

## Electrochemical oxidation of methanol on Pt<sub>3</sub>Co bulk alloy

S. LJ. GOJKOVIĆ<sup>#</sup>

*Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, P. O. Box 3503,  
11120 Belgrade, Serbia and Montenegro*

(Received 15 July 2003)

*Abstract:* The electrochemical oxidation of methanol was investigated on a Pt<sub>3</sub>Co bulk alloy in acid solutions. Kinetic parameters such as transfer coefficient, reaction orders with respect to methanol and H<sup>+</sup> ions and energy of activation were determined. It was found that the rate of methanol oxidation is significantly diminished by rotation of the electrode. This effect was attributed to the diffusion of formaldehyde and formic acid from the electrode surface. Stirring of the electrolyte also influenced the kinetic parameters of the reaction. It was speculated that the predominant reaction pathway and rate determining step are different in the quiescent and in the stirred electrolyte. Cobalt did not show a promoting effect on the rate of methanol oxidation on the Pt<sub>3</sub>Co bulk alloy with respect to a pure Pt surface.

*Keywords:* methanol, electrochemical oxidation, Pt<sub>3</sub>Co alloy, direct methanol fuel cell.

### INTRODUCTION

Methanol oxidation is an important electrochemical reaction from both practical and fundamental aspects because it is the anodic reaction in direct methanol fuel cells (DMFC) and a prototype of the oxidation of small organic molecules. The main features of the reaction and also the main obstacles for its application are the high overpotential needed in order to oxidize methanol at a measurable rate and the deactivation of all electrocatalysts with time. Methanol oxidation has been extensively investigated since the early 70's with two main topics: identification of the reaction intermediates, poisoning species and products, and modification of Pt surface in order to achieve higher activity at lower potentials and better resistance to poisoning. The results have been reviewed by several authors.<sup>1–5</sup>

Intermediates that have been identified by infrared spectroscopy,<sup>6–10</sup> electrochemical thermal desorption mass spectroscopy (ECTDMS)<sup>11,12</sup> and differential electrochemical mass spectrometry (DEMS)<sup>13–15</sup> are (C, O) species, which can be linearly or bridge bonded CO<sub>ads</sub>,<sup>6–11</sup> and (C, H, O) species, suggested to be CHO<sub>ads</sub><sup>15</sup> and COH<sub>ads</sub>.<sup>10,13,14</sup> Evidence of the methoxy CH<sub>3</sub>O<sub>ads</sub> intermediate was also found.<sup>9</sup> The main reaction product is CO<sub>2</sub>,<sup>16</sup> although significant amounts of formaldehyde<sup>17,18</sup> formic acid<sup>16</sup> and

<sup>#</sup> Serbian Chemical Society active member.

