Pt based anode catalysts for direct ethanol fuel cells

Weijiang Zhou a , Zhenhua Zhou a , Shuqin Song a , Wenzhen Li a , Gongquan Sun a , Panagiotis Tsiakaras b , Qin Xin a , c , ∗

a Direct Alcohol Fuel Cell Laboratory, Dalian Institute of Chemical Physics, CAS, P.O. Box 110, Dalian 116023, PR China
b Department of Mechanical and Industrial Engineering, University of Thessalia, Pedion Areos, GR 38334 Volos, Greece

c State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, CAS, P.O. Box 110, Dalian 116023, PR China

Received 15 January 2003; received in revised form 11 May 2003; accepted 11 May 2003

Abstract

In the present work several Pt-based anode catalysts supported on carbon XC-72R were prepared with a novel method and characterized by means of XRD, TEM and XPS analysis. It was found that all these catalysts are consisted of uniform nanosized particles with sharp distribution and Pt lattice parameter decreases with the addition of Ru or Pd and increases with the addition of Sn or W. Cyclic voltammetry (CV) measurements and single direct ethanol fuel cell (DEFC) tests jointly showed that the presence of Sn, Ru and W enhances the activity of Pt towards ethanol electro-oxidation in the following order: Pt/Sn/C > Pt/Ru/C > Pt/W/C > Pt/Pd/C > Pt/C. Moreover, Pt/Ru/C further modified by W and Mo showed improved ethanol electro-oxidation activity, but its DEFC performance was found to be inferior to that measured for Pt/Sn/C. Under this respect, several PtSn/C catalysts with different Pt/Sn atomic ratio were also identically prepared and characterized and their direct ethanol fuel cell performances were evaluated. It was found that the single direct ethanol fuel cell having Pt/Sn/C or Pt/Sn/C or Pt/Sn/C as anode catalyst showed better performances than those with Pt/Sn/C or Pt/Sn/C. It was also found that the latter two cells exhibited higher performances than the single cell using Pt/Ru/C, which is exclusively used in PEMFC as anode catalyst for both methanol electro-oxidation and CO-tolerance. This distinct difference in DEFC performance between the catalysts examined here would be attributed to the so-called bifunctional mechanism and to the electronic interaction between Pt and additives. It is thought that an amount of –OHads, an amount of surface Pt active sites and the conductivity effect of PtSn/C catalysts would determine the activity of PtSn/C with different Pt/Sn ratios. At lower temperature values or at low current density regions where the electro-oxidation of ethanol is considered not so fast and its chemisorption is not the rate-determining step, the Pt/Sn/C seemed to be more suitable for the direct ethanol fuel cell. At 75 °C, the single ethanol fuel cell with Pt/Sn/C as anode catalyst showed a comparable performance to that with Pt/Sn/C, but at higher temperature of 90 °C, the latter presented much better performance. It is thought from a practical point of view that Pt/Sn/C, supplying sufficient –OHads and having adequate active Pt sites and acceptable ohmic effect, could be the appropriate anode catalyst for DEFC.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Direct ethanol fuel cells; PtRu; PtSn; Nafion®; Proton exchange membrane; Anode catalyst

1. Introduction

Great attention has been paid the last decade to the proton exchange membrane fuel cells (PEMFCs) fueled by H2 or liquid fuels, such as low molecular
weight alcohols. Compared to the H2/O2 PEMFCs, direct alcohol PEMFCs are more compact without the heavy and bulky external fuel reformer and can be applied especially to power electric vehicles. Liquid fuels, such as low-molecular weight alcohols, featuring higher volumetric and gravimetric energy densities and better energy efficiency, can be easily handled, stored and transported in comparison with gaseous fuels. At present, direct methanol fuel cell (DMFC) is being widely investigated and considered as a possible power source for electric vehicles and other portable applications in the near future. However, it is well-known that methanol is volatile and relatively toxic, therefore it is not thought as a favorable and friendly fuel [1,2]. Other short chain organic chemicals, such as ethanol, ethylene glycol, propanol [3,4] and dimethyl oxalate [2], were also tested as fuels for direct liquid electro-oxidation PEMFCs. As one of the alternative fuels, ethanol is safer and has more energy density compared to methanol (8.01 kWh kg\(^{-1}\) versus 6.09 kWh kg\(^{-1}\)). Moreover, as a green fuel, ethanol can be easily produced in great quantity by fermentation of sugar-containing raw materials. Therefore, ethanol is more attractive than methanol for direct alcohol oxidation fuel cells operating at lower temperature values.

