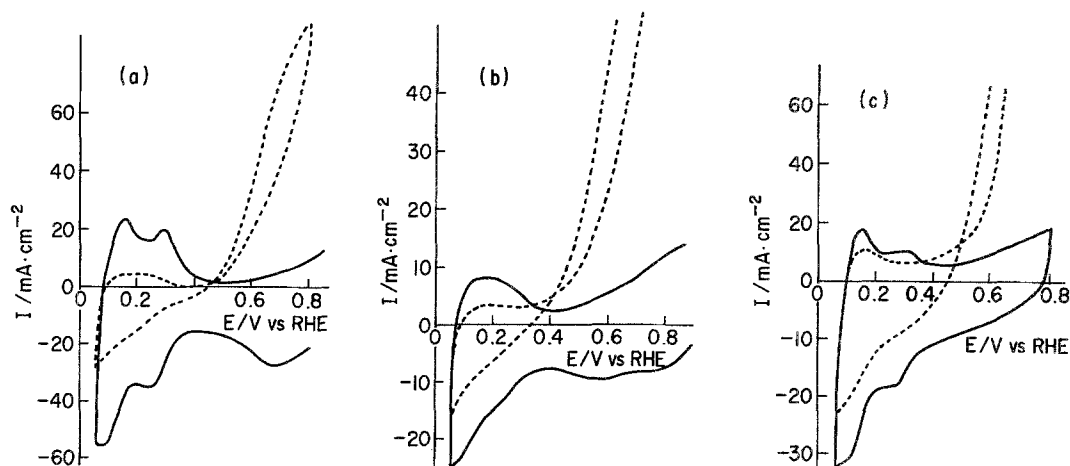


Fig. 3. Cyclic voltammograms on various Pt-SPEs with and without 1 M CH_3OH in 0.5 M H_2SO_4 . Dotted curves with 1 M CH_3OH and solid curves without CH_3OH . (a) Pt-SPE, (b) PtSn-SPE and (c) PtRu-SPE.