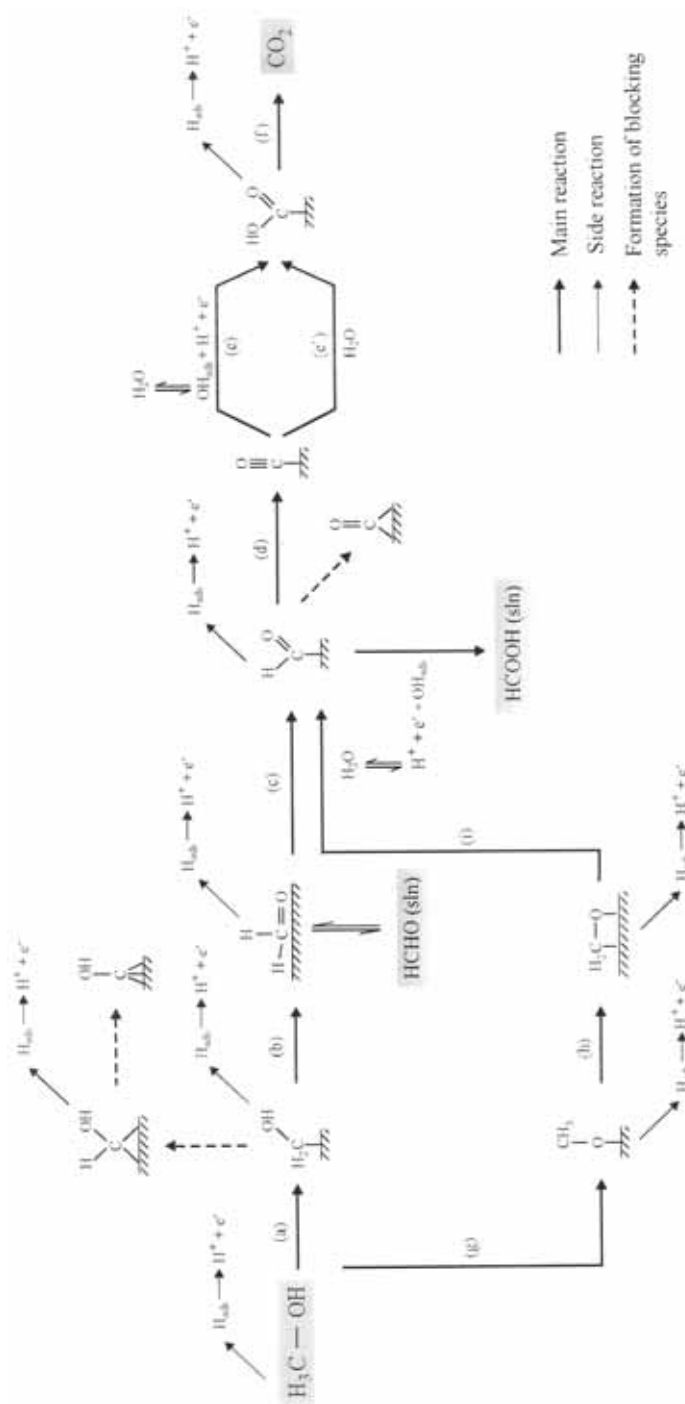


Fig. 1. Reaction pathways of methanol oxidation on a Pt surface.

methyl formate<sup>18,19</sup> were also detected. Some of the possible reaction steps for methanol oxidation that can be envisaged from the above mentioned intermediates and the products are given in Fig. 1.

Platinum is the most active metal for dissociative adsorption of methanol, but the potential where it adsorbs OH species, which are necessary for the oxidation of adsorbed methanol residues, is too high for the application of a single Pt electrocatalyst in a DMFC. Consequently, bimetal catalysts have been developed among which Pt–Ru was proved to be the best choice until now. However, Pate *et al.*<sup>20</sup> recently reported that the activity of a carbon supported Pt–Co catalyst approaches that of a Pt–Ru electrocatalyst at elevated temperatures. In the present paper, methanol oxidation was investigated on well defined smooth bulk Pt<sub>3</sub>Co alloy in acid solutions. The kinetic parameters and energy of activation of the reaction were determined in a quiescent and in a stirred electrolyte. A mass transfer effect on the reaction kinetics was found and correlated with a possible reaction pathway.

#### EXPERIMENTAL

A thermally prepared Pt<sub>3</sub>Co alloy electrode (prepared and characterized at Lawrence Berkeley National Laboratory, Berkeley, CA) was used in this study. A bulk composition of 75 % Pt was determined by means of X-ray fluorescence spectroscopy.

A disk electrode (0.127 cm<sup>2</sup> geometric surface area) was fabricated from the alloy and used in a rotating disk assembly (Tacussel). Prior to the experiment, the electrode surface was polished with an aqueous suspension of 0.05 μm Al<sub>2</sub>O<sub>3</sub>, then rinsed and ultrasonicated for 5 min in high purity water. In order to prevent possible changes in the surface composition of the alloy, the usual potential cycling of the electrode in the supporting electrolyte was not performed. Instead, the electrode was set into the methanol containing electrolyte under potential control and a positive going potential sweep at 1 mV s<sup>-1</sup> was immediately started. The starting potential was just at the beginning of hydrogen evolution and its value was adjusted for each supporting electrolyte concentration (*e.g.*, +20 mV vs. SHE in 0.1 M HClO<sub>4</sub> solution).

A standard glass cell was used with a Pt spiral as the counter electrode and a saturated calomel electrode as the reference electrode. All the potentials reported in this paper are expressed on the scale of the standard hydrogen electrode (SHE). The electrolyte contained 0.02 to 1 M HClO<sub>4</sub> as a supporting electrolyte and 0.01 to 1 M CH<sub>3</sub>OH. All solutions were prepared with high purity water (Millipore, 18 MΩ cm resistance). The electrolyte was deaerated by bubbling with N<sub>2</sub>, which had previously been purified by passing through an ammonium-metavanadate solution. When the polarization curves were recorded on a stationary electrode, the stream of N<sub>2</sub> was passed over the electrolyte in order to have complete quiescent conditions. The cell was thermostated at 25.0 to 45.0 °C. A potentiostat PAR 273A and an X–Y recorder Philips PM 8143 were used in all experiments.

