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An improved palladium-based DMFCs cathode catalyst

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A novel carbon-supported palladium-rich Pd_3Pt_1/C catalyst prepared by a modified polyol process showed a better cell performance than Pt/C in direct methanol fuel cells, which may be attributed to palladium's inactivity to methanol electro-oxidation while exhibiting good performance to oxygen reduction reaction.

There has been growing interest in using direct methanol fuel cells (DMFCs) as transport and portable power sources in recent years.[1] However, polymer electrolyte membranes (PEM) commonly employed, such as Nafion®, suffer from high methanol crossover, which not only lowers fuel utilization efficiency but also adversely affects the cathode performance, and thus results in a loss in the overall fuel cell efficiency. One effective way to overcome the crossover problem may be to adopt oxygen reduction selective catalysts for use as the DMFC's cathode.[2] Several transition metal compounds, such as pyrolysed transition metal macrocycles and transition sulfide, have been exploited as methanol-tolerant oxygen reduction reaction (ORR) catalysts[3] because of their good selectivity (~100%) against methanol oxidation reaction (MOR). But the activity of these ORR catalysts was considerably lower than platinum-based ones. Thus, many researchers have been trying to improve DMFCs cathode performance based on platinum catalysts.[4] Li *et al* obtained good cell performance through adopting multi-walled carbon-nanotube as carbon support; Neergat and his co-workers tried to alloy platinum with transition metal elements such as Co, Cr, Ni and Fe to improve ORR activity; Zhou *et al* got good DMFCs cathode performance by increasing the mass ratio of platinum metal to carbon support. However, platinum-based catalysts have not been considered ideal DMFCs cathode because of platinum's high intrinsic activity to ORR and MOR. Therefore, it is necessary to find a novel DMFCs cathode catalyst, which has good ORR performance and high selectivity against MOR.

Palladium and platinum have very similar properties because they belong to the same group in the periodic table. Savadogo had reported active palladium alloy catalysts without platinum for ORR in acid medium.[5] But the ORR on carbon supported palladium-based alloy in presence of methanol has not been announced hitherto. In this communication, carbon supported palladium-based catalyst as DMFCs cathode was investigated.

Pd–Pt/C catalyst with a molar ratio of palladium to platinum of 3 : 1 was prepared by a modified polyol synthesis strategy as described in previous papers.[4d] As a comparison, Pt/C was also prepared. The total metal content maintained about 20 wt.% for all the catalysts.

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Fig. 1 shows the X-ray diffraction (XRD) results of Pd_3Pt_1/C and Pt/C. The first peak at the low 2θ range (2θ ≈ 26°) was associated with the XC-72 carbon support. As displayed in Fig. 1, both the catalysts exhibited the characteristic diffraction fcc. crystalline structure. An angular shift of diffraction peaks to higher positions was found in the XRD pattern of Pd_3Pt_1/C as compared to those of Pt/C, which indicated the decreased lattice constant due to incorporation of palladium atoms. The (220) diffraction peak was used to calculate the metal particle sizes and lattice parameters according to the Scherrer and Bragg formula.[6] The particle sizes and lattice parameters of Pd_3Pt_1/C and Pt/C were 5.0 nm, 2.6 nm and 3.902 Å, 3.923 Å, respectively.†

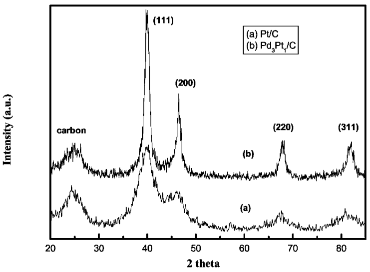

Fig. 1 XRD spectra of Pd_3 Pt_1/C and Pt/C catalysts, scan rate: 5° min^{-1}.

