Short communication

Room temperature preparation of carbon supported Pt-Ru catalysts

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Abstract

A carbon supported Pt-Ru (Pt-Ru/C-T) catalyst can be prepared by a chemical reduction method in an aqueous solution with tetrahydrofuran (THF) at room temperature. The Pt-Ru particles possess high alloying, small average size and a low relative crystallinity. The electrocatalytic activity of the prepared Pt-Ru/C catalyst for methanol oxidation is much higher than that of commercial Pt-Ru/C (Pt-Ru/C-E) catalysts which have a similar average size and relative crystallinity, but the alloying extent is much lower than that in our Pt-Ru/C-T catalyst. The results illustrate that the alloying extent of Pt and Ru in the Pt-Ru/C catalyst plays an important role in the electrocatalytic activity of the Pt-Ru/C catalyst for methanol oxidation.

1. Introduction

The Pt-Ru/C catalyst has been widely investigated for its superior electrocatalytic activities and CO tolerance for the methanol oxidation in a direct methanol fuel cell (DMFC) [1–3]. It is well known that the electrocatalytic activity of the Pt-Ru/C catalyst for methanol oxidation is strongly dependent on the component, average size and crystallinity, etc. of the Pt-Ru particles in the Pt-Ru/C catalyst [1–4]. However, the effect of the alloying extent of Pt and Ru on the electrocatalytic activity of the Pt-Ru/C catalyst for the methanol oxidation is not generally agreed upon [2,5].

Usually, Pt-Ru particles with a high alloying extent are prepared at a high temperature. However, the average size and the crystallinity of the Pt-Ru particles prepared at high temperature are usually large and high, respectively, leading to a low electrocatalytic activity. In this communication, it is reported for the first time that a Pt-Ru/C catalyst with high alloying, small average size and low crystallinity of the Pt-Ru particles can be prepared using a very simple chemical reduction method in an aqueous solution with tetrahydrofuran (THF) at room temperature. The

Pt-Ru/C catalyst prepared showed high electrocatalytic activity for methanol oxidation.

2. Experimental

The preparation method of a 20 wt.% Pt-Ru/C catalyst with an atomic ratio of Pt:Ru = 1:1 was as follows: 60 mg of Vulcan XC-72 carbon, 1.32 mL 0.0386 M H_2PtCl_6 and 0.52 mL 0.0963 M $RuCl_3$ were added to 10 mL solution of THF and H_2O with the volume ratio of THF:H_2O = 1:1. After the mixture solution was ultrasonicated for 1 h and mechanically stirred for 19 h, a 10 mL solution of $NaBH_4$ and Na_2CO_3 was added dropwise and stirred for 1 h at 10 °C. Then it was filtered and washed with triply distilled water and ethanol. Finally, it was dried in a vacuum oven at 60 °C. The catalyst obtained is called the Pt-Ru/C-T catalyst. For comparison, a Pu-Ru/C catalyst noted as the Pt-Ru/C-H catalyst was prepared with the above procedure except THF was not used. The commercial E-TEK Pt-Ru/C catalyst with a content of Pt and Ru similar to that in the Pt-Ru/C-T catalyst is called as the Pt-Ru/C-E catalyst. The energy dispersive X-ray analysis indicated that the atomic ratio of Pt and Ru in the Pt-Ru/C-T, Pt-Ru/C-E and Pt-Ru/C-H catalysts were 48.0:52.0, 49.0:51.0 and 48.6:51.2, respectively.