#### RESULTS

The cyclic voltammogram of the Pt<sub>3</sub>Co alloy in 0.1 M HClO<sub>4</sub> solution in the potential window relevant to methanol oxidation is given in Fig. 2. No current indicating dissolution of Co was observed, which nominated the alloy as a potential anode catalyst. Hydrogen adsorption/desorption peaks are present on the voltammogram but they do not have fine structure as on pure Pt. This demonstrates that alloying with Co not only reduces the number of Pt atoms on the electrode surface but also changes its ability for underpotential deposition of hydrogen atoms. This is in accordance with the results of Marković *et al.*<sup>21</sup> who compared voltammograms of Pt<sub>3</sub>Co and Pt materials prepared in the same way in the same laboratory.

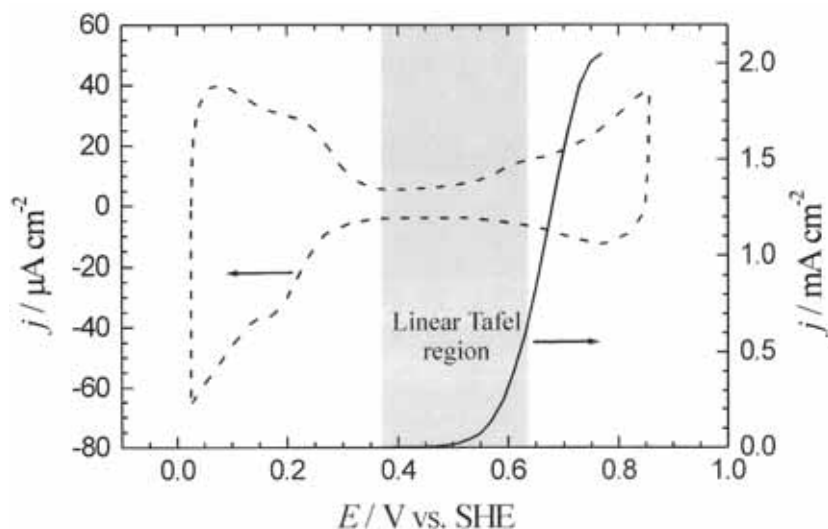


Fig. 2. Cyclic voltammogram of Pt<sub>3</sub>Co alloy in 0.1 M HClO<sub>4</sub> solution recorded at 20 mV s<sup>-1</sup> (dashed line) and the polarization curve for methanol oxidation in 0.1 M HClO<sub>4</sub> + 0.1 M CH<sub>3</sub>OH solution recorded at 1 mV s<sup>-1</sup> (solid line).

The polarization curve for the oxidation of 0.1 M methanol in 0.1 M HClO<sub>4</sub> is also presented in Fig. 2. The reaction starts at  $\approx 0.37$  V, which is in the double layer region of Pt and reaches a maximum rate at  $\approx 0.75$  V when the electrocatalyst is substantially oxidized. These two characteristic potentials are the same as on a pure Pt electrocatalyst,<sup>22</sup> which means that, at least at room temperature, Co does not improve the electrocatalytic properties of Pt.

It was reported earlier<sup>23</sup> that the open circuit potential of a Pt electrode in a methanol containing solution was more negative on a stationary electrode than on a rotating one. Also it was established<sup>22,24</sup> that the methanol oxidation current on Pt decreased when the electrode was rotated. The same phenomena were observed on the Pt<sub>3</sub>Co electrode and investigated in details in this work. Figure 3 presents the Tafel plots for methanol oxidation on a stationary disk electrode and on a disk electrode rotating at 1000 rpm in electrolytes containing 0.01 to 1 M methanol in 0.1 M HClO<sub>4</sub> at 30 °C. Several characteristics of these Tafel plots deserve attention. Methanol oxidation is strongly suppressed by the rotation of the electrode. No significant influence of the rotation rate of the electrode was found, *i.e.*, the current densities on the electrode rotating between 500 and 2000 rpm were the same within experimental error. The difference between the reaction rate in a quiescent and in a stirred solution is much more pronounced in the electrolytes with low methanol concentration than in more concentrated solutions. The onset of the reaction in the stirred electrolyte is shifted towards more positive potentials compared to the quiescent electrolyte. Well defined linear Tafel regions were obtained in both cases, but with different slopes. In the quiescent electrolytes, the Tafel slope changed from 75 to 90 mV dec<sup>-1</sup> when the methanol concentration was increased from 0.01 to 1 M. It should be noted that a Tafel

