Short Communication

Methanol electro-oxidation on platinum and platinum–tin alloy catalysts dispersed on active carbon

Zidong Wei [a], Hetong Guo [b], Zhiyuan Tang [b]

[a] *Chemical Engineering Department, Shandong University of Technology, Jinan, 250061, People's Republic of China*
[b] *Applied Chemistry Department Tianjin University, Tianjin, 300072, People's Republic of China*

Abstract

Platinum and platinum–tin alloy dispersed on active carbon are used as the catalysts for methanol electro-oxidation. Gas chromatographic and X-ray powder diffraction analysis show that the co-existence of Pt/C and PtSn/C in the catalysts yields better catalysis for methanol electro-oxidation than Pt/C alone. The electrochemical behaviour of the electrodes made from catalysts Pt/C and Pt–PtSn/C are investigated, together with platinum black for purposes of comparison. A new intermediate species is suggested to be present in the methanol electro-oxidation.

Keywords: Methanol electro-oxidation; Fuel cells; Electrocatalysis; Platinum; Active carbon

1. Introduction

Methanol fuel cells are an attractive alternative to hydrogen–air cells. An ideal electrolyte for methanol should have high conductivity, produce no corrosion of either the cell or the catalyst materials, and participate in no detrimental side reactions. In this context, alkaline electrolytes offer superior electrochemical performance compared with acidic systems. Alkaline electrolytes react, however, with carbon dioxide produced from methanol oxidation to form carbonates that foul the electrodes. Consequently, most research has been focused on acidic electrolyte systems [1–5].

In turn, corrosion-resistant catalysts and supports are required. Platinum seems to be the only material that has a significant amount of activity as well as stability for methanol electro-oxidation in acidic electrolytes. Unfortunately, methanol and mediates formed during methanol electro-oxidation adsorb on the platinum surface and effectively block the active sites. This causes a rapid decay in the initially high dehydrogen current. Considerable effort has been devoted to eliminate the poisoning effect. One strategy is to modify the platinum surface by under-potential deposition (UPD) of a foreign metal [1,3,6]. Janssen and Moolhuysen [6] summarized the UPD effects of 26 foreign metals on smooth platinum for methanol electro-oxidation. Results showed that the UPD of tin and ruthenium gave, respectively, 100 and 25 times more catalytic activity than platinum alone. It should

be pointed out, however, that this significant increase in catalysis was obtained on a smooth platinum sheet. The effective surface area of such an electrode is quite low. The current of methanol electro-oxidation is still too low for commercial usage.

Aramata and Masuda [7] and Swathirajan and Mikhail [8] reported the oxidation of methanol on platinum–tin alloy dispersed on different polymers. The adoption of high surface-area substrates in these two studies is an advancement on the use of smooth platinum. Various types of carbon material have been examined [9,10] as a support for platinum particle catalysts. In this communication, we discuss the electrochemical oxidation behaviour of methanol on platinum–tin catalysts dispersed on active carbon. Experiments have also been carried out on a platinum black electrode for the purposes of comparison. Gas chromatography is used to detect the results of methanol oxidation, and X-ray powder diffraction is employed to determine the composition of the platinum–tin catalyst powder. The optimum composition of the catalysts is obtained and a new intermediate species is deduced.

2. Experimental

2.1. Pt/C catalyst preparation

A solution of chloroplatinic acid ($H_2PtCl \cdot 6H_2O$) that contains the required amount (in wt.%) of platinum is taken
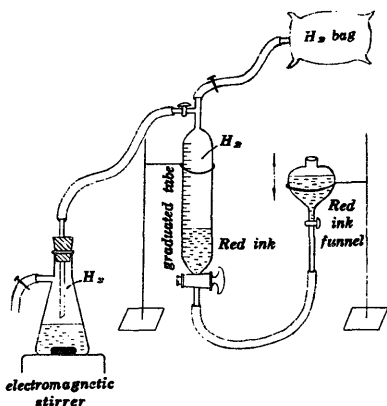
Fig. 1. Apparatus for Pt/C synthesis with hydrogen as a reducer.

from a 1% stock solution. Citric acid is added as a competitive adsorbant (the concentration of citric acid is controlled at ~0.08 M). To this mixture, the appropriate quantity of CO_2-treated active carbon (BET area: 500 m^2 g^{-1}) is added and mixed thoroughly by ultrasonic blending for 8 h. Platinum ions in the resulting slurry are reduced by hydrogen using the apparatus shown schematically in Fig. 1. The reaction is maintained until H_2 is no longer consumed. This can be observed through the movement of red dye in the graduated tube (Fig. 1). The mixture is filtered and washed with de-ionized water to pH: 6.5. The solid collected is then dried at 120 °C in a nitrogen stream. The carbon-supported platinum catalyst thus prepared contains 10 wt.% platinum.