The electrochemical measurements were performed using a CHI 600 electrochemical analyzer and a conventional three-

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electrode electrochemical cell. A Pt plate was used as the auxiliary electrode. The saturated calomel electrode (SCE) electrode was used as the reference electrode. The working electrode was prepared as follows: a glassy carbon electrode was polished with 0.3 and 0.05 μm Al_2O_3 sequentially and washed. Eight milligrams of Pt-Ru/C catalyst and 3.25 mL of a solution of 20% C_2H_5OH + 73.75% H_2O + 6.25% Nafion (5 wt.%) were mixed and sonicated for 30 min. Four microliter slurry was laid on the surface of a glassy carbon electrode. After drying, a working electrode was obtained. The apparent surface area of the glassy carbon electrode was 0.07 cm^2 and the specific loading of Pt-Ru on the electrode surface was about 28 μg cm^{-2}. For the electrochemical measurements of adsorbed CO, when the electrode potential was fixed at 0 V, CO was bubbled into the solution for 10 min until CO was fully adsorbed on the electrode. Thereafter, N_2 was bubbled for 10 min to remove the CO dissolved in the solution. All of the electrochemical measurements were carried out at 36 ± 1 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Pt-Ru/C-T, Pt-Ru/C-E and Pt-Ru/C-H catalysts. Four characteristic peaks corresponding to (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of the face-centered cubic crystalline of Pt were observed in each of the XRD patterns. However, the characteristic peaks shifted to the high 2θ direction compared with the peak position of pure Pt, indicating that Ru has entered into the Pt lattice and an alloy of Pt and Ru was formed. In Fig. 1, the insert clearly shows that the shift for the Pt-Ru/C-T catalyst is much higher than that of the Pt-Ru/C-E and Pt-Ru/C-H catalysts, illustrating that the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst is much higher than that in the Pt-Ru/C-E and Pt-Ru/C-H catalysts. From Fig. 1, some structural data on the Pt-Ru catalysts can be calculated [6–8]. The average size, relative crystallinity, lattice parameter of the Pt-Ru particles and the alloying extent of Pt and Ru for the Pt-Ru/C-T catalyst are 2.7 nm, 2.0, 0.3858 nm and 92%, respectively. While the corresponding data for the Pt-Ru/C-E catalyst are 2.5 nm, 1.6, 0.3910 nm and 8%, respectively. These

are 8.4 nm, 2.6, 0.3895 nm and 32%, respectively, for the Pt-Ru/C-H catalyst. It can be observed from the above data that the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst is much higher than that in the Pt-Ru/C-H catalyst, but the average size of the Pt-Ru particles in the Pt-Ru/C-T catalyst is much less than that in the Pt-Ru/C-H catalyst, illustrating that the existence of THF in the preparation solution can effectively prevent the metal particles from congregating and also increase the alloying extent of Pt and Ru. In addition, it was found that the average size and the relative crystallinity of the Pt-Ru particles in the Pt-Ru/C-T catalyst are similar to that in the Pt-Ru/C-E catalyst. Only the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst is much higher than that in the Pt-Ru/C-E catalyst. The measurements of the XPS spectra indicated that the binding energies of Pt$_{4f}$ in the Pt-Ru/C-T catalyst are higher than that in the Pt-Ru/C-E and Pt-Ru/C-H catalyst. It is more evident that the alloying extent of Pt and Ru in the Pt-Ru particles of the Pt-Ru/C-T catalyst is higher than that of the Pt-Ru/C-E and Pt-Ru/C-H catalysts.

The transmission electron microscope (TEM) measurements of the three catalysts indicated that the average size of the Pt-Ru particles in the Pt-Ru/C-T, Pt-Ru/C-E and Pt-Ru/C-H catalysts are 3.0, 2.7 and 8.6 nm, respectively. The dispersions of the Pt-Ru particles in the Pt-Ru/C-T and Pt-Ru/C-E catalysts are also better than that of the Pt-Ru particles in the Pt-Ru/C-H catalyst. The results are in the good agreement with that of the XRD measurement.