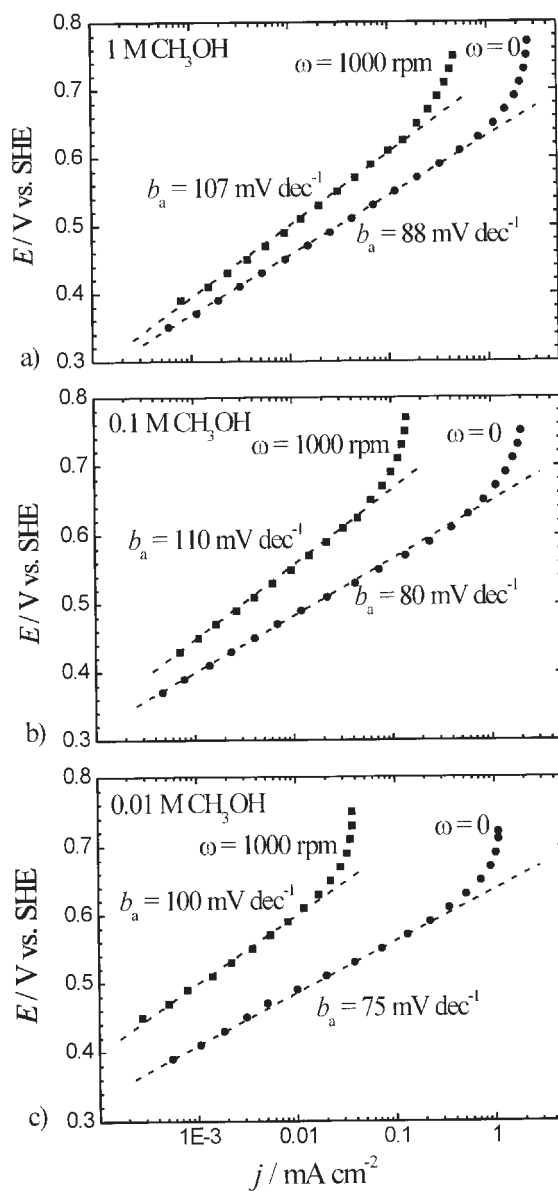


Fig. 3. Methanol oxidation in quiescent and stirred electrolytes containing 0.1 M HClO<sub>4</sub> and different concentration of methanol at 30 °C.

slope of 90 mV dec<sup>-1</sup> was also obtained on a pure Pt surface in 0.1 M methanol solution.<sup>22</sup> However, in the stirred electrolytes, the Tafel slope was 100–110 mV dec<sup>-1</sup> without systematic dependence on the methanol concentration. The end of the Tafel-like behavior at  $\approx 0.64$  V coincides with the plateau of the first step in the oxidation of the catalyst (Fig. 2). At more positive potentials when the catalyst is more oxidized, probably to Pt(OH)<sub>2</sub>, the increase of the methanol oxidation rate with potential becomes slower and finally a

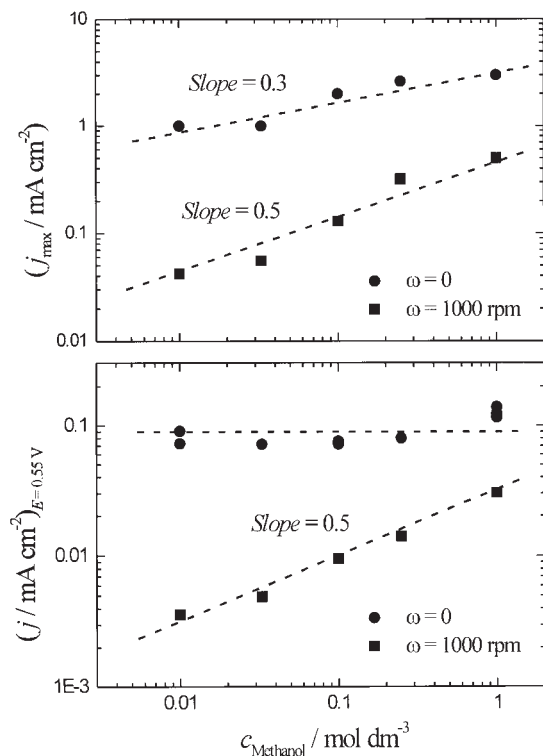


Fig. 4. Dependence of the methanol oxidation rate on the methanol concentration in quiescent and stirred electrolytes containing 0.1 M  $\text{HClO}_4$  at 30 °C. Top – maximum current densities and bottom – current densities in the Tafel region.

maximum current density is reached, which is followed by a decrease in the reaction rate (not shown in Figs. 2 and 3).

The influence of the methanol concentration on the reaction rate is summarized in Fig. 4 where the current densities at 0.55 V (approximately in the middle of the linear Tafel region) and the maximum current densities in both quiescent and stirred electrolytes are plotted as a function of methanol concentration. The reaction order with respect to methanol is 0.5 in the stirred electrolyte and the same value was calculated from the maximum current values. In the quiescent electrolytes the reaction rate is independent of the methanol concentration in the Tafel region and only slightly dependent at the maximum of the polarization curve. The potentials of the maximum on the polarization curves slightly increased with increasing methanol concentration, both in the quiescent and in the stirred electrolytes.