The adsorption and oxidation of ethanol for fuel cells at lower temperature values have already been investigated, but most of the prior studies were restricted to the analysis of ethanol anodic oxidation mechanism and the identification of the reaction intermediates and products. The complete ethanol electro-oxidation to CO\(_2\) involves 12 electrons per molecule and many adsorbed intermediates. Besides, ethanol is electrochemically oxidized through different pathways on different catalytic surfaces or in different media. Thus, it is more difficult to elucidate exactly the mechanism of ethanol electro-oxidation. High activity and stability of Pt, especially under acidic environment, makes it a suitable electrocatalyst for electro-oxidation of many small chemical molecules. However, as well-known, at room or moderate temperature values pure platinum is not a very good anode catalyst for ethanol or methanol electro-oxidation, because it is readily poisoned by the strongly adsorbed intermediates, among which CO\(_{ads}\) is always considered as one of the main poisoning species at low operating temperature. Making alloys with a second or a third metal is a convenient way to modify the electrocatalytic properties of platinum in order to overcome poisoning due to methanol or ethanol electro-oxidation intermediates, especially the adsorbed CO. It was found that several metals can definitely enhance Pt activity for alcohol oxidation [2]. Among them, Ru is the favorite metal. Tungsten represents also a potential additive to Pt for the alcohol electro-oxidation improvement. According to the electro-oxidation bifunctional mechanism [5], the synergistic effect is resulted from the fact that Ru or W activate water molecules and provides preferential sites for –OH\(_{ads}\) adsorption at lower potentials than Pt. Abundant –OH\(_{ads}\) species are necessary to completely oxidize the poisoning intermediates to CO\(_2\). It has been also very briefly reported [6] that Pt-Pd alloy catalyst dramatically enhances ethanol electro-oxidation activity in presence of basic electrolyte. For methanol electro-oxidation, Pt-Sn catalytic activity and their optimum atomic ratio are still controversial at present. In addition to the oxidation of intermediates, such as CO\(_{ads}\), the cleavage of C–C bond plays a very important role [7] in the reaction of ethanol complete electro-oxidation to CO\(_2\) increasing energy conversion efficiency and fuel utilization. The complexity of this reaction and the presence of so many intermediates require the development of novel anode catalysts, able to break the C–C bond at low temperature, to release 12 electrons and to completely oxidize the poisoning species at lower overpotentials. Many different platinum-based anode catalysts, such as Pt–Ru [8], Pt–Sn [9], Pt–Mo [10,11] and so on, have been investigated and demonstrated to display to a certain extent electrochemical activity for methanol and ethanol electro-oxidation. The electro-oxidation of ethanol on other catalysts, such as rhodium and iridium [12], has also been investigated and different reaction mechanisms have been proposed. As another potential catalyst, gold [13] was found to show higher selectivity for ethanol electro-oxidation while its activity is lower than platinum. It is very interesting to be mentioned that most results from above catalysts were obtained through half-cell experiments. So, it is worthy evaluating the electro-oxidation catalysts in single direct ethanol fuel cell (DEFC) tests by adopting them as anode catalysts. It has been recently reported by Lamy et al. [1] that the nature and structure of the anode catalysts play a key role in the
adsorption and electro-oxidation of ethanol and other aliphatic alcohols. Increasing the operating temperature of PEMFCs directly fed with liquid ethanol (direct ethanol fuel cell, DEFC) can effectively increase the ethanol electro-oxidation rate and decrease the overpotential. It was found [3] that at higher temperature of 170 °C, Pt-Ru catalyst shows almost comparable activity for both methanol and ethanol electro-oxidation. On the other hand, increasing operation temperature needs new solid electrolytes other than the usual Nafion® membranes [14] that cannot operate at higher temperatures for a long time. Thus, in order to improve the performance of DEFC based on Nafion® membrane used extensively at present, it is of great importance to hunt for more active anode catalysts for ethanol electro-oxidation at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.

In the present work, a novel method is used for the preparation of carbon-supported Pt and Pt-based catalysts in presence of higher metal loadings. Based on our previous exploratory works [17–20], several Pt-based binary and ternary metallic anode catalysts were studied by cyclic voltammetry and tested as anodes in single direct ethanol fuel cells at lower temperatures. Some methods have been demonstrated good to prepare Pt-based electrode catalysts [15,16], while it still remains a challenge to prepare highly dispersed supported Pt-based catalysts with uniform nanopaticle structure in the presence of high metal loading.
operated at 100 kV. More than 300 particles were calculated to get the integrated information about the overall distribution of every Pt-based catalyst samples.