Fig. 2 displayed the cyclic voltammetry (CV) curves of the catalysts in 0.5 M $HClO_4$ electrolyte (with/without 0.1 M CH_3OH) employing the thin porous coating microelectrode technique[7] with a potentistat/galvanostat (EG&G Model 273A). The diameter of the microelectrode is 0.4 cm and the metal loading was 0.15 mg cm^{-2}. It can be seen from Fig. 2 that the hydrogen adsorption–desorption range of Pt/C catalyst decreased greatly while hardly any change was observed on Pd_3Pt_1/C catalyst when 0.1 M CH_3OH was added to N_2-saturated 0.5 M $HClO_4$ electrolyte. Comparison of their full line voltammograms with/without methanol clearly revealed that less poison was formed on the Pd_3Pt_1/C catalyst than on Pt/C, which was indicated by a minor blocking of hydrogen adsorption–adsorption on the Pd_3Pt_1/C catalyst. This may be on account of palladium's inactivity to MOR and hence the palladium-rich catalyst was largely restrained from the oxidation of methanol in acid solution.

ORR polarization curves of Pd_3Pt_1/C and Pt/C catalysts in

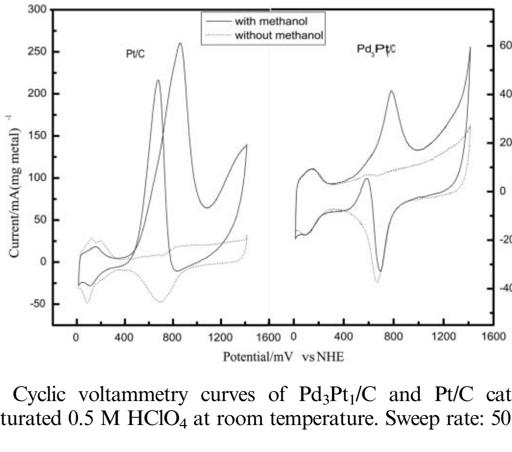

Fig. 2 Cyclic voltammetry curves of Pd_3Pt_1/C and Pt/C catalysts in N_2-saturated 0.5 M $HClO_4$ at room temperature. Sweep rate: 50 mV s^{-1}.

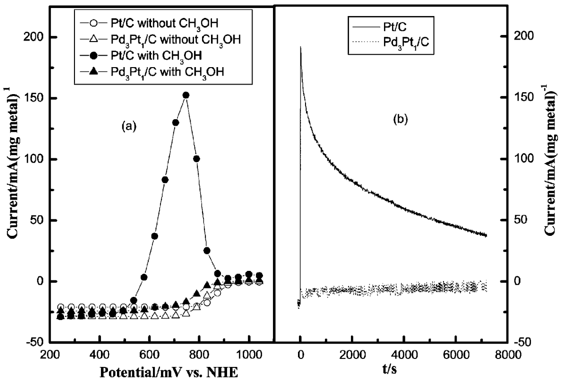

Fig. 3 (a) Polarization curves for ORR in O_2-saturated 0.5 $MHClO_4$ (with/without 0.1 MCH_3OH) at room temperature. Sweep rate: 5 mV s^{-1}. Oxygen feed: 5 mL min^{-1}, Rotation speed: 2500 rpm. (b) Polarization current *vs.* time plots for the Pd_3Pt_1/C and Pt/C in O_2-saturated 0.1 M CH_3OH + 0.5 M $HClO_4$ solution at 0.8 V (*vs.* NHE) at room tempetature, Oxygen feed: 5 mL min^{-1}, 2500 rpm.