The influence of the concentration of  $\text{H}^+$  ions was investigated in electrolytes containing 0.1 M methanol and different concentration of  $\text{HClO}_4$  at 30 °C. The Tafel slopes in the stirred electrolytes were about  $110 \text{ mV dec}^{-1}$ , irrespective of the  $\text{HClO}_4$  concentration, while in the quiescent electrolytes its value increased from  $75 \text{ mV dec}^{-1}$  in 0.02 M to  $105 \text{ mV dec}^{-1}$  in 1 M  $\text{HClO}_4$ . Increasing the concentration of  $\text{HClO}_4$  led to a decrease in the methanol oxidation rate. The current densities at 0.55 V are plotted as a function of  $\text{HClO}_4$  concentration in Fig. 5. The influence of  $\text{H}^+$  ion concentration on the reaction rate is similar

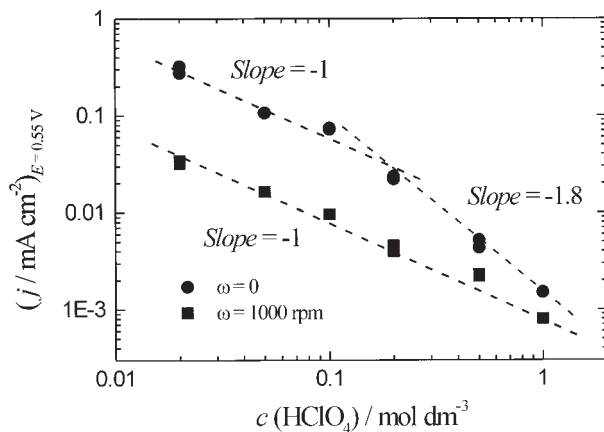


Fig. 5. Dependence of the methanol oxidation rate on the concentration of  $\text{HClO}_4$  in quiescent and stirred electrolytes containing 0.1 M methanol at 30 °C.

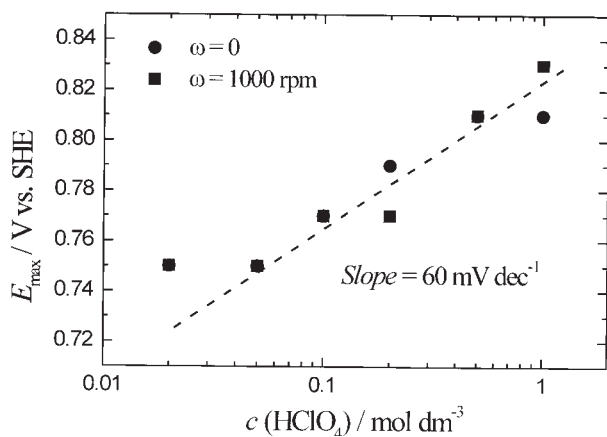


Fig. 6. Potential of the maximum of the polarization curve for methanol oxidation at 30 °C as a function of  $\text{HClO}_4$  concentration. Methanol concentration = 0.1 M.

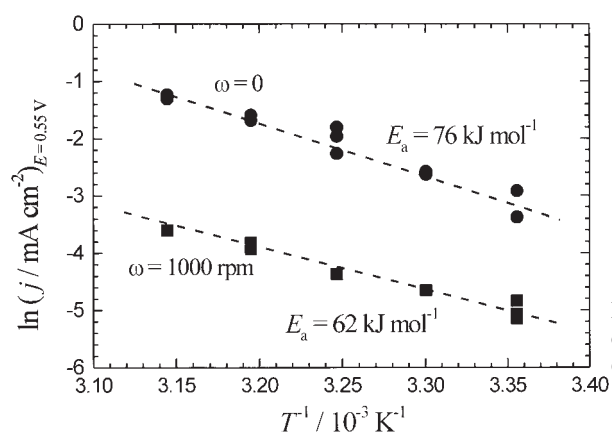


Fig. 7. Arrhenius plots for methanol oxidation in 0.1 M  $\text{HClO}_4$  + 0.1 M  $\text{CH}_3\text{OH}$  electrolyte.

in both the quiescent and stirred electrolytes, with the exception that in the first case the decrease in the current densities becomes steeper when the concentration of  $\text{HClO}_4$  is higher than 0.1 M. The reaction order with respect to  $\text{H}^+$  ions was calculated to be above  $-1$ . The potentials where the polarization curves reach their maximum are also dependent on the  $\text{HClO}_4$  concentration. Although the potentials of the maximum were not very reproducible, they were shifted toward more positive values with increasing  $\text{HClO}_4$  concentration and as shown in Fig. 6, a line with a slope of  $60 \text{ mV dec}^{-1}$  can be drawn, irrespective of the rotation of the electrode.