2.3. Cyclic voltammetry experiments

The cyclic voltammetry spectra were recorded using a potentiostat/galvanostat (EG&G Model 273A). Five milligram of Pt-based catalyst was suspended in 1 ml of ethanol and 50 μl of Nafion® solution (5 wt.% Aldrich solution) to prepare catalyst ink. Then 25 μl of ink was transferred with an injector to clean glassy carbon disk electrode (with area of 0.1256 cm²). After the ethanol volatilization, the electrode was heated at 75 °C for 10 min. A mixture solution containing 0.5 M H₂SO₄ and 1.0 M ethanol was used as electrolyte, which was saturated by pure argon in order to expel oxygen in the solution. During the experiment the temperature was kept constant at 25 °C. The scan rate was 10 mV/s, and a saturated calomel electrode (SCE) was used as reference electrode, and a platinum wire was used as counter electrode. The data were recorded after three cyclic curves overlapped each other.

2.4. The MEA preparation and single fuel cell test

The membrane electrode assembles (MEAs) were fabricated according to the method described in previous works [19,20,22]. The anode contained the in-house carbon-supported Pt-based catalysts with a Pt loading of 1.33 mg/cm² (except the case when pure Pt/C was used as anode catalyst where the platinum loading was 2.0 mg/cm²) purchased from Johnson Matthey with a Pt loading of 1.0 mg/cm², which was kept identical in all the MEAs. Nafion®-115 membrane was used as solid electrolyte, which was pre-treated with diluted H₂O₂ solution and H₂SO₄ solution successively [23]. Then, the sandwich of anode-membrane-cathode was assembled by hot-pressing constantly at 140 °C for 90 s. The single cell with an active area of 9 cm² was fed with an ethanol aqueous solution of 1.0 M. The fuel cell operating temperature was less than 100 °C, and the fuel flow rate controlled by a peristaltic pump was 1.0 ml/min. On the cathode side, unhumidified oxygen was used with a total flow rate of 120 ml/min and pressure of 0.2 MPa.

3. Results and discussion

The different diffractograms of the various carbon-supported Pt and Pt-based catalysts are shown in Figs. 1 and 2. The diffraction peak at 20°-25° observed in all the XRD patterns of the carbon-supported catalysts is due to the (002) plane of the hexagonal structure of Vulcan XC-72 carbon. The diffraction peaks at about 39°, 46°, 68° and 81° are due to Pt (111), (200), (220), and (311) plane, respectively, which represents the typical character of a crystalline Pt face centered cubic (fcc) phase. There are no other distinct reflection peaks in all spectra than those of the four peaks mentioned above, indicating that all in-house supported Pt and Pt-based catalysts have prevailed Pt (fcc) crystal structure. The (220) reflections of Pt are used to calculate the average particle size according to the Scherrer formula [24]. The particle mean size and lattice parameter obtained from XRD patterns and the TEM results are summarized in the Table 1.

By examining the XRD results reported in Fig. 1, there are obvious differences among the bimetallic catalysts in both the noble metal particle size and the shift of the reflection peak of (220) plane, while as is shown in Fig. 2 no differences are found among those Pt–Ru based ternary metallic catalysts. The PtRu/C catalyst has the smallest particle diameter calculated from the fitted (220) plane [24]. The lattice parameter of the (fcc) Pt/C 20 wt.% is estimated to be 3.9156 Å, while the lattice parameter of PtRu/C catalyst synthesized by the same method is 3.8830 Å, which indicates the improved interaction between Pt–Ru. It was also found that the addition of Ru and Pd to Pt/C can decrease the lattice parameter of Pt (fcc) crystal inducing the (220) reflection peak shift to higher position, while the addition of Sn and W to Pt/C induces opposite results, which indicates that the interaction between Sn and Pt is different from that between Pt and Ru. The calculated lattice parameters of PtRu/C and PtRu/W are 3.9873 and 3.9223 Å, respectively. The respective additions of W and Mo to PtRu/C have no obvious effect on its XRD pattern, showing that both additives do not change its
crystal structure. Furthermore, from the XPS results of these catalysts it was found that Sn was mainly in the oxidized state, while Pt and Ru were in reductive state.