2.2. Preparation of Pt–Sn/C alloy catalyst

The required amount of Pt/C catalyst is dispersed in de-ionized water. To this slurry is added an aqueous solution of $SnCl_2 \cdot 2H_2O$ with vigorous stirring. After adjusting the pH to 8.0 by slowly adding a dilute aqueous solution of hydrazine, stirring is continued for 2 h in order to deposit tin on the supported platinum catalyst. The resulting slurry is filtered and the solid collected is dried at 120 °C in a nitrogen atmosphere.

2.3. Electrode preparation

The catalysts are slurried with 2-propanol. Next, the required amount of Teflon emulsion is added with vigorous stirring for 30 min. The final slurry is spread on a support membrane made of graphite paper (previously wet-proofed with Teflon) to provide a platinum loading of 1.0 mg cm^{-2} of electrode area. The final electrode is pressed slightly and dried in air at 120 °C for 10 min and then sintered in air at 320 °C for 12 min.

2.4. Measurement

Polarization curves for methanol electro-oxidation are obtained galvanostatically in a nitrogen saturated 1 M $CH_3OH/2.5$ M H_2SO_4 solution at 60 °C and are not *IR* corrected. The counter electrode is a platinized platinum sheet. An Hg/Hg_2SO_4 electrode served as the reference electrode and has a potential of 0.68 V versus SHE.

X-ray diffraction (XRD) measurement is performed with a D/Max-A (Kigak Co. Jp) apparatus. Gaschromatography measurement is carried out with a GC-500 gaschromatography meter (Varian Co. US).

3. Results

3.1. Catalytivity of catalyst powder

It is important to predict the activity of the catalyst powder before it is fabricated into an electrode. It is also time-saving to abandon those catalyst powders that show poor catalytic ability. The following experiment is designed to examine the activity of catalyst powder. The catalyst powder is added to a 1% methanol aqueous solution into which oxygen is bubbled for 5 h at 40 °C. Methanol will be oxidized in the presence of the catalyst. The extent of methanol oxidation depends strongly on the activity of the catalyst powder. The resulting solution was analysed with a GC-500 gaschromatograph. The results are summarized in Table 1, where *RT* represents the residence time of the component in the chromatograph tube. The percentage of peak area corresponding to *RT* is calculated. The dependence of the relative rate of methanol oxidation on the tin content in the catalyst powder is illustrated in Fig. 2. It is apparent that the oxidation of methanol depends markedly on the catalyst. The oxidation of methanol does not take place in the absence of catalyst. The tin content has an optimum value for methanol oxidation near 4 wt.%. The XRD spectra of the catalyst powders (Fig. 3) show that almost all of the platinum in the 10%Pt–10%Sn/C catalyst is alloyed with tin. By contrast, only part of the platinum in the 10%Pt–3.3%Sn/C catalyst is alloyed with tin. The latter catalyst
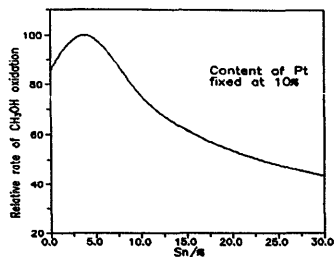

Fig. 2. Dependence of relative rate of methanol oxidation on tin content in Pt–Sn/C catalyst.

Table 1
Influence of catalyst type on methanol oxidation

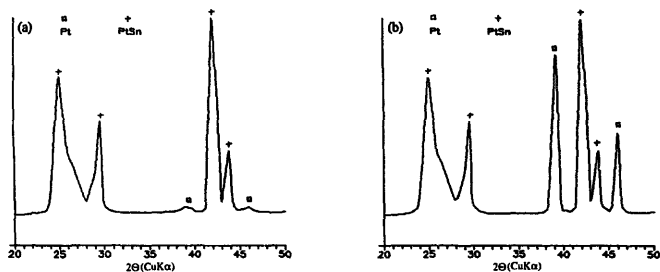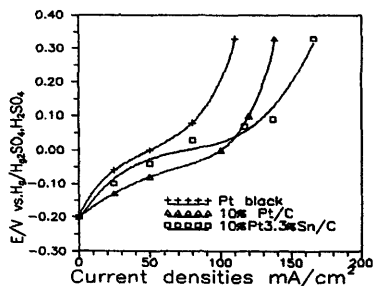| Residence time	Area of chromatographic peak (%)					Compound corresponding to residence time
(min)	no catalyst	10%Pt/C	10%Pt–10%Sn/C	10%Pt–3.3%Sn/C	10%Pt–30%Sn/C	
2.90	100	14.8	24.5	0	56.4	methanol
3.39	0	85.2	75.5	0	43.6	formaldehyde
5.04	0	0	0	100	0	to be detected

Fig. 3. XRD spectra for: (a) 10%Pt–10%Sn/C, and (b) 10%Pt–3.3%Sn/C.

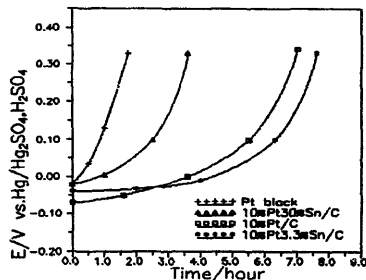Fig. 4. Current–potential profiles for methanol oxidation in 2.5 M H_2SO_4 and 1 M CH_3OH at 60 °C on electrodes made from given catalysts.