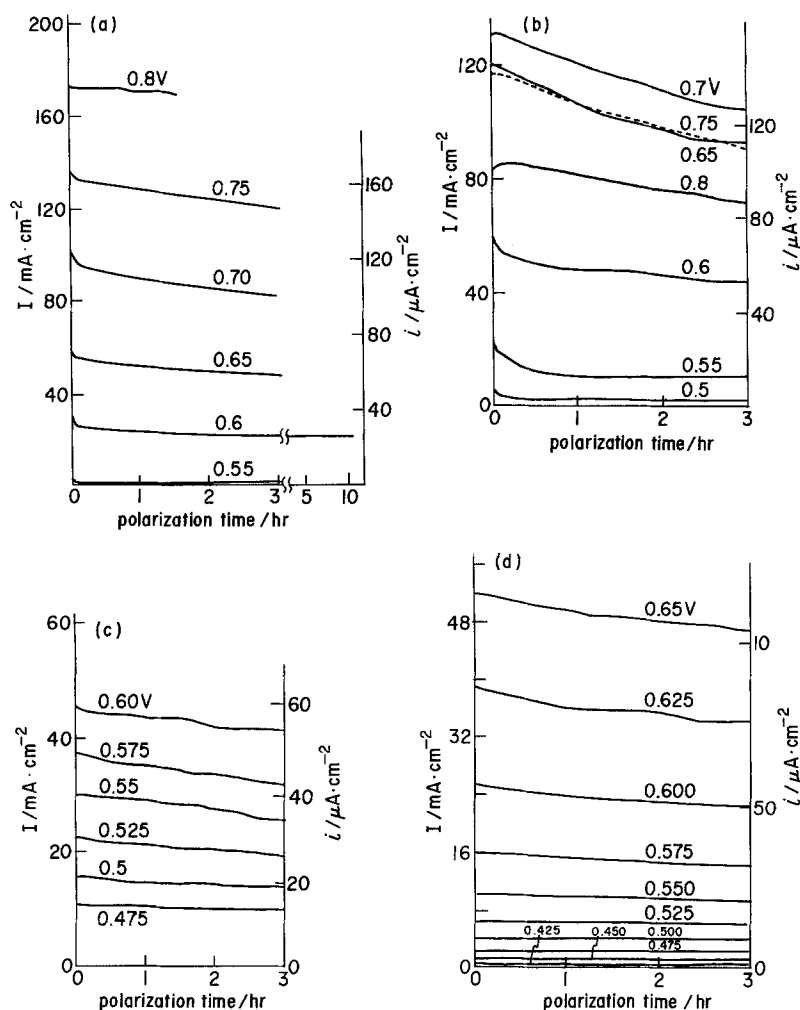


Fig. 4. Polarization at various potentials (vs RHE) on various Pt-SPEs in 1 M CH_3OH + 0.5 M H_2SO_4 . (a) Pt-SPE with roughness factor (RF) = 840, (b) PtIr-SPE with RF = 840, (c) PtSn-SPE with RF = 708 and (d) PtRu-SPE with RF = 500.

activation nor the current during CV are maintained at a constant potential polarization. Thus, the polarization current of Pt-SPE was measured at a constant potential versus time in 1 M CH_3OH + 0.5 M H_2SO_4 , for comparison of the maintenance of its electrocatalytic activity with that of Pt. At the beginning of polarization at 0.6 V, the activities were nearly identical, but Pt lost activity with time for prolonged polarization although Pt-SPE maintained activity for 10 h or more after approximately 2 h polarization, as already reported for the case of HClO_4 [23, 24]. The polarization characteristics of various Pt-SPEs were observed at constant potentials, as shown in Fig. 4. We found that the degree of decrease in current with time is large when the observed current is large. However, the ratio of the degree of decrease to the amount of current is nearly identical ($\pm 5\%$) over 3 h, except for the PtIr-SPE. This indicated that the logarithm of current with respect to electrode potential (Tafel plots) gives identical slopes during any period of polarization.

For the PtIr-SPE, Ir showed characteristic features toward methanol electrooxidation [26] which affected the polarization on the PtIr-SPE during the initial reaction stage. After 20 min polarization, the PtIr-SPE current decreased approximately 20% in 3 h and

this current, after 3 h polarization, could not be strictly classified as a steady value.

3.4. Tafel plots

We plotted reaction currents after 3 h of polarization and used these values as the steady state values (Tafel plots) for all Pt-SPEs in Fig. 5, where the current density is scaled with respect to the true area of Pt (Pt and Ir for PtIr-SPE). We found in Fig. 5 that the PtSn-SPE exhibits the highest catalytic activity among the observed Pt-SPEs. The order of activity is PtSn-SPE > PtRu-SPE > PtIr-SPE > Pt-SPE, at low potentials. At 0.5 V, the activities of PtSn-SPE and PtRu-SPE are, respectively, 20 and 10 times higher than that of Pt-SPE itself. It was shown that Pt-SPE maintained a catalytic activity 20 times higher than Pt [23, 24]. These facts indicated that the catalytic activity and longevity of PtSn-SPE and PtRu-SPE are quite pronounced. It has been reported for the platinum-tin system [22] that the higher oxidation states of platinum were induced by the presence of tin oxide. Pt species at high oxidation states, such as Pt^{2+} and Pt^{4+} , were shown to play an important role in the methanol oxidation by the redox processes $\text{Pt}^0/\text{Pt}^{2+}$ or $\text{Pt}^{2+}/\text{Pt}^{4+}$. In Fig. 3b we found a new reduction peak at 0.6 V,