The measurement of the UV–vis absorption spectroscopy indicated that the UV–vis absorption spectra of the H_2PtCl_6 solution is changed after THF is added to the H_2PtCl_6 solution (Fig. 2), illustrating the formation of complexes of H_2PtCl_6 with THF. In addition, the results of the electrochemical measurements demonstrated that in the aqueous solution, the onset reduction potential of H_2PtCl_6 is about 200 mV more positive than that of $RuCl_3$. However, in the THF and H_2O solution, the onset reduction potentials of H_2PtCl_6 shifted to the negative direction (Fig. 3) and is almost equal to that of $RuCl_3$ due to the formation of the complex of H_2PtCl_6 and THF. Thus, when H_2PtCl_6 and $RuCl_3$ in the aqueous solution with THF are reduced with $NaBH_4$, Pt and Ru can be reduced simultaneously

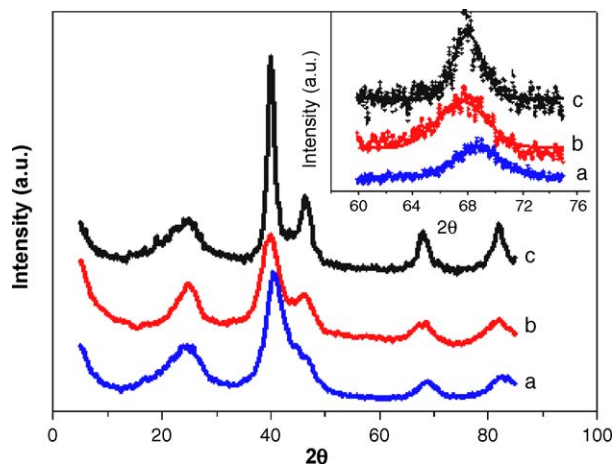
Fig. 1. The XRD patterns of (a) the Pt-Ru/C-T, (b) Pt-Ru/C-E and (c) Pt-Ru/C-H catalysts. *Insert*: the XRD patterns in the range of 2θ = 60–76.
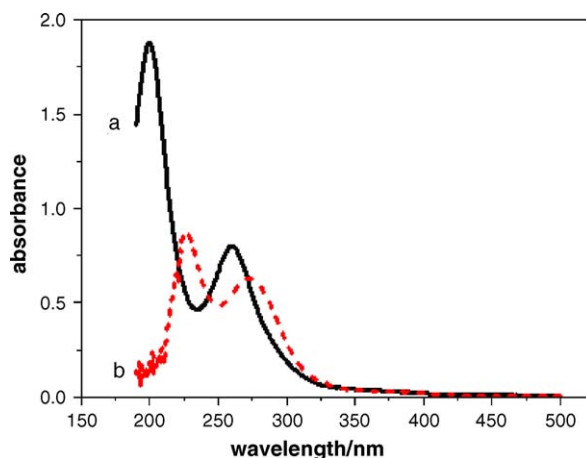

Fig. 2. The UV–vis absorption spectra of 1.0×10^{-4} M H_2PtCl_6 in (a) H_2O and (b) THF.
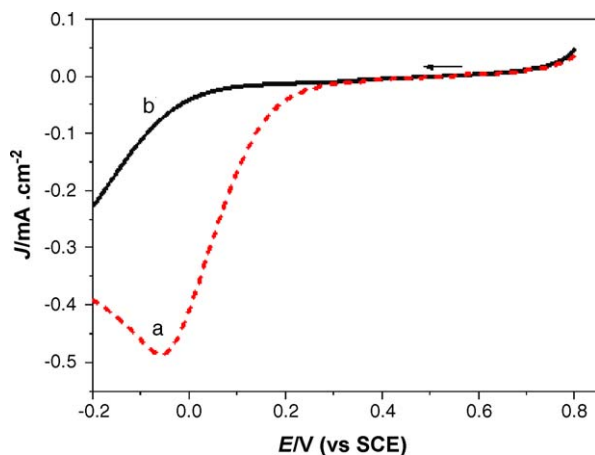
Fig. 3. The linear sweep curves of 0.0045 M H_2PtCl_6 + 0.05 M NaCl in (a) H_2O and (b) the mixture solution of THF and H_2O with the volume ratio of 5:5 at the glassy carbon electrode.

and the alloy of Pt and Ru is more easily formed. We believe that this is the reason why the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst is very high.