From the TEM micrographs, it was found that metal particles of all Pt-based catalysts were very uniform. Fig. 3 depicts a typical TEM image of in-house Pt<sub>1</sub>Ru<sub>1</sub>/C catalyst and its metal particle size.
Table 1
XRD and TEM Results of carbon-supported Pt and Pt-bimetallic catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mean particle size (nm)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/C</td>
<td>2.7</td>
<td>2.6</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>PtPd/C</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>PtW/C</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>PtSn/C (Pt/Sn = 1:1)</td>
<td>2.3</td>
<td>2.1</td>
</tr>
<tr>
<td>PtSn/C (Pt/Sn = 3:2)</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>PtSn/C (Pt/Sn = 2:1)</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>PtSn/C (Pt/Sn = 3:1)</td>
<td>2.2</td>
<td>1.9</td>
</tr>
<tr>
<td>PtSn/C (Pt/Sn = 4:1)</td>
<td>2.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

distribution with a mean particle size of about 1.9 nm and a sharp distribution. Other three PtRu-based catalysts have similar particle size. The mean particle size of PtSn/C was similarly found to be about 2.3 nm, slightly higher than that of PtRu/C. The samples of PtW/C and PtPd/C have mean size of 3.6 and 3.0 nm, respectively. The values of the mean particle size obtained by TEM analysis are almost in good agreement with those calculated from the XRD results, but the former are always higher. The TEM results show that the present method is suitable to prepare nanometer-sized Pt-based catalysts in the presence of high metal loadings. It is important to notice that nanoscaled noble metal catalysts were prepared in the present work without the employment of any expensive surfactants, which are used in previous preparation methods [25]. Furthermore, compared to the sulfite-complex route [26] that has been demonstrated suitable to prepare Pt and Pt-Ru nanosized catalysts, more various Pt-based catalysts, such as PtSn and so on can also easily be synthesized by the method used in the present work. Indeed, in the method proposed here inexpensive ethylene glycol plays the role of both reducing agent and protective agent during the metal reduction process. Given the above reasons and the results of XRD and TEM, the method adopted here is convenient and inexpensive, suitable to prepare various supported Pt-based catalysts with higher metal loading.

Furthermore, another interesting result is reported in Fig. 4 in which it is clear that in the Pt-Sn catalysts, the lattice parameter of Pt crystalline increases as the Sn content increases. The mean particle size and lattice parameter obtained from the XRD patterns and TEM results are listed in Table 1. As easily can be noticed,
Table 2
CV results of Pt/C and carbon-supported Pt-bimetallic catalysts (25°C)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Methanol (1.0 M)</th>
<th>Ethanol (1.0 M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Positive peak potential (mV vs. SCE)</td>
<td>Peak current density (mA/cm²)</td>
</tr>
<tr>
<td>Pt/C</td>
<td>680</td>
<td>27.63</td>
</tr>
<tr>
<td>Pt₁Ru₁/C</td>
<td>551</td>
<td>48.05</td>
</tr>
<tr>
<td>Pt₁Sn₁/C</td>
<td>638</td>
<td>36.72</td>
</tr>
<tr>
<td>Pt₁W₁/C</td>
<td>592</td>
<td>39.15</td>
</tr>
<tr>
<td>Pt₁Pd₁/C</td>
<td>625</td>
<td>34.56</td>
</tr>
</tbody>
</table>

According to the TEM micrographs, all Pt-Sn catalysts have almost very similar particle size ranging between 2.2 and 3.0 nm.

