Methanol Electrooxidation on Smooth Platinum Modified with Ru the Influence of Ru Coverage and Potentials on Oxidative Current and Products

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Methanol oxidation on smooth Pt electrode modified with different coverage of Ru was studied using cyclic voltammetry and potential step combined with differential electrochemical mass spectroscopy. The current efficiency of formed CO_2 was calculated from faraday current and ion current of $m/z = 44$. The results show that Ru modified Pt electrode with the coverage of *ca*. 0.3 has the highest catalytic activity for methanol electrooxidation i.e. faraday current and the current efficiency of CO_2 at the low potentials reach to the maximum. In addition Ru loses its co-catalytic properties at the high potentials.

Keywords　　methanol electrooxidation　Ru modified Pt　current efficiency of CO_2　differential electrochemical mass spectroscopy　cyclic voltammetry　potential step

Introduction

It is widely agreed that as a single component catalyst platinum is the only element to show a significant electrocatalytic activity on methanol oxidation and therefore has been studied extensively. The catalytic activity of platinum however is still too low to consider direct methanol fuel cells as a practical power source. Therefore a lot of studies have been conducted to promote the electrocatalytic activity of platinum. [1-17]

Adding secondary element has been one of the most common and successful methods. [1] Ruthenium and tin have been the elements most widely used to modify platinum. Ru always shows a steady and high catalytic activity toward methanol electrooxidation on Pt. At present Pt-Ru electrode is believed to be the best catalyst among the platinum binary catalysts for methanol oxidation. However the optimal composition of Pt-Ru alloy is remaining controversial. In the early years Entina *et al*. [2] indicated an optimum Ru composition of 25 atomic%. Nevertheless Motoo *et al*. [3] reported that Pt-Ru alloy with 50 atomic% ruthenium shows the maximal current towards methanol oxidation and gave an explanation based on the theory of bifunctional mechanism. At present it is well known that bifunctional mechanism could be used to explain CO oxidation on Pt-Ru more exactly. However unlike CO adsorption

methanol adsorption on Pt needs more than 2 sites hence Pt-Ru alloy surface with 50 atomic% does not seem to be the optimal catalyst. [4] Ross *et al*. [4] presented the optimum alloy surface composition of ~ 10 atomic% Ru for the electrooxidation of methanol at ambient temperature but the optimum composition of Pt-Ru also seems to depend on the temperature methanol concentration and the potential range chosen for comparison. Recently with normalisation of the porous catalyst surface Iudice de Souza *et al*. [5] pointed out that Pt-Ru alloy with 25 atomic% Ru bulk composition has the highest electrocatalytic activity on methanol oxidation in the lower potential range. Iwasita *et al*. [6] also found that with respect to methanol oxidation on Ru modified Pt 111 a maximum of high catalytic activity is observed between 10% and 40% Ru.

In this work in addition to faraday current the current efficiency of formed CO_2 during methanol oxidation at Ru modified smooth polycrystalline Pt was also detected by differential electrochemical mass spectroscopy DEMS . They were used for evaluating the catalytic activity of Pt-Ru electrodes. A maximum of catalytic activity was observed on Ru modified Pt with the coverage of ~ 0.3. However Ru loses its co-catalytic properties at the high potentials.

Experimental

A potentiostat Wenking LB75L Germany a home built function generator Institute of Physical Chemistry Bonn University and a quadruple mass spectrometer Balzers QMG-511 were used for differential electrochemical mass spectrometry. A new dual thin layer flow through cell made of titanium was used in the experiments of DEMS which was described in Refs. 7—9.