O_2-saturated 0.5 M $HClO_4$ with/without methanol employing a rotation disk electrode (RDE) at 2500 rpm are presented in Fig. 3a. The half-wave potential $E_{1/2}$ (the potential corresponding to one-half of the diffusion current) of Pt/C and Pd_3Pt_1/C were 860 mV and 820 mV, respectively, which means that Pt/C had better ORR activity in 0.5 M $HClO_4$ electrolyte and Pd_3Pt_1/C also displayed comparative ORR activity in comparison with that of Pt/C. When 0.1 M methanol was added to the electrolyte, the MOR peak of Pt/C catalyst was so large that the catalytic activity to ORR was decreased greatly in the potential range of 500 ~ 900 mV. However, it was very interesting to note that no MOR peak appeared in the ORR polarization curve of Pd_3Pt_1/C catalyst and the $E_{1/2}$ for ORR only negatively shifts a little (from 820 mV to 800 mV), which in principle indicated that Pd_3Pt_1/C possessed superior selective ORR activity in presence of methanol to Pt/C catalyst. The previous CV test had indicated that there existed weaker MOR peaks in N_2-saturated 0.5 M $HClO_4$ + 0.1 M CH_3OH solution on Pd_3Pt_1/C catalyst, as shown in Fig. 2. However, in the same solution saturated with O_2 in the RDE test, there were no longer any positive methanol oxidation peaks on Pd_3Pt_1/C. This meant that when both methanol and oxygen were present simultaneously, ORR had the priority to occur over MOR on Pd_3Pt_1/C catalyst, whereas the priority was the reverse on Pt/C catalyst. A chronoamperometric test (CA) for oxygen reduction in presence of methanol, carried out at a constant potential (0.8 V *vs.* NHE), also confirmed this phenomenon, as shown in Fig. 3b. Pt/C catalyst presented a large positive methanol oxidation current while that of Pd_3Pt_1/C was a negative oxygen reduction current.

I–V plots of DMFCs single cell employing the catalysts as cathodes at 75 °C are given in Fig. 4. Both the cathode catalysts metal loading maintained 1 mg cm^{-2} and the anode catalysts adopted Pt (20 wt%)–Ru (10 wt%)/C-JM with metal loading of 2.0 mg cm^{-2}. Nafion-115 (Dupont) was used as the membrane. Preparation of the membrane-electrode assemblies (MEAs) was based on the procedure of ref. 8 and the geometric active areas of both the MEAs used in this paper were 4 cm^2. As shown in Fig. 4, Pd_3Pt_1/C consistently revealed remarkable performance advantage over the reference Pt/C catalyst. The cell performance results were in good agreement with RDE and CA results and this may be attributed to the palladium–platinum synergistic effect.[9] It had been reported that palladium and platinum had similar behaviour to ORR,[10] but they showed a different electrochemical behavior to MOR in that palladium is completely inactive for methanol electro-oxidation in acid solution.[11] When too much palladium was added into the catalyst, most of the active sites of platinum catalyst to MOR can be separated and the activity to MOR decreased greatly. At the same time, palladium and platinum maintained their own active sites for ORR. Therefore, when palladium alloyed a small quantity of platinum to get a new catalyst Pd_3Pt_1/C, the selectivity against MOR combined with ORR activity could obtain good cell performance in DMFCs.

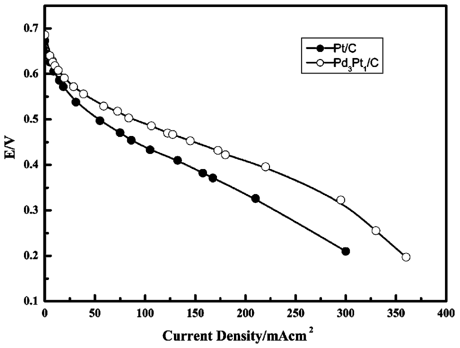

Fig. 4 Performance of Pd_3Pt_1/C and Pt/C as DMFCs cathode at 75 °C. Fuel feed: 1 M CH_3OH 1 mL min^{-1}; oxygen pressure: 0.2 Mpa;

In conclusion, palladium-rich Pd_3Pt_1/C catalyst enhanced DMFCs cathode performance for its selective ORR activity in the presence of methanol and may be an alternative methanol-tolerant cathode in DMFCs.

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Notes and references

† Pt: a_{fcc} = 3.923 Å; Pd: a_{fcc} = 3.890 Å from JCPDS.

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