The main results of CV test of carbon supported Pt and Pt-bimetallic catalysts are listed in Table 2 including the positive peak potentials and corresponding peak current densities of ethanol electro-oxidation. Peak position reported in Table 2 is for the first ethanol oxidation peak, and the second oxidation peak may appear at higher potential, where the bimetallic catalysts are not so stable. The CV results of methanol electro-oxidation on these catalysts are also listed in Table 2 in order to compare their activity with respect to the electro-oxidation of ethanol. From Table 2 and Fig. 5, it is clear that the addition of the second metal to Pt results in the negative shift of the first ethanol electro-oxidation peak. The first oxidation peak on Pt₁Ru₁/C appears at the most negative potential, at about 0.53 V (versus SCE), and the peak potential is about 0.23 V lower than that on Pt/C catalyst. The first electro-oxidation peak of ethanol on Pt₁Pd₁/C is around 0.65 V (versus SCE), higher than that on Pt₁Ru₁/C. The current density at the first peak of the ethanol electro-oxidation on Pt₁Ru₁/C is higher than that on Pt₁Pd₁/C, but less than these on Pt₁Sn₁/C, Pt₁W₁/C and Pt/C, respectively. The Pt₁Sn₁/C shows the highest current density, but also has a higher overpotential (0.71 versus SCE). Pt₁W₁/C catalyst also exhibits a higher current density than these of Pt/C and Pt₁Ru₁/C and Pt₁Pd₁/C, but has a similar overpotential (0.75 versus SCE) to Pt/C. Pt₁Pd₁/C shows lower activity to ethanol oxidation than Pt₁Ru₁/C and Pt₁Sn₁/C. The positive peak current density of ethanol on Pt₁W₁/C is close to that on Pt₁Sn₁/C, but...
the peak appears at higher positive potential. It is clear that \( \text{Pt}_1\text{Sn}_1/C \) presents a higher positive peak current density, and consequently higher activity to ethanol electro-oxidation from the point of current density. \( \text{Pt}_1\text{Ru}_1/C \) shows the lowest overpotential to ethanol electro-oxidation among the above electrocatalysts, which indicates that \( \text{Pt}_1\text{Ru}_1/C \) is also a promising catalyst for ethanol electro-oxidation. It is also found from Table 2 and Fig. 5 that ethanol electro-oxidation on the \( \text{Pt}_1\text{Sn}_1/C \) and \( \text{Pt}_1\text{Ru}_1/C \) catalyst seem opposite from methanol electro-oxidation on them. \( \text{Pt}_1\text{Ru}_1/C \) catalyst shows higher activity to methanol oxidation than \( \text{Pt}_1\text{Sn}_1/C \), while the latter shows higher activity to ethanol oxidation than \( \text{Pt}_1\text{Ru}_1/C \). As one can observe in Fig. 5, the negative peaks of \( \text{Pt}_1\text{Sn}_1/C \) and \( \text{Pt}_1\text{W}_1/C \) also differ from those of \( \text{Pt}_1\text{Ru}_1/C \) and \( \text{Pt}_1\text{Pd}_1/C \), indicating that there are different interactions between the catalyst surfaces and ethanol electro-reaction intermediates. The positive peak positions of ethanol oxidation on ternary metallic catalysts were 600 mV (vs. SCE) for \( \text{Pt}_1\text{Ru}_1\text{Mo}_1/C \), 700 mV for \( \text{Pt}_1\text{Ru}_1\text{W}_1/C \). The CV test identifies that \( \text{Pt}_1\text{Sn}_1/C \) is the more suitable electro-catalyst for ethanol electro-oxidation among these four Pt-bimetallic catalysts.

Then, the four Pt-based bimetallic catalysts and Pt/C were employed as anode catalysts for the MEA preparation and their DEFC performances were tested. In Fig. 6 are reported the performances of single ethanol cells with different anode catalysts at 90 °C. As identified in the CV test, \( \text{Pt}_1\text{Sn}_1/C \) shows higher activity with respect to Pt/C and to the other bimetallic catalyst in the single fuel cell tests. In Fig. 6, it can be distinguished that adopting \( \text{Pt}_1\text{Sn}_1/C \) as the anode catalyst, the open circuit voltage (OCV) of the single fuel cell approaches 810 mV, about 140 mV more than the fuel cell employing \( \text{Pt}_1\text{Ru}_1/C \). The OCVs of the single cells with \( \text{Pt}_1\text{W}_1/C \) and \( \text{Pt}_1\text{Pd}_1/C \) as anode catalysts are 540 and 505 mV, respectively. The performance of the single cell with Pt/C as anode catalyst is similar to that of single cell with \( \text{Pt}_1\text{Pd}_1/C \). The single cell test demonstrates that, from a practical point of view, Pt/C and \( \text{Pt}_1\text{Pd}_1/C \) do not seem to be good catalysts for ethanol oxidation. W and Ru can dramatically enhance the activity of Pt with respect to methanol oxidation due to the so-called synergetic effect. In the present work, as one can observe from the Fig. 6, the addition of the two additives (Ru and W) to Pt also enhances the ethanol oxidation activity, and by examining the single cell
performances Ru is better activator than W. As far as Sn is concerned, its effect on Pt activity for methanol electro-oxidation is yet controversial in recent literature. Here, as observed Table 2, the methanol CV test on Pt1Sn1/C demonstrates the promoting effect of Sn towards methanol electro-oxidation on Pt although it is inferior to that of Ru. But the single fuel cell experiment result in Fig. 6 and the ethanol CV results in Fig. 5 jointly indicate that adding Sn to Pt can remarkably increase the electro-oxidation of ethanol on Pt. Thus, as far as ethanol electro-oxidation is concerned, Pt1Sn1/C is evidently the more suitable anode catalyst among the four bimetallic catalyst mentioned above. As concerned the life time, it was found from the experiments that the power output of almost all single direct ethanol fuel cells was constant for three days at least. More precisely the performance of single cells with different anode on the second day was comparable to that on the third day and both were relatively improved compared to the single cell performance on the first day. Here the results for every anode catalyst were recorded on the second day after the single cell fixed and tested.