All solutions were prepared from Millipore water and analytical grade or suprapure chemicals from Merck or Fluka and deaerated by 99.999% argon. 0.5 mol/L H_2SO_4 p.a. was used as supporting electrolyte. A smooth polycrystalline platinum $\phi = 10$ mm and roughness factor is

ca. 1.8 was used as working electrode. The working electrode was first cleaned by cyclic sweep between 0.05—1.5 V in 0.5 mol/L H$_2$SO$_4$ solution at the scan rate of 50 mV/s and exchanging solution at 1.5 V. Ru adsorption was carried out directly in DEMS-cell by introducing 5 × 10^{-3} mol/L RuCl$_3$ + 0.5 mol/L H$_2$SO$_4$ solution. Adsorption time was 5 min. Different coverage of Ru could be obtained by changing adsorption potentials between 0.3 and 0.8 V. After Ru adsorption the electrode was thoroughly rinsed with 0.5 mol/L H$_2$SO$_4$ solution. Here only fresh prepared Ru-solution was used for adsorption. Ru coverage on polycrystalline platinum was determined according to Ref. 15 and checked with the method of Motoo.[3] All experiments were carried out at room temperature.

Results and discussion

Cyclic voltammograms of smooth polycrystalline platinum with different coverage of Ru *in* 0.5 *mol/L* H$_2$SO$_4$ *solution*

Fig. 1 shows the cyclic voltammograms of smooth polycrystalline platinum with different coverage of Ru in 0.5 mol/L H$_2$SO$_4$ solution. Pt-Ru electrodes were prepared by constant potential deposition of Ru in fresh 5 ×

10^{-3} mol/L RuCl$_3$ + 0.5 mol/L H$_2$SO$_4$ solution for 5 min at different potentials which are 0.8 b 0.7 c 0.6 d 0.5 e and 0.3 V f respectively.

Compared to the double layer charge of smooth polycrystalline platinum the one of Ru modified smooth polycrystalline platinum becomes larger due to OH adsorption and desorption on Pt-Ru while the hydrogen adsorption/desorption peaks reduce. The change in Ru coverage can obviously be observed from the change in the double layer charge. With the decreasing adsorption potential Ru coverage increases.