Polarization curves for methanol oxidation in an electrolyte containing 0.1 M methanol and 0.1 M  $\text{HClO}_4$  were recorded in the temperature range from 25 to 45 °C. No significant shift in the onset of the methanol oxidation with temperature was observed. Over the entire temperature range, Tafel plots with slopes of  $80 \text{ mV dec}^{-1}$  were obtained. The corresponding Arrhenius plots for 0.55 V in the quiescent and stirred electrolytes are given in Fig. 7. An activation energy of about  $76 \text{ kJ mol}^{-1}$  was estimated for the quiescent electrolyte and  $62 \text{ kJ mol}^{-1}$  for the stirred electrolyte.

#### DISCUSSION

Methanol oxidation on  $\text{Pt}_3\text{Co}$  bulk alloy is similar to that on pure Pt electrocatalyst. The reaction begins when hydrogen is desorbed from the electrode surface and attains a maximum rate when the Pt is significantly covered by an oxide, probably  $\text{Pt}(\text{OH})_2$ . Cobalt did not show a promoting effect on the potential of the onset of methanol oxidation.

Being a very slow reaction, the rate of methanol oxidation should not be limited by the mass transfer of methanol from the electrolyte toward the electrode surface. A simple calculation shows that the limiting diffusion current density for the oxidation of 0.1 M methanol in a quiescent electrolyte should be about  $50 \text{ mA cm}^{-2}$ , which is 25 times higher than the maximum current density observed in this solution (Fig. 3b). On the contrary, agitation of the electrolyte provoked a pronounced decrease in the current densities over the entire potential region. This indicates that some intermediate which can diffuse away from the electrode is involved in the reaction mechanism.

Before discussing this hypothesis, possible artifacts that could produce such an unusual effect of the electrode rotation on the methanol oxidation current have to be mentioned. The first possibility is some impurity in the electrolyte the adsorption of which is facilitated on the rotating electrode. The supporting electrolyte used in this work was  $\text{HClO}_4$  which could contain traces of  $\text{Cl}^-$  ions. However, Biegler<sup>24</sup> reported the same phenomenon, although his experiments were performed in  $\text{H}_2\text{SO}_4$  solutions and additional purification of the electrolyte had no influence on the effect. In this work, when the polarization curve was being recorded on a rotating electrode, the current increased when the rotation was stopped and decreased when the rotation was started again. This reversible effect of the rotation is also inconsistent with the influence of impurities. Recently Iwashita<sup>5</sup> pointed the necessity of thoroughly eliminating traces of oxygen in the electrolyte because the peroxide species produced



during oxygen reduction on Pt can oxidize adsorbed organic residues. However, the amount of oxygen in the electrolyte in this work was estimated to be  $< 10^{-6}$  M which is too low to act as a scavenger for some reactive intermediate in the oxidation of methanol. Moreover, Wasmus and Vielstich<sup>25</sup> showed that oxygen in the electrolyte can enhance the catalytic properties of Pt towards the oxidation of CO and methanol, because oxygen containing species are required for the removal of poisoning species formed during methanol oxidation. However, this effect was established when pure oxygen was bubbled through the electrolyte.

Hence, it seems that the lower current densities in the stirred electrolyte is genuine to methanol oxidation on Pt and similar electrocatalysts and that the phenomenon originates from a weakly adsorbed intermediate. Desorption of carbon monoxide can be ruled out, because  $\text{CO}_{\text{ads}}$  is a rather stable species that can survive removal of the electrode from the electrolyte, its transfer into a UHV chamber and re-immersion in the electrolyte.<sup>3</sup> According to the reaction scheme in Fig. 1, other species that can diffuse away from the electrode are formaldehyde and formic acid. Since both of them were detected in the electrolyte,<sup>16–18</sup> it is likely that they are responsible for the lower reaction rate when the electrode is rotated. The difference between the current density on a stationary electrode and that of a rotating one is more than an order of magnitude in electrolytes with a low methanol concentration, which is much larger than the difference in the number of electrons transferred when methanol is completely oxidized to  $\text{CO}_2$  and only partially to HCOH. This is an indication that the intermediate which diffuses away from the electrode surface is formed before the occurrence of the rate determining step (rds).

