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Methanol Tolerant PWA-Pt/C Catalyst with Excellent Electrocatalytic Activity for Oxygen Reduction in Direct Methanol Fuel Cell

Yan Zhuo LU[1], Tian Hong LU[1,2], Chang Peng LIU[1], Ya Wen TANG[2], Wei XING[1]*

[1]Changchun Institute of Applied Chemistry, Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Changchun 130022
[2]Environmental Friendship Laboratory, College of Chemistry and Environmental Science, Nanjing Normal University, Nanjing 210097

Abstract: It was reported for the first time that phosphorictungstenic acid (PWA) could promote the oxygen reduction reaction (ORR) and inhibit the methanol oxidation reaction at the cathodic Pt/C catalyst in the direct methanol fuel cell (DMFC). When the weight ratio of PWA to Pt/C is 1, the composite catalyst increases the reduction current of oxygen by about 38% and decreases the oxidation current of methanol by about 76% compared with that of the Pt/C catalyst.

Keywords: DMFC, phosphorictungstenic acid, methanol tolerance, oxygen reduction.

There are several problems preventing DMFC from the commercial applications. One of them is "methanol crossover", which causes a mixed potential due to the electrocatalytic oxidation of methanol at the Pt/C cathode and even poisoning the Pt/C catalyst[1]. Thus, it is important to find a cathodic electrocatalyst, which possesses the good electrocatalytic activity for ORR and methanol tolerant ability. In this paper, it was reported that the PWA-Pt/C composite catalyst shows the above ability.

All electrochemical measurements were performed using a Princeton Applied Research Model 273A potentiostat/Galvanostat and a three-electrode electrochemical cell. The Ag/AgCl electrode and a Pt foil were used as the reference electrode and the auxiliary electrode, respectively. The working electrode was prepared as follows. 1, 3, 5, 7 or 10 mg PWA and the 5 mg of Pt/C catalyst were mixed in the 0.4 mL of 5 wt.% Nafion solution. The mixtures obtained are called as Pt-PWA1/C, Pt-PWA3/C, Pt-PWA5/C, Pt-PWA7/C and Pt-PWA10/C catalyst, respectively. 5 μL of the catalyst ink prepared was transferred onto the glassy carbon electrode (5 mm in diameter)(GCE). After evaporating the solvent under air, the working electrode was ready to be used.

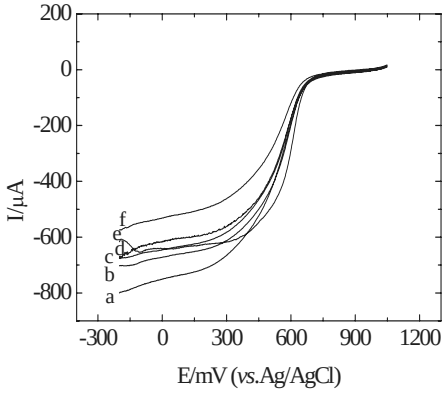
Figure 1 shows the oxygen reduction activity at the different electrodes in the 0.5 mol/L H_2SO_4 solution saturated with oxygen. It can be clearly observed from **Figure 1** that the onset potentials of ORR at the different electrodes are almost the same, but the limiting currents are different. The limiting current at the Pt-PWA5/C electrode is about 800 μ A at -0.2V. It is the largest among all the electrodes and about 38% larger than

* E-mail:xingwei@ciac.jl.cn

that at the Pt/C electrode.

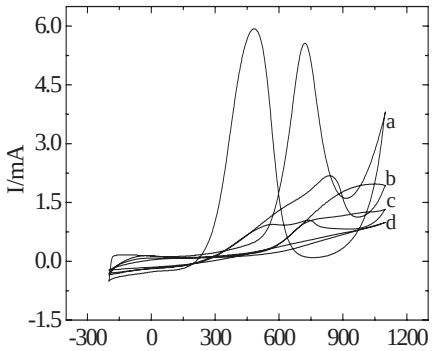
Figure 2 shows the cyclic voltammograms of the 0.5mol/L H_2SO_4 solution with 1 mol/L CH_3OH and saturated oxygen at the different electrodes. Two strong peaks for the methanol oxidation in the positive and negative scan directions were observed at the Pt/C electrode (**Figure 2**, Curve a). However, the oxidation peaks of methanol at other Pt-PWA/C electrodes (**Figure 2,** Curve b, c and d) are much weaker than that at the Pt/C electrode. The peak current at the Pt-PWA5/C electrode is about 76% less than that at the Pt/C electrode. Especially, the oxidation peaks of methanol at the Pt-PWA10/C electrode almost disappear. It is illustrated that PWA can significantly inhibits the oxidation of methanol at the Pt/C electrode. From the above results, it can be concluded that the Pt-PWA5/C catalyst shows the best performance for the electrocatalytic activity for ORR and the methanol tolerance among all the composite catalysts with the different weight ratio of PWA and Pt/C.

Figure 1 Linear sweeping voltammograms of oxygen saturated in the 0.5 mol/L H_2SO_4 solution at (a) Pt-PWA5/C, (b) Pt-PWA3/C, (c) Pt-PWA1/C, (d) Pt-PWA7/C, (e) Pt/C, (f) Pt-PWA10/C electrodes.



Rotation speed: 1000 rpm, Scan rate: 10 mV/s.

Figure 2 Cyclic voltammograms of the (a)Pt/C, (b) Pt-PWA1/C, (c) Pt-PWA5/C (d) Pt-PWA10/C electrodes in the 0.5mol/L H_2SO_4 solution with 1 mol/L CH_3OH and saturated oxygen.



Scan rate: 100 mV/s.

The reason for PWA to promote ORR and inhibit the methanol oxidation is not very clear so far. Perhaps, PWA possesses the *pseudo*-liquid behavior, such as high oxygen affinity[2]. Thus, PWA would promote ORR. However, methanol, as the relatively large molecule is difficult to permeate through PWA to the Pt surface and its oxidation is prevented in certain degree.

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