Effect of Molybdenum and Tungsten on the Activity of Pt/ceramic Membrane Electrodes for Anodic Oxidation of Alcohol*

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Abstract: A new type of ceramic-based electrode that could be utilized in anodic oxidation of alcohol was prepared by electrodepositing platinum onto a ceramic membrane. Tungsten and molybdenum were incorporated into the electrode by immersing the membrane in a sol of tungsten oxide or tungstosilicic acid or silicomolybdic acid. The tungsten and molybdenum promoted the activity of the electrode to a considerable degree. The current density of the Pt-Mo-Si/C/M electrode could be as high as 187 mA/cm^2 during the oxidation of methanol, and it was five times more active than that of Pt/C/M at the same working conditions. Similar results were obtained in the oxidation of ethanol.

Key words: anodic oxidation; alcohols; molybdenum; membrane; electrode
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1 Introduction

Anodic oxidation of alcohol currently attracts much attention, since the direct methanol fuel cell is recognized as one of the most promising vehicular power systems of the future. Generally the oxidation of methanol on the anode is more difficult than the anodic oxidation of hydrogen, and the oxidation of ethanol is more difficult than methanol. Platinum was demonstrated as the most active catalyst, but it is easy poisoned by the intermediates of methanol oxidation[1]. Ruthenium was found to be a good promoter of platinum catalysts because it could prevent the poisoning of the catalyst, but the activity of Pt – Ru catalysts still needs to be improved as their performance is not yet high enough for real application. It was reported by some researchers that the addition of tungsten could improve the activity significantly[2]. Although there are some reports about promotion with tungsten, no reports about using molybdenum as promoter has been found yet.

It is widely recognized that the anodic oxidation of ethanol is much more difficult than that of methanol, therefore methanol but not ethanol is considered for use as the fuel of choice for fuel cells. If the anodic oxidation of ethanol could easily be realized, a new type of fuel, which has many more advantages than methanol, may be used as the fuel of choice for fuel cells.

In the present work, the effect of addition of molybdenum or tungsten on the electrochemical activity of a ceramic based membrane electrode was investigated for the anodic oxidation of methanol and ethanol, and some important and interesting results were obtained.

2 Experimental

The ceramic membrane used as substrate is a type of extra thin alumina-zirconia membrane with a stainless steel mesh frame. The electrode was prepared as follows. Firstly, the substrate was carbonized in a tubular furnace in a flow of liquid petroleum gas (LPG) at 900 ℃, in order to render it conductive. An alternative method used was to sputter a gold film on the surface of the membrane. Thus, it was possible to avoid the high temperature treatment to the membrane, as in the case of proton conductive membranes, a high temperature treatment would cause the loss or partial loss of conductivity. Secondly, the membrane was treated with a silicomolybdic or a tungstosilicic acid solution or a tungsten sol, which was followed by air drying and then drying at 110 ℃ for 24 hours in an oven. Thirdly, platinum or platinum ruthenium alloy was electroplated upon the membrane surface in a bath of either platinum or a mixture of platinum and ruthenium.

The evaluation of the activity of electrodes for the anodic oxidation of methanol was carried out on an AUTO LAB PGST-30 potentiostat/ galvanostat (ECO Chemie B V, The Netherlands) at room temperature. Potentiostatic

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scans, including linear and cyclic scans, were performed. A platinum wire was used as counter electrode and a saturated calomel electrode (SCE) was used as reference electrode. The electrolyte solution used in the present work was composed of 0.5 mol/L H_2SO_4 or Na_2SO_4 and 0.5 mol/L methanol or ethanol, and all potentials were presented in the SCE scale.

The electrode was characterized by SEM and EDS on an S-650 Electron Micrograph (Hitachi, Japan) fitted with an EDX-4 electron dispersed spectrometer (United State).

3 Results

It was found that the addition of tungsten and molybdenum could improve the activity of electrodes for the oxidation of methanol and ethanol greatly. As shown in Fig. 1, the peak current density of the molybdenum modified electrode for the oxidation of methanol could be as high as 187 mA/cm^2, which is almost five times more than that of a Pt/C/M electrode. A current density of 93 mA/cm^2 was achieved in the case of the tungsten modified electrode, almost two times more than that of the Pt/C/M electrode. All these results show that the addition of tungsten and molybdenum could improve the performance of electrodes significantly.

