Simple and controllable synthesis of highly dispersed Pt–Ru/C catalysts by a two-step spray pyrolysis process

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A carbon supported Pt–Ru catalyst with uniform distribution and small average size of the Pt–Ru particles was synthesized using a two-step spray pyrolysis (SP) method; the electrocatalytic activity of the prepared catalyst for methanol oxidation is better than that of the standard commercial catalyst.

Supported and unsupported Pt–Ru catalysts have been investigated for their superior electrocatalytic activities for methanol oxidation and good CO tolerant ability related to direct methanol fuel cells (DMFCs).[1–3] It is well known that the electrocatalytic activities are strongly dependent on the shape, size and size distribution of the metal particles.[4] Numerous works have been devoted to the preparation and structure–activity relationship study of this type of catalyst.[3,5–11] Among the preparation methods reported in the literature for carbon supported Pt–Ru (Pt–Ru/C) catalysts, the impregnation method[12,13] and colloidal method[14,15] are the most adopted routes. Pt–Ru catalysts prepared by the impregnation method do not show good control of the particle size, size distribution or chemical composition. The colloidal method and solid phase reaction method,[11] however, are generally somewhat complex. In particular, repeated filtering and washing procedures are time-consuming and easily cause the loss of noble metals.

Spray pyrolysis (SP) is a useful tool for the large- or small-scale production of particles with controlled particle size since the properties of the final product can be controlled through the choice of precursor and solution concentration or by changing the conditions of the aerosol decomposition. Generally, in an SP process, the reaction temperature and the composition of the carrier gas are the basic operating variables. In addition, the solution properties, such as the precursor composition, concentration, or the addition of a co-solvent is crucial to achieve the desired composition and morphology of the final product.[16]

In this communication we report a two-step SP process based on the use of a special solvent to prepare Pt–Ru/C catalysts from metal salt precursors with the addition of reducing gases (hydrogen–nitrogen).

The synthesis procedure for the Pt–Ru/C catalysts is as follows. First, H_2PtCl_6 and $RuCl_3$ (atomic ratio of Pt:Ru = 1:1) as the precursors were dissolved in poly(ethylene glycol) (PEG, molecular weight (MW) = 200 or 600, A.R.) and mixed with carbon black (Vulcan XC-72R, Cabot Corp., $S_{BET} = 250\ m^2\ g^{-1}$) suspended in distilled water. The mixture was maintained at 80 °C and stirred for at least 3 h. An atomizer (Büchi Mini B-191) was used to generate the aerosol droplets of the precursor solution with a delivery rate of 150 mL h^{-1} and the flow rate of the gas carrier was 10 L min^{-1}. The suspension of the precursor droplets in the gas carrier was passed through a diffusion driver and then passed through a quartz tube heated externally by tube furnaces forming metal nanoparticles on the carbon by solvent evaporation and precursor decomposition. The furnace temperature for these experiments was 180 °C. Finally, the as-prepared particles obtained by spray pyrolysis were post-treated with a heating rate of 10 °C min^{-1} to 600 °C for 3 h under hydrogen–nitrogen to obtain the Pt–Ru/C catalysts (denoted as Pt–Ru/C(SP)). The loading of Pt and Ru in the catalyst was varied from 10 to 50% by varying the H_2PtCl_6 and $RuCl_3$ content in the initial solution. This communication reports mainly the results of the Pt–Ru/C (SP) sample with 20 wt% Pt + 10 wt% Ru.

The size and morphology of the Pt–Ru/C catalysts were characterized by TEM (JEOL JEM 2010). The bulk composition of the prepared catalysts was evaluated by energy dispersive X-ray analysis (EDX) in a scanning electron microscope (JEOL JAX-840). The XRD pattern of the catalysts were obtained using a Rigaku-D/MAX-PC 2500 X-ray diffractometer with the Cu-Kα ($\lambda = 1.5405$ Å) radiation source operating at 40 kV and 200 mA. In order to compare the electrocatalytic activity of the Pt–Ru/C(SP) catalyst with that of the commercial Pt–Ru/C catalyst (E-TEK Co.) (denoted as Pt–Ru/C(E)), the performance of a single DMFC with the anodic Pt–Ru/C(SP) catalyst (20 wt% Pt + 10 wt% Ru) and the cathodic Pt/C(E) catalyst (30 wt% Pt) was measured and compared with that with the anodic Pt–Ru/C(E) catalyst (20 wt% Pt + 10 wt% Ru) and the cathodic Pt/C(E) catalyst (30 wt% Pt). The loading of Pt–Ru on both anode and cathode was 2 mg cm^{-2}. A 1.0 M CH_3OH solution with a flow rate of 1.0 mL min^{-1} and oxygen with a flow rate of 5 mL min^{-1} at 0.2 M Pa were used. The surface area of the electrode was 30 × 30 mm. The preparation of the membrane electrode assembly and the operation of the single fuel cell is the same as that in the literature.[16] The operation temperature of the cell was 90 °C.