It is rather difficult to identify the rds in such a complex reaction as methanol oxidation where numerous intermediates, steps and pathways are possible (see Fig. 1). However, the negative reaction order with respect to  $\text{H}^+$  ion concentration can be attributed to the participation of  $\text{OH}_{\text{ads}}$  in the rds. Thus, the chemical steps



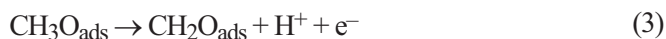
or



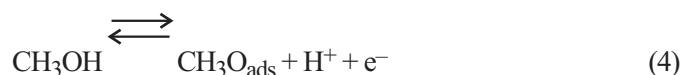
might be suggested as the possible rds. They should result in a Tafel slope of about 60 mV  $\text{dec}^{-1}$ , while the experimentally observed values were 75 to 90 mV  $\text{dec}^{-1}$  in the quiescent electrolytes. An explanation of this discrepancy cannot be proposed at the moment, except the complexity of the reaction mechanism with several adsorbed species, the surface coverage of which can be potential dependent and influence the Tafel behavior.

If step (1) is the rds, the desorption of HCOH should be the main cause of the current drop in stirred electrolyte, and if step (2) is the rds then both the desorption of HCOH and HCOOH could be responsible for this effect. On a stationary electrode, the diffusion of these species from the electrode surface is slow and a high coverage of  $\text{CHO}_{\text{ads}}$  or  $\text{CO}_{\text{ads}}$  is achieved, which is indicated by the zero reaction order with respect to methanol. However,

when the diffusion of HCOH and HCOOH is enhanced by rotation, the surface coverage of the participant in the rds is diminished to a medium value which results in a one-half reaction order with respect to methanol. The Tafel slope under these conditions is about 110 mV dec<sup>-1</sup> and also energy of activation is slightly changed. This leads to the assumption that the rds might be different in the stirred electrolyte. According to the scheme in Fig. 1, two pathways are conceivable for methanol oxidation. The first one is (a)–(f) and the other is (g)–(i)–(d)–(f). They take place in parallel up to the CHO<sub>ads</sub> intermediate, after which they merge into a single reaction sequence. Since the pathway (g)–(i)–(d)–(f) circumvents formaldehyde as an intermediate, it could be proposed that in the stirred electrolyte where HCOH leaves the vicinity of the electrode, pathway (g)–(i)–(d)–(f) becomes significant and even takes over the whole reaction. Under these conditions the electrochemical step

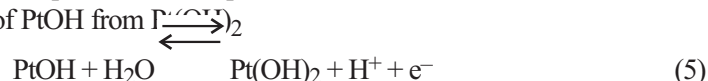


could be slow. The negative reaction order with respect to the concentration of H<sup>+</sup> ions is in accordance with this assumption because the formation of CH<sub>3</sub>O<sub>ads</sub> is dependent on the H<sup>+</sup> concentration:



A reaction order with respect to methanol of 1/2 and a Tafel slope of 110 mV dec<sup>-1</sup> indicate that the surface coverage of CH<sub>3</sub>O<sub>ads</sub> has a medium value and that it is independent of the potential.

The maximum on the polarization curve for methanol oxidation is in the potential region where Pt is substantially oxidized. A role of Pt(OH)<sub>2</sub> in the deactivation of the Pt surface is indicated by the dependence of the potential of the maximum on the H<sup>+</sup> concentration. The formation of PtOH from Pt(OH)<sub>2</sub>



follows the same dependence of a 60 mV per tenfold increase in the H<sup>+</sup> concentration as the maximum on the polarization curve of methanol oxidation (Fig. 6). Pt(OH)<sub>2</sub> is less active for the adsorption of methanol and this step becomes rate determining at more positive potentials, which results in the insensitivity of the reaction rate on the potential.

#### CONCLUSIONS

Cobalt does not show a promoting effect on the rate of methanol oxidation on Pt<sub>3</sub>Co bulk alloy with respect to a pure Pt surface. However, this statement should be reconsidered on nanoscale alloy particles.

The methanol oxidation rate is significantly diminished by rotation of the electrode in electrolytes containing a low concentration of methanol. This was ascribed to the diffusion of formaldehyde and formic acid from the electrode surface. Mass transfer effects on the reaction rate should also be investigated on nanoscale electrocatalysts. This is important because in the porous structure of gas diffusion electrodes all catalyst particles are not

evenly available to the fuel and some of them can operate at low methanol concentrations. In the optimization of the fuel flow in DMFC, one should be aware of a possible negative effect of convection on the methanol oxidation current.

The dependence of the methanol oxidation kinetics on the stirring of the electrolyte can help in the postulation of the reaction pathway. On the basis of the kinetic parameters of methanol oxidation and its dependence on the stirring of the electrolyte, it was speculated that the reaction on Pt<sub>3</sub>Co bulk alloy follows parallel pathways. In the quiescent electrolyte, the pathway which includes formaldehyde and formic acid is predominant. When the electrolyte is stirred, this reaction pathway is suppressed and the reaction occurs *via* CH<sub>3</sub>O<sub>ads</sub> as the intermediate.