Fig. 4 shows the cyclic voltammograms of 0.5 M CH_3OH in the 0.5 M H_2SO_4 solution for the Pt-Ru/C catalyst electrodes. It can be observed from Fig. 4 that in the positive scan direction, the potentials of the oxidation peaks of CH_3OH at the three Pt-Ru/C catalyst electrodes are almost the same, at 0.47 V. However, the peak current densities are different. They are 3.88 mA cm^{-2} at the Pt-Ru/C-T catalyst electrode, 2.46 mA cm^{-2} at the Pt-Ru/C-E catalyst electrode and 0.92 mA cm^{-2} at the Pt-Ru/C-H catalyst electrode. It is obvious that the electrocatalytic activity of the Pt-Ru/C-T catalyst for methanol oxidation is higher than that of the Pt-Ru/C-E and Pt-Ru/C-H catalysts.

The results from the chronoamperometric curves of 0.5 M CH_3OH in the 0.5 M H_2SO_4 solution at the Pt-Ru/C catalyst electrodes at 0.40 V indicated that the current density at the Pt-Ru/C-T catalyst electrode at 1000 s is almost twice and four times larger than that at the Pt-Ru/C-E and Pt-Ru/C-H catalyst electrodes, respectively. The data further demonstrate that
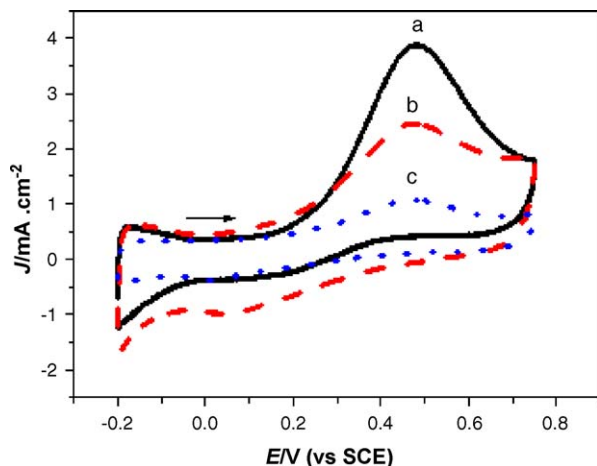

Fig. 4. The cyclic voltammograms of 0.5 M CH_3OH in the 0.5 M H_2SO_4 solution at (a) the Pt-Ru/C-T, (b) Pt-Ru/C-E and (c) Pt-Ru/C-H catalyst electrodes.
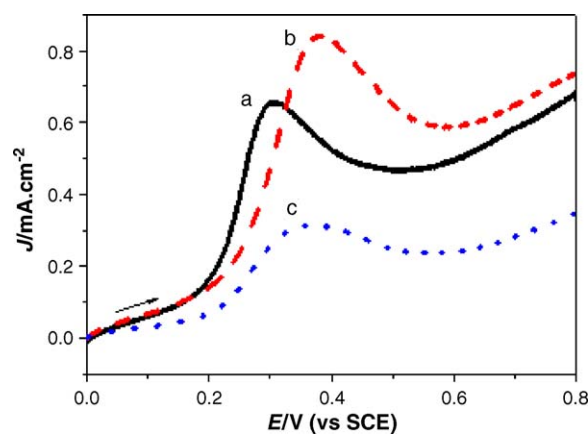

Fig. 5. The linear sweep voltammograms of the adsorbed CO at (a) the Pt-Ru/C-T, (b) Pt-Ru/C-E and (c) Pt-Ru/C-H calatlyst electrodes.

the electrocatalytic activity of the Pt-Ru/C-T catalyst for the methanol oxidation is higher than that of the Pt-Ru/C-E and Pt-Ru/C-H catalysts.