Methanol oxidation on Ru *modified smooth polycrystalline platinum*

In the previous papers [8] [9] we have investigated methanol oxidation on Ru modified smooth polycrystalline platinum $\vartheta_{Ru} \approx 0.35$ in 0.1 mol/L methanol + 0.5 mol/L H$_2$SO$_4$ solution. It was indicated that in addition to promoting methanol oxidation on smooth Pt at low potentials *i.e.* enhancing faraday current Ru-adatoms also increase the current efficiency of formed CO$_2$ during methanol oxidation. Here we further investigated the influence of Ru coverage and potentials on faraday current and the current efficiency of formed CO$_2$ during methanol oxidation on smooth Pt.
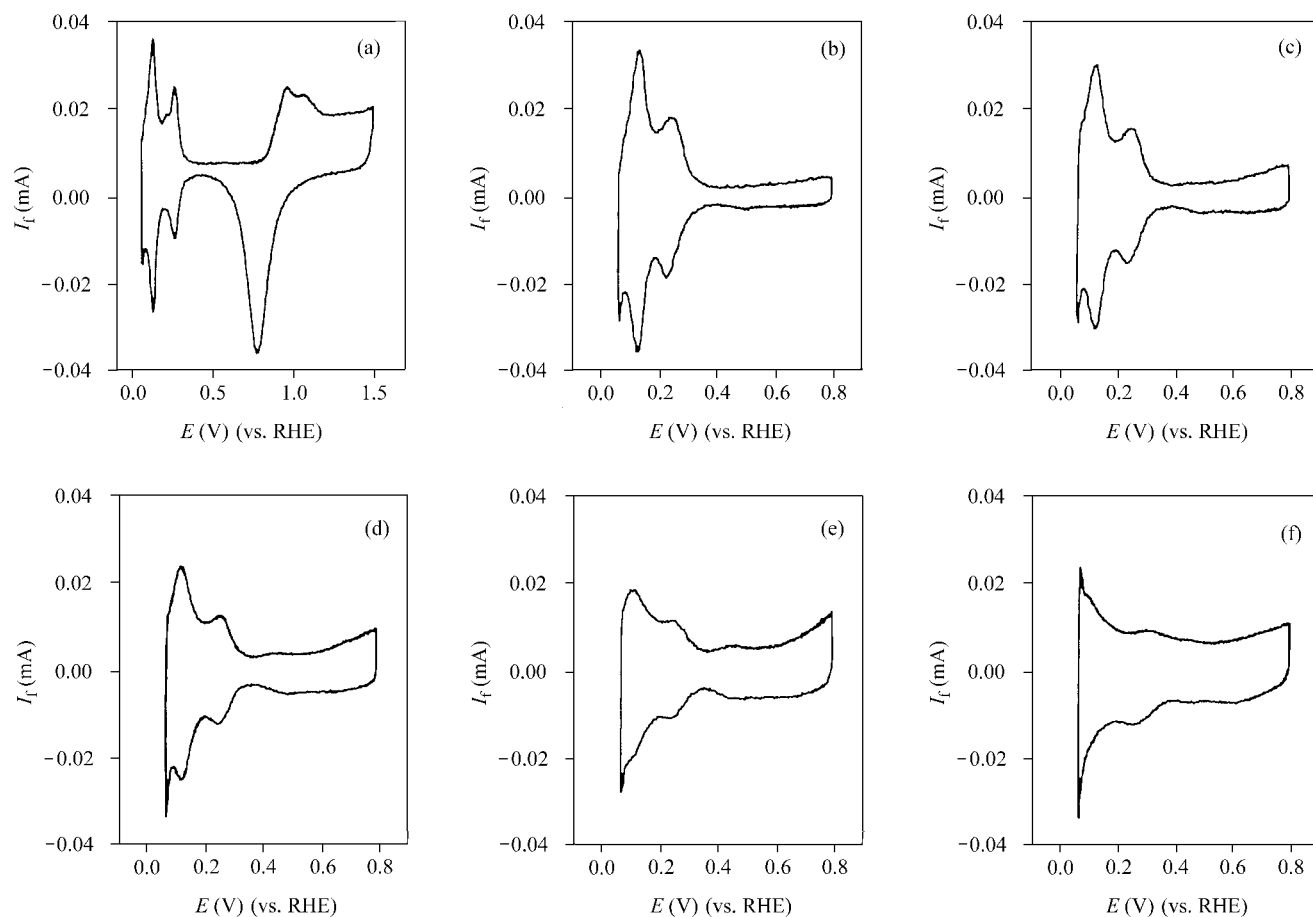

Fig. 1 Cyclic voltammograms of smooth polycrystalline platinum modified with different coverage of Ru in 0.5 mol/L H$_2$SO$_4$ solution. Scan rate 50 mV/s. a Pt b Pt-Ru $\vartheta \approx 0.12$ c Pt-Ru $\vartheta \approx 0.25$ d Pt-Ru $\vartheta \approx 0.35$ e Pt-Ru $\vartheta \approx 0.5$ f Pt-Ru $\vartheta \approx 0.7$.