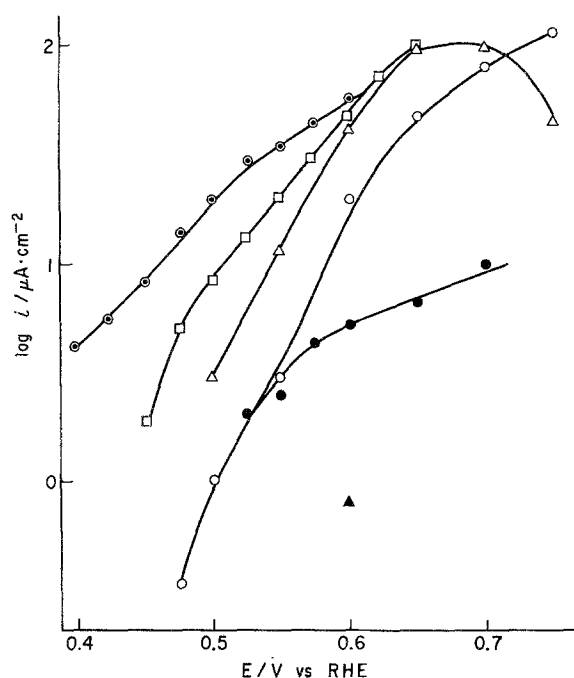


Fig. 5. The Tafel plots on various Pt-SPEs in 1 M CH₃OH + 0.5 M H₂SO₄. Current density, i , was evaluated from adsorbed hydrogen on Pt in 0.5 M H₂SO₄ except that for the case of PtIr-SPE adsorbed hydrogen on Ir and Pt was used. ○: PtSn-SPE; □: PtRu-SPE; △: PtIr-SPE; ○: Pt-SPE; ●: IrPd-SPE; ▲: pt-Pt after 20 h polarization.

which may be attributed to the interaction between Pt and Sn, i.e. the valence state of Pt is likely to be modified. In the case of PtRu-SPE, the oxidation state of Pt is also thought to be modified by the presence of Ru from the XPS results of the PtRu alloys, on which surface Pt is oxidized to PtO₂ [27]. Even on PtIr alloys, its surface Pt is oxidized easier than Pt itself although the oxidizable degree of Pt is lower than that of the PtRu alloys [27]. These results suggest that the Pt species redox process assists the mechanism for the enhancement of the methanol oxidation. For comparison, the results of the IrPd-SPE are also given in Fig. 6. Since Pd has no activity during methanol electrooxidation in H₂SO₄ [28] and Ir itself shows twice as much activity as Pt itself at 0.6 V [26], IrPd-SPE was also shown to exhibit enhanced catalytic activity due to the SPE matrix. The decrease in current at $E > 0.75$ V is due to Ir [26].

The slope of the Pt-SPE Tafel plots, $2.303RT/\beta F$, was 100–140 mV, where the Tafel constant, β , was 0.58–0.41. For the mechanistic investigation of the enhanced modification by Sn and Ru on Pt-SPE, the methanol concentration and pH dependences were observed. At a methanol concentration, [CH₃OH], of 1–0.125 M,

$$\left(\frac{\partial \log i}{\partial \log [\text{CH}_3\text{OH}]}\right)_\phi = 0.2\text{--}0.6 \quad (1)$$

and

$$\left(\frac{\partial \log i}{\partial \log [\text{H}^+]}\right)_E = \sim 0 \quad (2)$$

at 0.5–0.01 M H₂SO₄ for all the Pt-SPEs, where ϕ is the potential with respect to NHE and E is the potential versus RHE. For a Pt electrode over a wide range of pH the mechanistic parameters were observed by Bagotzky *et al.* [15]. In an acidic solution the Tafel

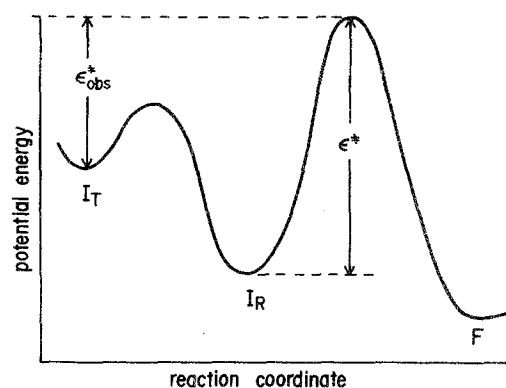


Fig. 6. Potential energy curve for illustration of the relative state of the observed activation energy ϵ_{obs}^* and the activation energy of the rate-determining step ϵ^* .