At present Pt-Ru catalysts are still used extensively as anode catalysts for fuel cells fueled with methanol or synthesis gas. Based on Pt-Ru, many ternary and quaternary metallic catalysts have been prepared, among which PtRuW and PtRuMo showed excellent behavior. In the present study, Pt1Ru1W1/C and Pt1Ru1Mo1/C with Pt weight loading of 20% were also prepared by adopting the same method. As shown in Fig. 7, the single fuel cells employing the two tri-metallic catalysts, respectively, as anode catalysts demonstrate really improved performance. From the Fig. 7, it can be also seen that the addition of Mo increases the open circuit voltage, while the addition of W can greatly increase the maximum power density.

The results of single direct ethanol fuel cell tests adopting the different catalysts mentioned above are summarized in Table 3, in which is including the open circuit voltage of various single cells, the working output voltages at current densities of 30 and 60 mA/cm², the corresponding power densities, and the maximum power densities and its corresponding current densities. Although compared to Pt1Ru1/C, the addition of W to Pt-Ru can greatly improve the activity of Pt-Ru toward ethanol electro-oxidation, the performance of the single DEFC with Pt1Ru1W1/C is still inferior to that employing Pt1Sn1/C.

![Fig. 7. Comparison of the performance of single cell with PtRu-based anode catalysts at 90°C. Solid electrolyte is Nafion®-115 membrane. Ethanol aqueous solution is 1.0 mol/l and its flow rate is 1.0 ml/min; cathode contains Pt/C (Johnson Matthey Co.) with 1.0 mgPt/cm².](image-url)
Table 3
Summary of performance of single fuel cell tests adopting different catalysts (90 °C)

<table>
<thead>
<tr>
<th>Anode catalysts</th>
<th>Open circuit voltage (mV)</th>
<th>At 30 mA/cm²</th>
<th>At 60 mA/cm²</th>
<th>Maximum power density (mW/cm²)</th>
<th>Current density at maximum power density (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Output voltage (mV)</td>
<td>Corresponding power density (mA/cm²)</td>
<td>Output voltage (mV)</td>
<td>Corresponding power density (mA/cm²)</td>
</tr>
<tr>
<td>Pt/C</td>
<td>547</td>
<td>275</td>
<td>8.25</td>
<td>177</td>
<td>10.62</td>
</tr>
<tr>
<td>Pt/Pd/C</td>
<td>500</td>
<td>285</td>
<td>8.53</td>
<td>193</td>
<td>11.58</td>
</tr>
<tr>
<td>Pt/W/C</td>
<td>540</td>
<td>312</td>
<td>9.36</td>
<td>252</td>
<td>13.92</td>
</tr>
<tr>
<td>Pt/Ru/C</td>
<td>677</td>
<td>461</td>
<td>13.83</td>
<td>368</td>
<td>22.06</td>
</tr>
<tr>
<td>Pt/Sn/C</td>
<td>811</td>
<td>662</td>
<td>19.86</td>
<td>576</td>
<td>34.56</td>
</tr>
<tr>
<td>Pt/Ru/W/C</td>
<td>698</td>
<td>503</td>
<td>15.09</td>
<td>425</td>
<td>25.50</td>
</tr>
<tr>
<td>Pt/Ru/Mo/C</td>
<td>720</td>
<td>486</td>
<td>14.58</td>
<td>389</td>
<td>23.34</td>
</tr>
</tbody>
</table>