Cyclic voltammetry

Methanol oxidation on Ru modified smooth Pt is shown in Fig. 2. The formation of CO_2 on Ru modified smooth polycrystalline Pt starts at 0.4 V, *i. e.* over 150 mV more negative than that on smooth polycrystalline Pt. With the increasing Ru coverage, faraday current and ion current of formed CO_2 during methanol oxidation at low potentials < 0.7 V first increase, then decrease. Thus an optimum Ru coverage should exist. It could be seen that Pt-Ru electrode with a coverage of Ru $\vartheta_{Ru} \approx 0.3$ has a highest catalytic activity on methanol electrooxidation at the low potentials.
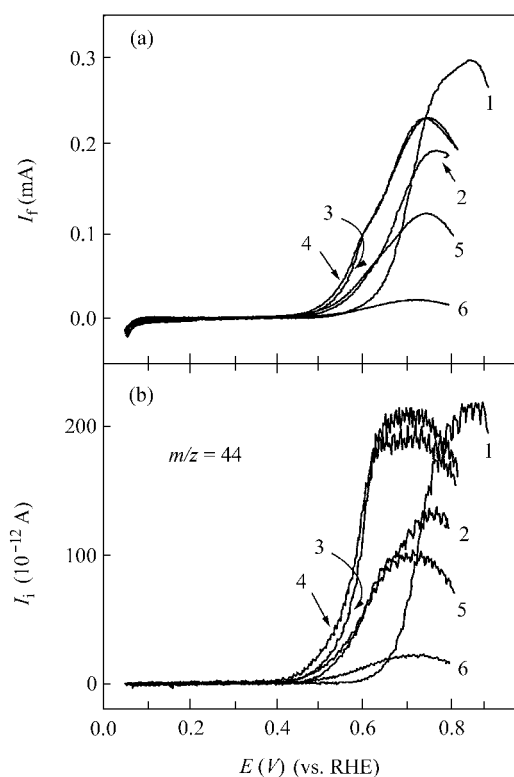
Fig. 2   Positive sweep part of simultaneously recorded CVs (a), MSCVs $m/z = 44$ (b) on smooth polycrystalline platinum modified with different coverage of Ru in 0. 1 mol/L methanol + 0.5 mol/L H_2SO_4 solution. Scan rate 10 mV/s. Electrolyte flow rate 5 μL/s. 1 Pt; 2 Pt-Ru $\vartheta \approx$ 0.12; 3 Pt-Ru $\vartheta \approx 0.25$; 4 Pt-Ru $\vartheta \approx 0.35$; 5 Pt-Ru $\vartheta \approx 0.5$; 6 Pt-Ru $\vartheta \approx 0.7$.

Potential step

Fig. 3 shows the simultaneously recorded transients of faraday current and ion current $m/z = 44$ on smooth polycrystalline Pt and Ru modified smooth polycrystalline Pt in 0.1 mol/L methanol + 0.5 mol/L H_2SO_4 solution after the step of potential from 0.05 to 0.6 V. Like the case of cyclic voltammetry, with the increasing Ru coverage, faraday current and ion current of formed CO_2 during methanol oxidation first increase, reach the maximum with Ru coverage of ~ 0.3, then decrease. At the second minute after potential step, faraday currents and ion currents of CO_2