slope was 60 mV at $E < 0.5$ V and 120 mV at $E > 0.6$ V, and the methanol concentration dependence was less than unity. Our results are in reasonable agreement with the results of Ref. [15] at $E > 0.6$ V. It is interesting that the mechanistic parameters are almost identical among the Pt-SPEs and pt-Pt with different catalytic activities of the order of 2 or more, when the extrapolated value of the PtSn-SPE curve at $E < 0.5$ V to $E = 0.6$ V is compared to the point of pt-Pt (Fig. 5).

From the pH dependence with respect to E , we obtained the pH dependence with respect to ϕ at constant temperatures as [29]

$$\left(\frac{\partial \log i}{\partial \log [\text{H}^+]}\right)_\phi = -\beta + \left(\frac{\partial \log i}{\partial \log [\text{H}^+]}\right)_E \quad (3)$$

from the relations

$$i \propto \exp(\beta FE/RT), \quad E = \phi - \phi_c + k,$$

and

$$\left(\frac{\partial \log i}{\partial \log a}\right)_\phi = \left(\frac{\partial \log i}{\partial E}\right)_a \left(\frac{\partial E}{\partial \log a}\right)_\phi + \left(\frac{\partial \log i}{\partial \log a}\right)_E$$

where the activity, a , is equated to [H⁺], ϕ_c is expressed by the Nernst equation and k is constant by the difference of equilibrium potentials between the hydrogen and methanol electrode reactions, and the stoichiometric coefficient is set to unity. Thus, $(\partial \log i / \partial \log [\text{H}^+])_\phi = -\beta = -0.41 \sim -0.58$. Accordingly, our observed rate expression is given by

$$i = K[\text{CH}_3\text{OH}]^{(0.2\text{--}0.6)}[\text{H}^+]^{-\beta} \exp(\beta F\phi/RT) \quad (4)$$

where β equals 0.41 ~ 0.58. This indicates that the large difference in catalytic activity is included in K of Equation 4, where the factor K is a function of the surface coverage of the intermediates, the activation energy, ϵ^* , and the pre-exponential factor. As the surface coverage amounts to between 0.3 and 0.6 by the adsorbed species derived from methanol, which may be a poison of the reaction [26], the different catalytic activities, of the order of 20 times among the Pt-SPEs, are not simply due to the poisoning effect of the adsorbed species.

An activation energy, ϵ_{obs}^* , of 20–33 kJ mol⁻¹ was observed at 0.55 and 0.60 V between 20 and 50°C, and

was nearly identical for Pt-SPE and PtRu-SPE. The value of $\epsilon_{\text{obs}}^\ddagger$ might indicate that the rate-determining step is a diffusion-controlled step. Hence, the effect of diffusion was observed by He gas bubbling on the PtRu-SPE in a cell. Vigorous stirring by the bubbling caused a negative effect by decreasing the current by 5–10%. This negative bubbling effect may be accounted for by the reaction of formic acid, formed by methanol oxidation [30], which was removed from the electrode surface by the He bubbling. This negative bubbling effect does not affect our discussion at the steady state condition for the constant amount of the intermediate, since the reactivity of formic acid is higher than that of methanol. Accordingly, the $\epsilon_{\text{obs}}^\ddagger$ is not identical to the rate-determining step ϵ^\ddagger which may be varied among the Pt-SPEs [31]. As shown in Fig. 6, this suggested that the potential energy of the initial state, I_R , of the rate-determining step (intermediate of the reaction) is quite low, compared with that of the initial state of the overall reaction, I_T .

In the present investigation, it was found that Sn, Ru and Ir enhanced the catalytic activity of Pt-SPEs for methanol oxidation. The enhancement is ascribed to a two-fold effect, not only of H₂O and CH₃OH activation by the SPE matrix [23], but also modification of the oxidation state of Pt by Sn and Ru [22]. This feature gives a dual effect on the catalytic activity. As an additional effect, it is likely that the large mixing effect, as provided by the swelling phenomenon of SPE, affects the state of H₂O. The reaction scheme and mechanism of the electrooxidation of methanol on Pt-SPEs will be studied in further work.