Fig. 5. Potential–time function for methanol electro-oxidation at current density of 50 mA cm^{-2} in 2.5 M H_2SO_4 and 1 M CH_3OH at 60 °C on electrode made from given catalysts.

exhibits better activity for methanol oxidation. This means that the co-existence of platinum and PtSn alloy is beneficial for methanol oxidation.

3.2. Methanol electro-oxidation

Methanol electro-oxidation on the prepared electrodes is shown in Fig. 4, together with data for platinum black. The short-term polarization behaviour of electrodes made from 10%Pt/C and 10%Pt–3.3%Sn/C has much lower overpotentials than that made from platinum black. The lifetime test is shown in Fig. 5. Compared with the rapid decay of the platinum black electrode, the electrodes made from 10%Pt/C and 10%Pt–3.3%Sn/C exhibit considerable improvement

in terms of life. By contrast, the electrode made from 10%Pt–3.3%Sn/C gave only slightly better lifetime performance than the electrode from 10%Pt/C. This is identical with the observation of direct methanol oxidation by oxygen in the presence of catalyst powder. An increased content of tin in Pt–Sn/C alloy catalysts improves the electrode catalysis for methanol electro-oxidation.
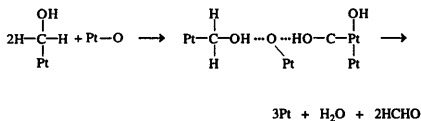
3.3. Mechanism of the reaction

According to Goodenough and Hamnett [2], four bound species are present on platinum during the electro-oxidation of methanol. These species are:

OH	H	Pt	
$|$	$|$	$|$	
Pt—C—Pt	O=C	O=C	O=C—Pt
$|$	$|$	$|$	
Pt	Pt	Pt	
1	**2**	**3**	**4**
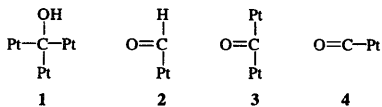
Given that formaldehyde is detected in the oxidized solution of methanol (see Table 1), a fifth bound species should be present on the platinum. It may be formed through the following reaction:

$$CH_3OH + Pt \longrightarrow \begin{array}{c} OH \\ | \\ H-C-H \\ | \\ Pt \end{array} + H^+ + e^-$$
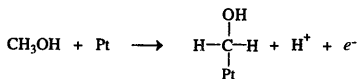
In the presence of oxide-rich platinum (expressed as Pt–O), the fifth species is oxidized to formaldehyde:

$$2H-\begin{array}{c} OH \\ | \\ C \\ | \\ Pt \end{array}-H + Pt-O \longrightarrow Pt-\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}-OH \cdots O \cdots HO-\begin{array}{c} OH \\ | \\ C \\ | \\ Pt \end{array}-Pt \longrightarrow$$

$$3Pt + H_2O + 2HCHO$$

In order to explain the enhanced activity of Pt/C when tin is present, a very common view is that tin in the platinum surface weakens the adsorption of stable media ≡C–OH and =C=O [11]. Obviously, further study is required to understand the complete mechanism of methanol electro-oxidation.

4. Conclusions

Platinum and platinum–tin alloy dispersed on active carbons enhance methanol electro-oxidation. The co-existence of platinum and platinum–tin alloy on active carbons exhibits better catalysis than either platinum alone on active carbons or bulk platinum electrodes. It is recommended that the content of tin in the mixed catalysts is kept below 4 wt.%, relative to the amount of active carbon.

References

[1] S.-R. Wang and F. Peters, J. Electrochem. Soc., 139 (1992) 2519.
[2] J.B. Goodenough and A. Hamnett, Electrochim. Acta, 32 (1987) 1235.
[3] A. Aramata, T. Kodera and M. Masuda, J. Appl. Electrochem., 18 (1988) 577.
[4] M. Watanabe, M. Uchida and S. Motoo, J. Electroanal. Chem., 229 (1987) 395.
[5] K. Ota, Y. Nakagawa and M. Takashi, J. Electroanal. Chem., 179 (1984) 179.
[6] M.M. Janssen and J. Moolhuysen, Electrochim. Acta, 21 (1976) 861; 21 (1976) 869.
[7] A. Aramata and M. Masuda, J. Electrochem. Soc., 138 (1991) 1949.
[8] S. Swathirajan and Y.M. Mikhail, J. Electrochem. Soc., 139 (1992) 2105.
[9] Z. Wei, A Study on electrocatalysts of fuel cells and the mass transfer in air electrode, Thesis, Tianjin University, People's Republic of China, 1993, p. 21.
[10] Z. Wei, H. Guo and Z. Tang, J. Power Sources, 52 (1994) 123.
[11] G. Kokkindis, J. Electroanal. Chem., 201 (1986) 211.