were used to calculate the current efficiencies of formed CO_2 which was described in details in Ref. 7. As results, the effect of Ru coverage on faraday current and current efficiency during methanol electrooxidation is shown in Fig. 4. On smooth Pt, current efficiency of formed CO_2 is only ca. 20%. Small coverage of Ru ad-atoms markedly enhances current efficiency of formed CO_2. When Ru coverage reaches ~ 0.3, a maximum current efficiency of CO_2 is obtained. With the higher coverage of Ru > 0.35, current efficiency of CO_2 reduces on the contrary, however, it is still higher than 40%. Therefore, potential step experiments also show Pt-Ru electrode with a coverage of Ru $\vartheta_{Ru} \approx 0.3$ has a highest catalytic activity on methanol electrooxidation.
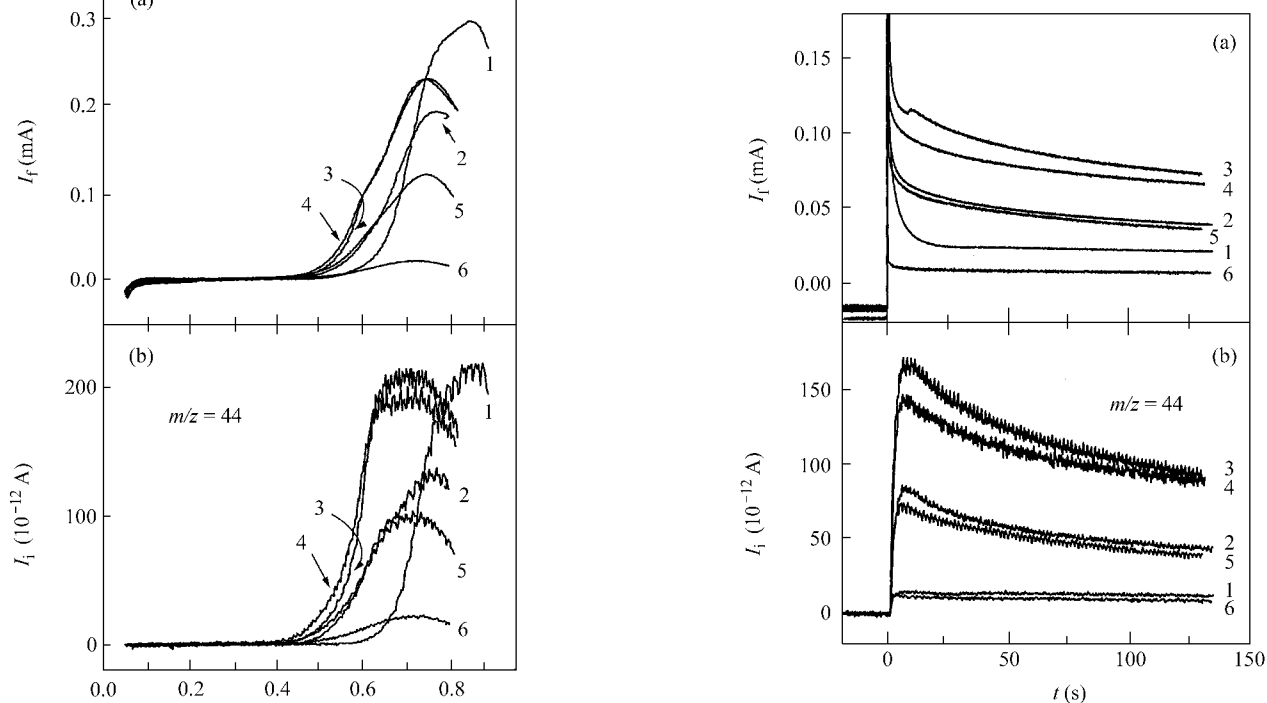
Fig. 3   Simultaneously recorded transients of faraday current (a), ion current $m/z = 44$ (b) on smooth polycrystalline platinum and Ru modified smooth polycrystalline platinum in 0.1 mol/L methanol + 0.5 mol/L H_2SO_4 solution after the step of potential from 0.05 to 0.6 V. Electrolyte flow rate 5 μL/s. 1 Pt; 2 Pt-Ru $\vartheta \approx 0.12$; 3 Pt-Ru $\vartheta \approx 0.25$; 4 Pt-Ru $\vartheta \approx 0.35$; 5 Pt-Ru $\vartheta \approx 0.5$; 6 Pt-Ru $\vartheta \approx 0.7$.

The current efficiency of formed CO_2 as a function of the potential was also studied. In Fig. 5, on Pt faraday current increases sharply, and current efficiency of CO_2 increases slightly with the increase of potentials till 0.8 V. On Ru modified Pt $\vartheta_{Ru} \approx 0.35$, the higher current efficiency of CO_2 is observed at low potentials, however, it drops at higher potentials $\geqslant 0.7$ V to the same value as that on pure Pt, although faraday current increases till 0.75 V. Above the potential of 0.7 V, faraday current on Pt-Ru is lower than on pure Pt. This demonstrates that Ru loses its co-catalytic properties at the high potentials $\geqslant 0.7$ V, perhaps due to the transformation of a Ru ac-

