Tin oxide nanoparticle-modified commercial PtRu catalyst for methanol oxidation

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The electrocatalytic performance of commercial PtRu/C is significantly enhanced by directly mixing a few SnO_2 nanoparticles. The composite catalysts show enhanced CO oxidation, higher activity and better stability than commercial PtRu/C. Among the different ratios of SnO_2 nanoparticles (10–40%), the SnO_2–PtRu/C (20%) composite catalyst shows the best catalytic activity for methanol oxidation. The effect of temperature on methanol oxidation was also investigated and the apparent activation energy (E_a) value of catalyst was obtained. The results here suggest a simple route to enhance the catalytic efficiency for commercial PtRu/C catalyst.

1. Introduction: Direct methanol fuel cells (DMFCs) are being actively considered for automotive and stationary power applications as they offer high efficiency with little or no pollution [1]. The main challenge of DMFCs is to seek and improve catalysts with good activity and anti-poisoning ability. Various strategies have been developed to improve the performance for methanol electrooxidation, for example, the addition or incorporation of a second element in Pt electrocatalysts, or the proper morphological (shape and size) control [2]. At present, PtRu catalyst has been considered as the most active catalyst, which is indeed the state-of-the-art anode catalyst for DMFCs [3]. However, because there is still room relating to the efficiency and cost of PtRu, further improvement is required for its practical application.

Recently, metal oxides (such as IrO_2, V_2O_5, WO_3, CeO_2, MoO_3 and RuO_2) were introduced into the PtRu system and a great number of experiments indicated that its catalytic activity for methanol electrooxidation was greatly improved [4–9]. The metal oxides possess a good capacity for storing and releasing oxygen, which plays an important role in intermediate CO_{ad} electrooxidation. Furthermore, the low price and the abundance of metal oxides can reduce the cost of catalyst. Therefore they are promising additives for Pt-based catalysts [10]. However, they often synthesise the metal oxides/carbon composite as a support first, then depositing nanoparticles on the surface of synthesised composite material [4, 7, 8]. Or, they were depositing metal nanoparticles and metal oxides on the support simultaneously [5, 6, 9]. The adding methods of the metal oxides in catalysts are quite complicated.

In the present work, the composite catalysts are prepared by directly mixing commercial PtRu/C catalyst with SnO_2 nanoparticles. It is reported that tin oxide nanoparticles (SnO_2) in the vicinity of Pt could offer oxygen species conveniently to remove the CO-like species [11]. Cyclic voltammetry, chronoamperometry and CO-stripping were adopted to characterise the electrocatalytic activities of the composite catalysts for methanol oxidation. The results suggest that directly mixing SnO_2 nanoparticles can dramatically enhance the catalytic efficiency of commercial PtRu/C. The effect of temperature on methanol oxidation was also investigated and the apparent activation energy (E_a) value of catalyst was obtained.

2. Experimental

2.1. Preparation: The SnO_2–PtRu/C composite catalysts electrode were prepared by a directly mixing method as follows: certain amounts of the SnO_2 nanoparticles (50–70 nm, Aladdin Chemistry Co. Ltd) and the commercial PtRu (Johnson Matthey Company, 30 wt% metal loaded, Atom ratio Pt : Ru = 1 : 1) catalyst were put into a vial with various PtRu/SnO_2 mass ratios (PtRu : SnO_2 = 100 : 0, 90 : 10, 80 : 20, 70 : 30 and 60 : 40). The mixture catalyst was dispersed ultrasonically for 1 h in 1 ml Nafion/ethanol (0.25% Nafion). Then, 8 µl suspensions were quantitatively transferred to the surface of polished glassy carbon electrode, followed by drying in air at room temperature. The commercial PtRu/C was used as a reference.

2.2. Characterisation: The morphology of the catalyst was analysed by a Tecnai G220S–TWIN (FEI Company) transmission electron microscope (TEM) operating at 200 kV. The electrochemical experiments were performed using an Autolab electrochemical work station (PGSTAT128N, Eco Chemie, The Netherlands). A conventional three-electrode cell was used, including an Ag/AgCl (3 M KCl) electrode as the reference, a platinum wire as the counter and a modified glass carbon (5 mm in diameter) as the working electrode.