Fig. 5 shows the linear sweep voltammograms of the adsorbed CO at the Pt-Ru/C calalyst electrodes. It is observed from Fig. 5 that the peak potentials for the oxidation of the adsorbed CO at Pt-Ru/C-T, Pt-Ru/C-E and Pt-Ru/C-H catalyst electrodes are 0.304, 0.388 and 0.361 V, respectively. It was found that the order of the potential of the oxidation peak of the adsorbed CO at the three Pt-Ru/C catalyst electrodes is the same as the order of the alloying extent of Pt and Ru in the three Pt-Ru/C catalysts. This illustrates the adsorption strength of the adsorbed CO on the Pt-Ru/C catalysts is related to the alloying extent of Pt-Ru. Therefore, the high electrocatalytic activity of the Pt-Ru/C-T catalyst for the methanol oxidation is due to the weak adsorption of CO on the Pt-Ru/C-T catalyst because CO is one of the intermediates of the methanol oxidation and can be strongly adsorbed on Pt, leading to the poisoning of the Pt catalyst [9,10].

4. Conclusions

In conclusion, the Pt-Ru/C-T catalyst with a very high alloying extent, small average size and low relative crystallinity of the Pt-Ru particles can be prepared with a very simple chemical reduction method in THF and H_2O solution at the room temperature because THF can prevent the metal particles from the congregating and increase the alloying extent of Pt and Ru. The fact that the electrocatalytic activity of the Pt-Ru/C-T catalyst for methanol oxidation is much higher than that of the Pt-Ru/C-E catalyst can only be attributed to the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst which is much higher than that in the Pt-Ru/C-E catalyst because the structural data, such as the relative crystallinity and the average size of Pt-Ru particles in the Pt-Ru/C-T and Pt-Ru/C-E catalysts are similar except that the alloying extent of Pt and Ru in the Pt-Ru/C-T catalyst is much higher than that in the Pt-Ru/C-T catalyst. Therefore, the alloying extent of Pt and Ru in the Pt-Ru/C catalyst is an important factor affecting the electrocatalytic activity of the Pt-Ru/C catalyst for methanol oxidation. This is the main reason that the increase in the alloying extent of Pt and Ru can decrease the

adsorption strength of the intermediate of the methanol oxidation, CO, on the Pt-Ru/C catalyst.

Because this preparation method of the Pt-Ru/C catalyst is very simple and the elelctrocatalytic activity of the prepared Pt-Ru/C catalyst for the methanol oxidation is very high, this preparation method should be considered for practical applications.

Acknowledgements

References

[1] W.D. King, J.D. Corn, O.J. Murphy, D.L. Boxall, E.A. Kenik, K.C. Kwiatkowski, S.R. Stock, C.M. Lukehart, J. Phys. Chem. B 107 (2003) 5467.
[2] C. Roth, N. Martz, A. Morlang, R. Theissmann, H. Fuess, Phys. Chem. Chem. Phys. 6 (2004) 3557.
[3] Q.Y. Lu, B. Yang, L. Zhuang, J.T. Lu, J. Phys. Chem. B 109 (2005) 1715.
[4] H. Sophie, K. Tetyana, F. Brian, G. Johnson, J. Chem. Soc. Dalton Trans. 21 (2001) 3295.
[5] D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, Langmuir 15 (1999) 774.
[6] E. Antolini, F. Cardellini, J. Alloys Compd. 315 (2001) 118.
[7] V. Radmilovic, H.A. Gasteiger, P.N. Ross, J. Catal. 15 (1995) 98.
[8] J.H. White, A.F. Sammells, Perovskiteand, J. Electrochem. Soc. 140 (1993) 2167.
[9] S.D. Lin, T.C. Hsiao, J.R. Chang, A.S. Lin, J. Phys. Chem. B 103 (1999) 97.
[10] P.A. Christensen, J.M. Jin, W.F. Lin, J. Phys. Chem. B 108 (2004) 3391.