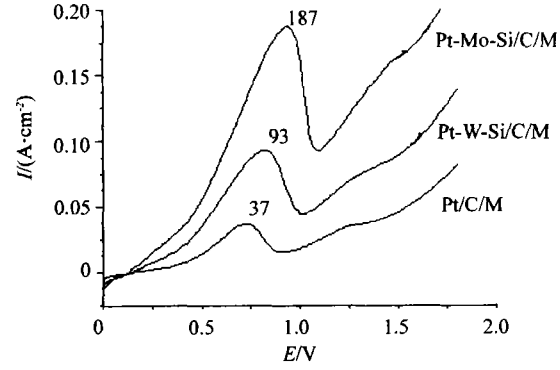


Fig.1 Comparison of the electrochemical activity of electrodes

Even to the anodic oxidation of ethanol, good results also are achieved by addition of tungsten and molybdenum. The newly prepared electrodes were applied in the anodic oxidation of ethanol and exciting results were achieved as is shown in Fig. 2. In contrast to the oxidation of methanol where a single peak was observed, the oxidation of ethanol shows two peaks. Again, in the case of the Pt/C/M electrode, the current density was less than 20 mA/cm^2 during the oxidation of ethanol; thus only half of that observed during the oxidation of methanol under similar conditions.

The addition of tungsten and molybdenum could raise the current density to 50 mA/cm^2 and 100 mA/cm^2 respectively. Hence, the addition of tungsten and molybdenum could enhance the activity of the electrode greatly in the anodic oxidation of ethanol.

It is interesting that the activity of the Pt-W/C/M electrode was not enhanced but decreased when the addition of tungsten was carried out by treating the membrane with a solution of sodium tungstate, and we have not got an exact explanation for this phenomenon yet.

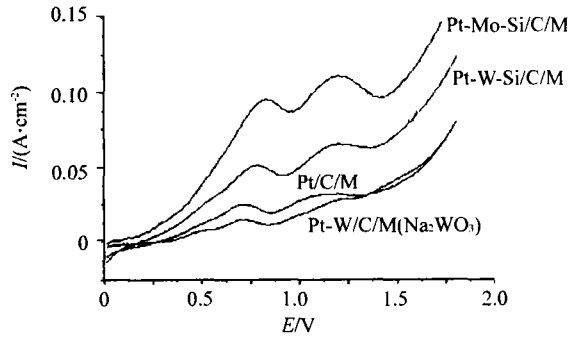


Fig.2 Effects of temperature and molybdenum on the electro oxidation of ethanol

At present we know a very little bit to the mechanism of promotion of Mo, but we have studied the morphology of the Pt-W-Si/C/M electrode by SEM and the surface composition by EDS. It was found that the addition of tungstosilicic acid resulted in an effective particle distribution and morphology of the active component. It was determined by EDX analysis that the addition of tungsten could enhance the percentage of Pt atoms on the surface of the electrode.

About the mechanism of promotion of molybdenum, it will be the important object of our future research works.

As is shown in Fig. 3, the activity of the electrode was affected by temperature. When the temperature was raised from 298 K to 308 K, the peak current density could be increased from 187 to 290 mA/cm^2, and for a temperature increase from 298 K to 318 K, the peak current density could be increased from 187 to 423 mA/cm^2. Thus it seems that the anodic oxidation is a kinetic controlled reaction.

Fig. 4 shows the $E - I$ curve of the oxidation of ethanol on a Pt-Mo-Si/C/M electrode at various scanning rates. It is clear that the peak current density rose with an increase of the scanning rate.

4 Discussion

The promotion of tungsten and silicotungstic acid were recognized by some researchers before and some investigations about its mechanism have been reported.

Hammnett et al[3] originally found improvement by addition of tungsten oxide in the oxidation of methanol;

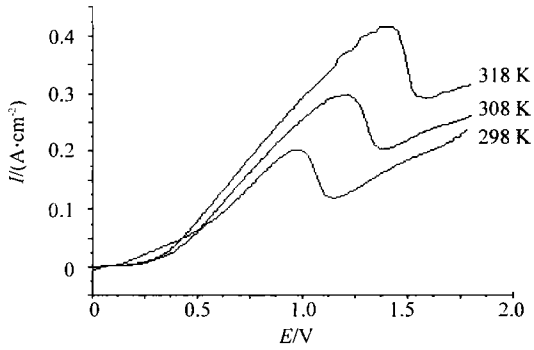


Fig.3 Effects of temperature on the activity of Pt-Mo-Si/C/M for oxidation of methanol at sweep rate of 30 mV/s

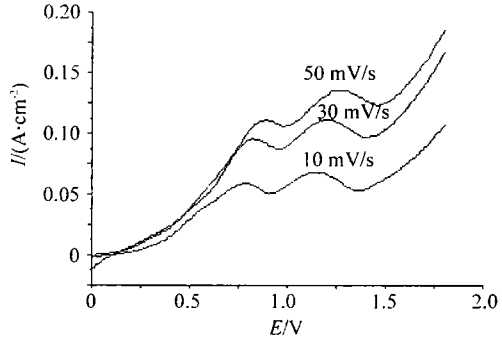
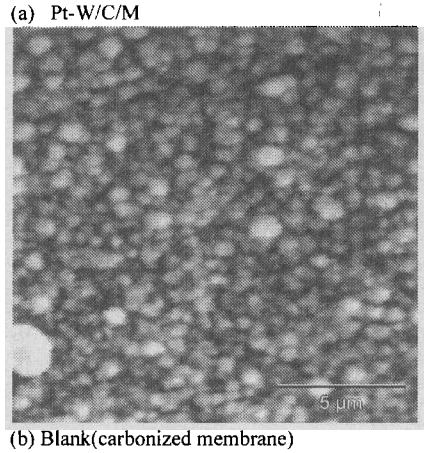