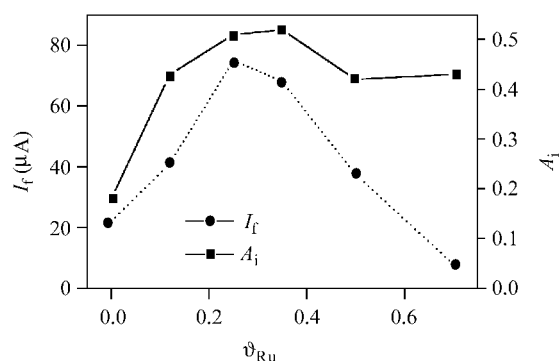tive hydrous oxide to an inactive anhydrous oxide at high potentials.[13]

Fig. 4 Correlation of faraday currents and current efficiencies of formed CO_2 during methanol electrooxidation on smooth polycrystalline platinum with the coverage of Ru. I_f faraday current A_i the current efficiency of formed CO_2.
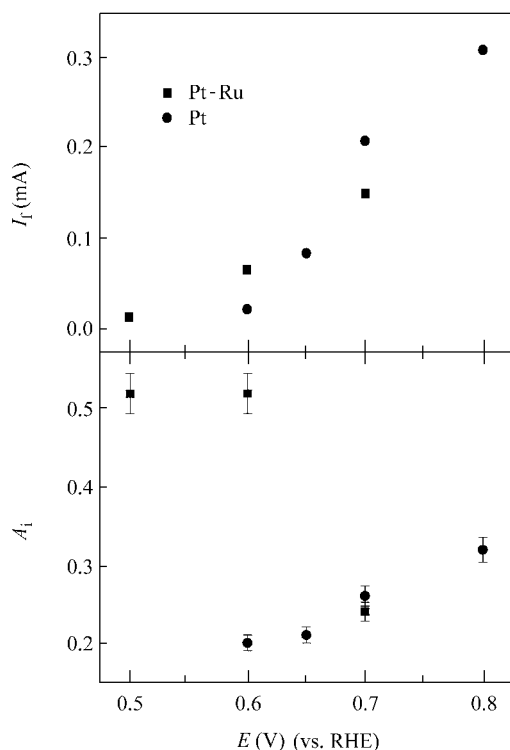

Fig. 5 Potential dependence of faraday currents and the current efficiencies of CO_2 during methanol electrooxidation on Pt and Ru modified Pt. I_f faraday current A_i the current efficiency of formed CO_2.

Mechanism of methanol oxidation on Ru modified smooth polycrystalline platinum

As shown in Scheme 1 [7-9] methanol electrooxidation on Pt proceeds via a parallel path mechanism.

Methanol oxidation on smooth Pt electrode at low potentials and high concentration of methanol proceeds mainly via dissolved intermediates i.e. formaldehyde and formic acid. The low current efficiency of CO_2 such as 20% supports this viewpoint. It is well known that on pure

Scheme 1
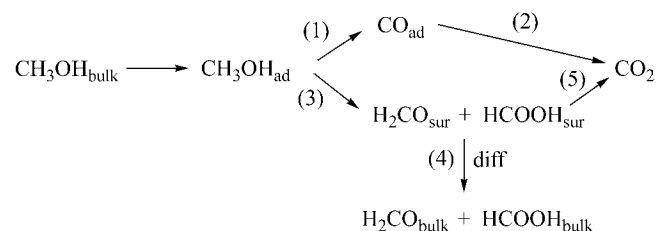
Pt the oxidative removal of adsorbed CO formed from methanol decomposition is the rate-determining step for the first consecutive reaction. Since the adsorption of oxygen-like species on pure Pt does not occur to any appreciable extent below ~ 0.7 V the oxidative removal of adsorbed CO takes place very slow in the low potential range resulting in methanol oxidation mainly via dissolved intermediates.