*Acknowledgements:* The author is grateful to P. N. Ross, N. M. Marković and V. Stamenković from the Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, USA, for supplying the alloy used in this work and their kind contribution to its preparation and characterization. This work was financially supported by the Ministry of Science, Technology and Development of the Republic of Serbia, Contract No. 1796.

## ИЗВОД

ЕЛЕКТРОХЕМИЈСКА ОКСИДАЦИЈА МЕТАНОЛА НА ЛЕГУРИ Pt<sub>3</sub>Co

С. Љ. ГОЈКОВИЋ

*Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, б. бр. 3503, 11120 Београд*

Електрохемијска оксидација метанола је испитивана на легури Pt<sub>3</sub>Co у киселим растворима. Одређени су кинетички параметри реакције: коефицијент прелаза, редови реакције по метанолу и H<sup>+</sup> јону и енергија активације. Утврђено је да се брзина реакције значајно смањује када електрода ротира. Тај ефекат је приписан дифузији формалдехида и мравље киселине са површине електроде. Мешање електролита такође утиче на кинетичке параметре реакције. Дискутована је могућност да су доминантан реакциони пут и спори ступањ у механизму реакције различити у мирном и мешаном електролиту. Присуство кобалта у легури није утицало на повећање брзине оксидације метанола у поређењу са чистом платином.

(Примљено 15. јула 2003)

## REFERENCES

1. R. Parsons, T. VanderNoot, *J. Electroanal. Chem.* **257** (1988) 9
2. S. Wasmus, A. Kuver, *J. Electroanal. Chem.* **461** (1999) 14
3. T. Iwashita in *Advances in Electrochemical Science and Engineering, Vol. 1*, H. Gerisher, C. Tobias, Eds., VCH, 1990
4. T. D. Jarvi, E. M. Stuve, in *Electrocatalysis*, J. Lipkowski, P. N. Ross, Eds., Wiley-VCH, New York, 1998
5. T. Iwashita, *Electrochim. Acta* **47** (2002) 3663
6. B. Beden, C. Lamy, A. Bewick, K. Kunimatsu, *J. Electroanal. Chem.* **121** (1981) 343
7. P. A. Christensen, A. Hamnett, G. L. Troughton, *J. Electroanal. Chem.* **362** (1993) 207
8. T. Iwasita, F. C. Nart, *J. Electroanal. Chem.* **317** (1991) 291
9. M. I. S. Lopes, B. Beden, F. Hahn, J. M. Leger, C. Lamy, *J. Electroanal. Chem.* **313** (1991) 323
10. X. H. Xia, T. Iwashita, F. Ge, W. Vielstich, *Electrochim. Acta* **41** (1996) 711
11. W. Vielstich, P. A. Christensen, S. A. Weeks, A. Hamnett, *J. Electroanal. Chem.* **242** (1987) 327
12. S. Wilhelm, T. Iwashita, W. Vielstich, *J. Electroanal. Chem.* **238** (1987) 383
13. J. Willsau, O. Wolter, J. Heitbaum, *J. Electroanal. Chem.* **185** (1985) 163

14. T. Iwashita, W. Vielstich, E. Santos, *J. Electroanal. Chem.* **229** (1987) 367
15. J. Wilsau, J. Heitbaum, *Electrochim. Acta* **31** (1986) 943
16. T. Iwashita, W. Vielstich, *J. Electroanal. Chem.* **201** (1986) 403
17. C. Korzeniewski, C. Childers, *J. Phys. Chem. B* **102** (1998) 489
18. K. Ota, Y. Nakagava, M. Takahashi, *J. Electroanal. Chem.* **179** (1984) 179
19. Y. Jusys, J. Kaiser, R. J. Behm, *Electrochim. Acta* **47** (2002) 3693
20. T. Page, R. Johnson, J. Hormes, S. Noding, B. Rambabu, *J. Electroanal. Chem.* **485** (2000) 34
21. U. A. Paulus, A. Wokaun, G. G. Schere, T. J. Schmidt, V. Stamenković, N. M. Marković, P. N. Ross, *Electrochim. Acta* **47** (2002) 3787
22. S. Lj. Gojković, T. R. Vidaković, *Electrochim. Acta* **47** (2001) 633
23. D. M. Dražić, V. Dražić, *Electrochim. Acta* **11** (1966) 1235
24. T. Biegler, *Aust. J. Chem.* **26** (1973) 2571
25. S. Wasmus, W. Vielstich, *J. Appl. Electrochem.* **23** (1993) 120.