References

- [1] P. W. Lu and S. Srinivasan, *J. Appl. Electrochem.* **9** (1979) 269.
- [2] R. S. Yeo, *ACS Symp. Ser.* **180** (1982) 453.
- [3] B. K. Kipling, *ACS Symp. Ser.* **180** (1982) 479.
- [4] I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.* **103** (1981) 5007.
- [5] N. Oyama, T. Simomura, K. Shigehara and F. C. Anson, *J. Electroanal. Chem.* **112** (1980) 271.
- [6] H. S. White, J. Leddy and A. J. Bard, *J. Am. Chem. Soc.* **104** (1982) 4811.
- [7] H. Nakajima, Y. Takabuwa, H. Kikuchi, K. Fujikawa and M. Kita, *Electrochim. Acta*, **32** (1987) 791.
- [8] K. A. Mauritz, C. J. Hora and A. J. Hopfinger, *Adv. Chem. Ser. ACS* **187** (1980) 123.
- [9] T. D. Gierke and W. Y. Hsu, *ACS Symp. Ser.* **180** (1982) 283.
- [10] In Ref. [9] the void cages are called clusters.
- [11] M. Falk, *Can. J. Chem.* **58** (1980) 1495.
- [12] M. Falk, *ACS Symp. Ser.* **180** (1982) 139.
- [13] W. G. F. Grot, G. E. Munn and P. N. Walmsley, *Extended Abstracts*, 141st Meeting of Electrochem. Soc., Houston (1972).
- [14] H. Takenaka and E. Torikai, *Kokai Tokkyo Koho* (Japan Patent) **55** (1980) 38934.
- [15] V. S. Bagotzky and Yu. B. Vassiliev, *Electrochim. Acta* **12** (1967) 1323.
- [16] B. B. Damaskin, O. A. Petrii and V. V. Batrakov, 'Adsorption of Organic Compounds on Electrodes', Plenum Press, New York (1971) Chaps 8 and 10.
- [17] M. W. Breiter, *Electrochim. Acta* **8** (1963) 973.
- [18] J. O'M. Bockris and H. Wroblowa, *J. Electroanal. Chem.* **7** (1964) 428.
- [19] K. J. Cathro, *J. Electrochem. Soc.* **116** (1969) 1608.
- [20] M. M. P. Janssen and J. Moolhuysen, *Electrochim. Acta* **21** (1976) 861, 869.
- [21] M. M. P. Janssen and J. Moolhuysen, *J. Catalysis* **46** (1977) 289.
- [22] A. Katayama, *J. Phys. Chem.* **84** (1980) 376.
- [23] A. Aramata and R. Ohnishi, *J. Am. Chem. Soc.* **105** (1983) 658.
- [24] A. Aramata and R. Ohnishi, *J. Electroanal. Chem.* **162** (1984) 153.
- [25] R. Woods, *Israel J. Chem.* **18** (1979) 118.
- [26] A. Aramata, T. Yamazaki, K. Kunimatsu and M. Enyo, *J. Phys. Chem.* **91** (1985) 2309.
- [27] L. Hilaire, G. D. Guerrero, P. Legare, G. Maire and G. Krill, *Surf. Sci.* **146** (1984) 569.
- [28] A. Aramata and I. Toyoshima, *J. Electroanal. Chem.* **135** (1982) 111.
- [29] H. Kita and A. Aramata, 'Electrochemical Reactors' (edited by M. Ismail), Elsevier, Amsterdam, Vol. 1, Chap. 3, in press.
- [30] K. Ota, Y. Nakagawa and M. Takahashi, *J. Electroanal. Chem.* **179** (1984) 179.
- [31] S. Glasstone, K. J. Laidler and H. Eyring, 'The Theory of Rate Processes', McGraw-Hill, NY (1941) p. 376.