Fig.4 $E - I$ corves of electrode Pt-Mo-Si/C/M at various sweeping rate

(a) Pt-W/C/M



(b) Blank(carbonized membrane)

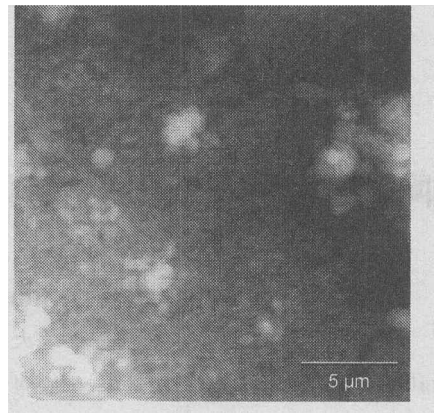


Fig.5 SEM images of electrode Pt-W/C/M and carbonized membrane

Shen and Tseung[4] indicated the substantial promotional effect of hydrous WO_{3-x}. Shukla et al[5] codeposited Pt and WO_{3-x} onto a porous carbon substrate, and they also observed promotion of the reaction rate.

Tseung et al. reported that tungsten seems to be providing a redox couple that changes between W(Ⅳ) or W(Ⅴ) and W(Ⅳ). This may be the earliest explanation of the role of tungsten as promoter.

Savadogo et al[6] found that the anodic oxidation of methanol could be accelerated by adding a small amount of silicotungstic acid to the electrolyte when using a Pt-Ru electrode. The presence of 10 mmol/L silicotungstic acid increased the reaction rate by around 50% and 100%, and this promotion was permanent, without a reduction in the promoting effect even after exposure for 48 hours.

Burstein et al[1] indicated that the anion of tungstosilicic acid was adsorbed onto the Pt-Ru catalytic surface and acted as promoter at this level; the promoting effect may result from the variable oxidation states of tungsten bound into a Keggin unit. By SEM observation, we found the addition of tungsten resulted in a very uniform distribution of the active components on the surface of the electrode (Fig.5). This may be one of the reasons for the promoting effect of tungsten.

We analyzed the surface compositions of a Pt/C/M electrode and a Pt-W/C/M electrode by EDS, it was found that the Pt contents on the surface of Pt/C/M and Pt-W/C/M are 7.23% (at atom) and 8.78% respectively when the loaded amounts of platinum are 1.62 and 1.35 mg/cm^2 respectively. It is clearly the addition of tungsten enhanced the surface concentration of Platinum, and it may be the second reason that tungsten show good promotion to Pt catalyst.

Since we have not yet found a report on the mechanism of promotion of silicomolybdic acid, this report may be the first which shows this effect. Although we have not determined the mechanism of silicomolybdic acid as promoter, we believe that it may be similar to that of tungstosilicic acid.

5 Conclusion

From the above results and discussion, we could conclude that the activity for anodic oxidation of methanol and ethanol of a Pt/C/M electrode could be improved significantly by the addition of tungstosilicic acid or silicomolybdic acid.

Moreover, fundamental and applicatory studies of Pt-Mo-Si/C/M and Pt-W-Si/C/M electrodes are worth

further investigation.

Tab.1 Performance data of electrodes for the oxidation of ethanol at 298 K in a 0.5H_2SO_4 solution

Electrode	Peak potential V	Peak current density ($mA \cdot cm^{-2}$)	Peak area ℃
Pt-Mo-Si/C/M	0.822	95.2	1.29
	1.196	111.3	1.557
Pt-W-Si/C/M	0.78	51.3	0.57
	1.207	65.2	0.48
Pt/C/M	0.716	26.4	0.25
	1.196	37.5	0.13

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Pt/陶瓷电极上醇类的阳极氧化作用及其钼和钨的添加对电极活性的影响

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摘 要:采用电沉积 Pt 在陶瓷膜的方法制得了一种新型的可用于醇类阳极氧化的陶瓷基底电极,采用在电沉积前用氧化钨的溶胶或硅钨酸或硅钼酸的溶液浸渍陶瓷膜的方法可将钨和钼添加到电极中。实验发现:钨和钼的添加可以十分显著地提高催化剂的活性,如:对于甲醇的阳极氧化,添加硅钼酸的电极上的电流密度可达到 187 mA/cm^2,为相同条件下不含硅钼酸的电极的 5 倍多。对于乙醇的阳极氧化也得到了相同的结果。

关键词:阳极氧化;醇;钼;无机膜;电极

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