Based on the fact that Pt₁Sn₁/C demonstrated to be a very active anode catalyst for the direct electro-oxidation of ethanol in PEM, additional work has been done to investigate the effect of Pt/Sn atomic ratio. Fig. 8 shows the performances of single fuel cells with different PtSn/C catalysts as anode catalysts. The results of these single ethanol fuel cells at different operation temperature values are depicted in Fig. 9. This part of work demonstrates again that the PtSn/C catalysts are more suitable for ethanol electro-oxidation than PtRu/C. Moreover, even Pt₄Sn₁/C, which is the less active catalyst for ethanol electro-oxidation, exhibits higher performance in single fuel cell operation than Pt₁Ru₁/C. The single fuel cell with Pt₄Sn₁/C as anode catalyst shows a comparable performance to that with Pt₁Ru₁/W₁/C, which, as mentioned above, is an improved PtRu-based catalyst supported on carbon for ethanol electro-oxidation.
In Fig. 9 it is also observed that at 60 °C, the power densities of single fuel cell at 30 and 40 mA/cm² increase with the Sn content in PtSn/C catalysts, and the best cell performance (according to the peak power density) appears when Pt3Sn2/C is employed as anode catalyst. When the temperature increases to 75 °C, the best performances are exhibited by the single fuel cell with Pt2Sn/C and Pt3Sn2/C. At 90 °C, the maximum power densities and power densities at 30, 60 and 90 mA/cm² all indicate that Pt2Sn1/C is the optimum anode catalyst for direct ethanol fuel cell.

A possible explanation of the behavior observed above is the following: it is well known that CO ads is one of the main and common intermediates during the electro-oxidation of ethanol, methanol and formic acid. Thus the oxidation of CO-like intermediates is crucial to ethanol electro-oxidation. According to XPS results about these in-house Pt-based catalysts as mentioned above, Pt and Ru of PtRu/C catalyst surface are in metallic states while Sn of PtSn/C catalyst surfaces is in oxide state. It is easy, as demonstrated in previous works, for Ru and W to provide –OHads species during methanol or ethanol electro-oxidation [27]. Sn or its oxides [5] are also helpful to the formation of surface oxygen-containing species. It is reported [28] that alloying Pt with Ru leads to a downshift of the Pt d states, increasing CO-tolerance of Pt and improving its activities to CO, methanol and ethanol electro-oxidations. At the same time the Ru d-band is shifted to higher energy levels leading to a stronger adsorption of CO on the Ru sites. Thus, a fraction of Ru surface active sites are probably not free for –OHads formation. By combining calculated binding energy values [28] and experimental results [29] it is assumed that CO does not prefer to bind with Sn surface atoms. Consequently, the Sn surface sites are always free to supply adsorbed –OHads species. Furthermore, as mentioned earlier, –OH species prefers to be adsorbed mostly on Sn than on Pt sites. It is obvious that Sn (or Sn-oxide [30]), Ru and W are able to form oxygen-containing species at lower overpotentials than Pt. These oxygen-containing surface species are necessary for the oxidation of adsorbed CO-like intermediates. This is the so-called bifunctional mechanism and explains partially the enhanced effect of Sn, Ru and W on the ethanol electro-oxidation. However, the enormous difference between single fuel cells performance with...
the three bimetallic catalysts, Pt1Sn1/C, Pt1Ru1/C and Pt1W1/C, could not be explained adequately in terms of bifunctional mechanism alone.

It is observed from the XRD results that the addition of Sn, Ru and W produces different changes of Pt lattice parameters. Thus, a plausible explanation is that the stretch of Pt lattice parameter catalyzes the cleavage of C–C bond and consequently increases the efficiency of ethanol electro-oxidation. Electronic interaction between Pt and the modifier may be another main cause. It has been reported that charge transfer from Sn to Pt would attract the oxygen-containing species to the surface at the more electropositive Sn atoms [31]. Another effect is probably due to the fact that the addition of Sn could decrease oxidative Pt state from catalyst surface and increase the free active Pt sites for ethanol chemisorption and the consequent dehydrogenation reaction. Xia [32] found enhanced catalytic effect of tin adatoms for the oxidation of adsorbed formic acid and explained it in terms of combination of bifunctional mechanism and electronic interaction between Sn adatoms and Pt substrate. The electronic interaction is emphasized in the initial oxidation region. The electronic interaction between Pt and Sn is proportional to the Sn content, and the performance of single fuel cell with Pt1Sn1/C or Pt1Sn2/C or Pt1Sn/C as anode catalyst is better than that with Pt1Sn/C or Pt1Sn/C at a temperature value close to 90 °C.