Figs. 1 and 2 show TEM images of the different Pt–Ru/C(SP) catalysts. It can be observed from Fig. 1 that the Pt–Ru particles are homogeneously distributed on the carbon carrier and the corresponding histogram of the Pt–Ru particle size is shown in Fig. 3. This reveals the narrow and log-normal particle size distribution. Based on the measurements of 300 particles in random regions, the average size of the Pt–Ru particles is 2.5 ± 0.2 nm. It was found that the length of PEG chains was responsible for the morphology of the Pt–Ru particles on the carbon carrier. When the PEG chains are long enough (MW = 600), they form a large network leading to a

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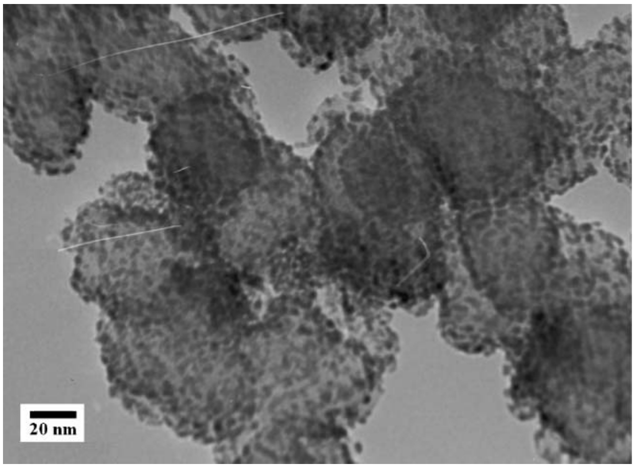

Fig. 1 TEM image of Pt–Ru/C(SP), MW = 600.

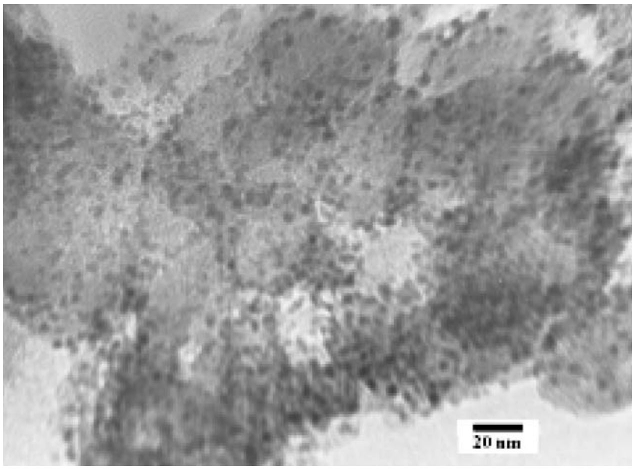

Fig. 2 TEM image of Pt–Ru/C(SP), MW = 200.

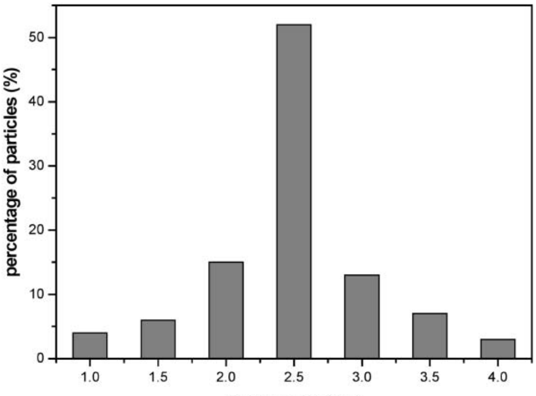

Fig. 3 Histograms from the TEM images of the Pt–Ru/C(SP) catalysts.

homogeneous dispersion of the Pt–Ru particles on the carbon carrier. However, when the PEG chains were short (MW = 200), the coverage of PEG only occurred partially on the surface of the carbon carrier, leading to a broad particle size distribution and the partial aggregation of the Pt–Ru particles on the carbon carrier. In addition, it was found that the average size of the Pt–Ru particles can be controlled by changing the concentration of the precursors, H_2PtCl_6 and $RuCl_3$, when the concentration of PEG was fixed at 0.10 g mL^{-1}. The average size of the Pt–Ru particles was found to increase slightly with an increase of the precursor concentration. For example, when the precursor concentration is 0.02, 0.04, 0.06 M, the average size of the Pt–Ru particles obtained is 2.00 $\pm$ 0.3, 2.50 $\pm$ 0.2, 3.2 $\pm$ 0.2 nm, respectively.