Ru ad-atoms not only promote the methanol oxidation on smooth Pt at low potentials but also increase the current efficiency of formed CO_2. It is well known that Ru can lower the oxidation potential of CO_{ad} on Pt. It is also found that small coverage of Ru can promote methanol decomposition into CO_{ad} on Pt at the low potentials.[9] Therefore it seems that Ru induces a shift from the reaction path via dissolved intermediates to that via adsorbed CO.

It must be noted that Ru ad-atoms can promote the oxidation of adsorbed CO on Pt but meanwhile block Pt surface which seems to be unfavorable for CO_{ad} formation from methanol decomposition since methanol adsorption does not occur on pure Ru at room temperature.[16] Therefore on Ru modified Pt electrode there should be a competition between the formation rate and the rate of oxidative removal of adsorbed CO which depends on Ru coverage. On Pt modified with low coverage of Ru below ~ 0.35 CO_{ad} formation from methanol decomposition is not inhibited even enhanced due to the electron effect [9] therefore the rate of the first reaction pathway is increased leading to the increase in the current efficiency of CO_2. On Ru modified Pt with the coverage of ~ 0.3 the formation rate and the rate of oxidative removal of CO_{ad} from methanol decomposition probably reach the optimum balance. As results a maximum current efficiency of CO_2 as well as faraday current for methanol oxidation is obtained in the low potential range. However as Ru coverage is much higher than 30% methanol decomposition into CO_{ad} on Pt is possibly inhibited due to the lack of adsorption sites. Thus the rate-determining step for the first consecutive reaction changes from the oxidative removal of CO_{ad} to CO_{ad} formation. Methanol oxidation via adsorbed CO becomes low again relative to methanol oxidation via dissolved intermediates which leads to the drop in the current efficiency of formed CO_2 as well as faraday current.

At present the optimal ratio Ru/Pt is still not definitely established but it was assumed by several authors that a Pt-Ru electrode with a low Ru content ca. 10% has the highest activity for methanol electrooxidation.[4] Howev-

er they used the peak current in CVs to evaluate the catalytic activity. Their potential step experiments showed that at the low potentials Pt-Ru electrode with the Ru coverage of 0.33 reveals the highest activity for methanol electrooxidation. Iudice de Souza et al.[5] found that at room temperature Pt-Ru $\vartheta_{Ru} \approx 0.25$ layer electrodeposited on gold substrates has the highest activity for methanol oxidation. Iwasita et al.[6] studied the electrooxidation of methanol on Pt 111 /Ru electrodes with different Ru coverage and found that a maximum of high catalytic activity was observed between 10% and 40%. These results are consistent with the results of this work. However it seems that the optimal ratio Ru/Pt varies with the different preparation of Pt-Ru electrodes i.e. co-deposition ad-atom alloy and carbon supported Pt-Ru colloid. Ru distribution and segregation on the surface appears to play a roll on the optimal ratio Ru/Pt. In addition methanol concentration and temperature do also affect the optimum Pt-Ru composition.[4,16] Ross' group[4] has ever proposed a model for the catalytic effect of Ru on methanol oxidation a surface structure possessing one Ru neighboring three Pt sites represents the optimum geometry for methanol oxidation. According to this optimum alloy surface composition of ~10 atomic% Ru for the electrooxidation of methanol was predicted. The result of this work does not support such a prediction. It seems that such an ideal ordered surface structure as proposed does not formed in real Pt-Ru system. In addition this model is based on the assumption that methanol oxidation proceeds only via adsorbed CO and the dissociative adsorption of methanol is the rate-determining step for methanol oxidation on Pt-Ru electrodes. The electron effect of Ru on methanol adsorption was not considered either. In fact at the low potentials the oxidation of methanol adsorbates could also control the methanol oxidation on Pt-Ru electrodes.[6]

In general under present experimental condition Pt-Ru electrode with a small coverage of Ru $\vartheta_{Ru} \approx 0.3$ has the highest catalytic activity for methanol electrooxidation i.e. faraday current and the current efficiency of CO_2 at the low potentials reach to the maximum.

Acknowledgement

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