At higher temperatures or at higher current density regions, the performance of a single fuel cell with Pt1Sn1/C as anode catalyst is superior to the performance of a single fuel cell with Pt1Sn2/C or Pt1Sn1/C catalysts. It is assumed that separate SnO2 phase could occur on the catalyst surface, and the separate oxide phase would cover active Pt sites and impede ethanol chemisorption. The decrease of Pt sites would result in the shift of rate determining step (RDS) of ethanol electro-oxidation to the chemisorption step. Besides, Sn oxide content increases with the Sn content in PtSn/C catalysts, and Sn oxide, on the other hand, probably results in the decrease of conductivity of anode catalyst, which consequently brings the increase of ohmic resistance of electron-conductor [33] and single cell internal resistance. The resistance increase, although has no correlation with chemical process, unavoidably results in the fuel cell resistance-overvoltage and worsens the performance of single cell, which partially counteracts the promotion of Sn. At lower temperatures, when the electro-oxidation of ethanol is not fast and the effect of resistance-overvoltage is not very obvious, the cleavage of C–C bond and the oxidation of adsorbed intermediates other than chemisorption of ethanol represent the RDS of the entire reaction process. Thus, higher Sn content is helpful to the formation of abundant –OHads and accelerates the entire reaction. This explains why the performance of single fuel cell with Pt1Sn1/C is better than that with Pt1Sn2/C at 60 °C. Thus, the experimental results that the performance of the single fuel cell with Pt1Sn1/C at higher temperature values is inferior to those with Pt1Sn2/C and Pt1Sn3/C are due probably to both the ohmic effect and the less active sites of Pt surface for ethanol chemisorption.

### 4. Conclusion

In the present work, the novel catalyst preparation method is demonstrated to be suitable to prepare nanometer-sized carbon supported Pt-based bimetallic and trimetallic catalysts in the presence of higher metal loadings. The results of the cyclic voltammetry tests are coordinated with those of single fuel cells from the point of current. The addition of a second element to Pt can evidently improve the reaction of ethanol electro-oxidation. It was found that Sn, Ru and W are good additives, affecting the activity of ethanol electro-oxidation in the following sequence: Pt1Sn1/C > Pt1Ru1/C > Pt1W1/C > Pt1Mo1/C > Pt/C.

Although considered as a good catalyst for methanol electro-oxidation in DMFCs, Pt1Ru1/C does not show the best activity for ethanol electro-oxidation. The addition of W and Mo, especially W, improves Pt1Ru1/C activity for ethanol electro-oxidation and its performance in direct ethanol single cell, but the activity of Pt1Ru1W1/C is still inferior to that of Pt1Sn1/C. The current density–voltage characteristics of single direct ethanol fuel cell show evidently that the Pt1Sn1/C is a better catalyst than carbon supported Pt1Ru1 and other PtRu-based ternary metallic catalysts.

Besides supplying abundant –OHads at catalyst surface, the different interactions between Pt and Sn or Ru result in the obvious difference between the
performances of single fuel cells employing \( \text{Pt}_{3}\text{Sn}_{1}/\text{C} \) and \( \text{Pt}_{4}\text{Sn}_{1}/\text{C} \) as anode catalysts, respectively. The amount of \(-\text{OH}_{\text{ads}}\), the amount of surface Pt active sites and the ohmic effect of \( \text{PtSn}/\text{C} \) catalysts determine the activity of \( \text{PtSn}/\text{C} \) with different Pt/Sn ratios and their performances in single ethanol cells. The single direct ethanol fuel cell tests show that \( \text{Pt}_{2}\text{Sn}_{1}/\text{C} \) or \( \text{Pt}_{3}\text{Sn}_{2}/\text{C} \) or \( \text{Pt}_{1}\text{Sn}_{1}/\text{C} \) is better than \( \text{Pt}_{1}\text{Sn}_{1}/\text{C} \) or \( \text{Pt}_{4}\text{Sn}_{1}/\text{C} \) as a result of \(-\text{OH}_{\text{ads}}\) supplying. At lower temperatures or in low current density region, the \( \text{Pt}_{3}\text{Sn}_{2}/\text{C} \) seems to be more suitable for the direct ethanol fuel cell. At 75°C, the single cell with \( \text{Pt}_{3}\text{Sn}_{2}/\text{C} \) as anode catalyst gives performance comparable to the cell with \( \text{Pt}_{2}\text{Sn}_{1}/\text{C} \) at higher temperature, the single fuel cell with \( \text{Pt}_{3}\text{Sn}_{2}/\text{C} \) shows the best performance. It is confirmed that \( \text{Pt}_{3}\text{Sn}_{2}/\text{C} \), supplying sufficient \(-\text{OH}_{\text{ads}}\), having adequate active Pt surface sites and acceptable ohmic effect, is the appropriate anode catalyst for direct ethanol fuel cell.

Acknowledgements

The authors would like to thank the “Greece-China Joint Research and Technology Programme 2000–2005” for funding. We also thank the financial support of National Natural Science Foundation of China (Grant No. 20173060).

References