A typical EDX spectrum of the Pt–Ru/C(SP) catalysts is shown in Fig. 4, from which the atomic ratio of Pt and Ru is found to be 1.02:1, nearly the same as the atomic ratio of Pt and Ru of the precursor salts. No traces of Cl were detected.

Fig. 5 compares the XRD pattern of the Pt–Ru/C(SP) catalyst with that of the Pt–Ru/C(E) catalyst. The broad diffraction peaks for the Pt–Ru/C(SP) catalyst reflect the smaller average size of the Pt–Ru crystal particles. This result is consistent with the TEM analysis in Fig. 1. A shift of the peak positions in the XRD patterns of Pt–Ru/C(SP) catalyst towards higher Bragg angles was observed with respect to that of the Pt–Ru/C(E) catalyst. This indicated that the alloying degree of the Pt–Ru particles in the Pt–Ru/C(SP) catalyst is higher than that in the Pt–Ru/C(E) catalyst. Crystallographic parameters, average size of the crystal particles and the degree of alloying can be calculated according to the relationship described in refs. 17 and 18.

Fig. 6 shows the current density–voltage curves of the single DMFC with different anodic catalysts. It was observed that when the current density is 300 mA cm^{-2}, the voltage of the cell with the anodic Pt–Ru/C(SP) catalyst is 0.39 V, *cf.* 0.34 V for the anodic

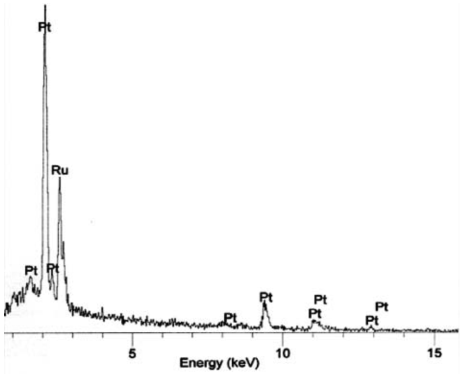

Fig. 4 EDX spectrum of the Pt–Ru/C(SP), MW = 600 catalyst.

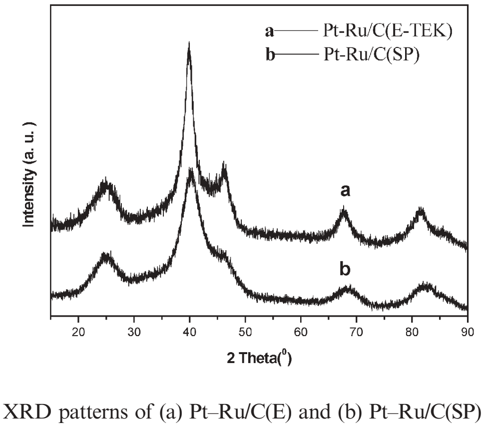

Fig. 5 XRD patterns of (a) Pt–Ru/C(E) and (b) Pt–Ru/C(SP) catalysts.

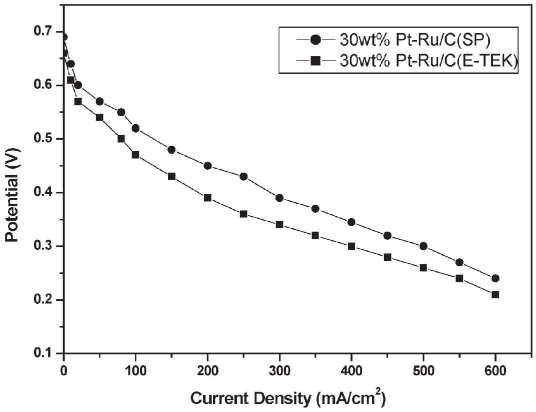

Fig. 6 The performance of a single DMFC with Pt–Ru/C(SP) and Pt–Ru/C(E) anodic catalysts.

Pt–Ru/C(E) catalyst. This result demonstrates that the electrocatalytic activity of the Pt–Ru/C(SP) catalyst for methanol oxidation is better than that of the Pt–Ru/C(E) catalyst. The high electrocatalytic activity of the Pt–Ru/C(SP) catalyst for the methanol oxidation can be attributed to the uniform distribution, small average size and high alloying degree of the Pt–Ru crystal particles in the Pt–Ru/C(SP) catalyst.[19–23]

In conclusion, two-step SP is a useful method to synthesize Pt–Ru/C catalysts. The electrocatalytic activity for methanol oxidation of the Pt–Ru/C catalysts obtained with this method is high. This arises from the uniform distribution, small average size and high alloying degree of the Pt–Ru particles on the carbon carrier.

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