Before each measurement, the solution was purged with high-purity N_2 for at least 30 min to ensure the N_2 saturated. All measurements were recorded at a rotation speed of 300 rpm after a stable response was established at room temperature (except for the effect of temperature on the methanol oxidation study). The cyclic voltammogram and CO-stripping were characterised in a 0.5 M H_2SO_4 solution. The CO pre-adsorption was performed with bubbling CO for 10 min, and then removed by purging the electrolyte with N_2. Electrooxidation of CO was measured by

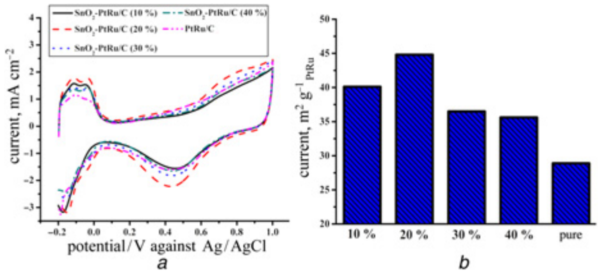

Figure 1 *Cyclic voltammograms of pure PtRu/C, 10, 20, 30 and 40% SnO_2–PtRu/C composite catalysts; scan rate: 50 mV/s (Fig. 1a); corresponding ECSA of catalysts histogram (Fig. 1b)*

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cycling the potential between −0.2 and 1.0 V (against Ag/AgCl). Electrocatalytic activities for methanol oxidation were measured in the solution of 0.5 M H_2SO_4 + 0.5 M methanol.

3. Results and discussion: Fig. 1*a* shows representative cyclic voltammogram curves in N_2-purged 0.5 M H_2SO_4 electrolyte of the pure PtRu/C, SnO_2–PtRu/C (10, 20, 30 and 40%) electrocatalysts from −0.2 to 1.0 V (against Ag/AgCl). All the SnO_2–PtRu/C composite electrodes have the higher current response for the hydrogen adsorption and deposition than that of the commercial PtRu/C. The electrochemically active surface area (ECSA) was calculated according to the literature [12]. As shown in Fig. 1*b*, the ECSA per unit weight of PtRu metal is 28.9 m^2/g for commercial PtRu/C. The ECSA of SnO_2–PtRu/C composite catalysts were calculated based on the PtRu mass, and they are 40.1, 44.8, 36.5 and 35.6 m^2/g for different contents of SnO_2 nanoparticles (10, 20, 30 and 40%, respectively) in the SnO_2–PtRu/C system. The SnO_2–PtRu/C (20%) catalyst shows the greatest specific ECSA, which is 1.5 times greater than that of the commercial PtRu/C catalyst. Whereas in the oxygen adsorption and desorption region, the SnO_2–PtRu/C composite catalysts with different SnO_2 ratios exhibit higher current density to a different degree than commercial PtRu/C. This suggests that SnO_2 nanoparticles offer oxygen-containing species which promote the adsorption of oxygen on Pt [10]. The oxygen-containing groups Sn–OH_{ads} species formed from SnO_2 can effectively assist Pt catalyst during the methanol oxidation reaction [13].

The electrocatalytic activities of SnO_2–PtRu/C composite were investigated and compared by investigating their electrooxidation of methanol, which is directly related to application in DMFCs. Fig. 2*a* shows representative typical cyclic voltammograms of SnO_2–PtRu/C composite electrode. As shown in Fig. 2*b*, the peak current of commercial PtRu/C catalysts is 0.118 A/mg PtRu. The oxidation peak current densities varied with different degrees when a different amount of SnO_2 nanoparticle was added. They are 0.201, 0.224, 0.189 and 0.151 A/mg PtRu for different contents of SnO_2 nanoparticles (10, 20, 30 and 40%, respectively) in the SnO_2–PtRu/C system. The SnO_2–PtRu/C (20%) catalyst shows the best activity for methanol oxidation, which is 1.9 times greater than that of the commercial PtRu/C catalysts. These results prove that mixing SnO_2 nanoparticles is a promising way to enhance the activity of PtRu/C catalyst. Previously, it was thought that the current density of the catalyst system increased with the increasing ratio of SnO_2 nanoparticles. However, the decrease of the current density was observed with the further increase of SnO_2 nanoparticles (30 and 40%). As observed in the preceding discussion, an increase in the content of SnO_2 would provide more oxygen-containing groups of Sn–OH_{ads} species, which may lead to an increase of the activity of catalyst. However, the SnO_2 is non-conductive, and the higher content of SnO_2 nanoparticles results in reducing conductivity of the carbon support, which is unfavourable for the activity of methanol oxidation. At an appropriate content of SnO_2, the two opposite factors reach equilibrium, that is, the highest activity of the SnO_2–PtRu/C catalysts.

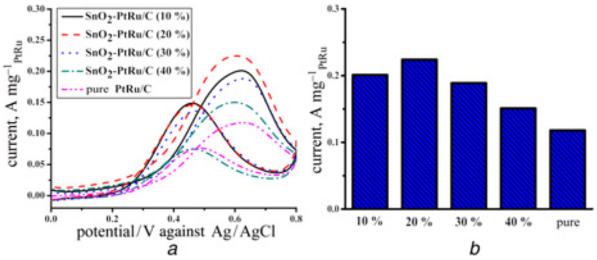

Figure 2 *Methanol electrooxidation of pure PtRu/C, 10, 20, 30 and 40% SnO_2–PtRu/C composite catalysts; scan rate: 50 mV/s (Fig. 2a); corresponding peak current histogram (Fig. 2b)*

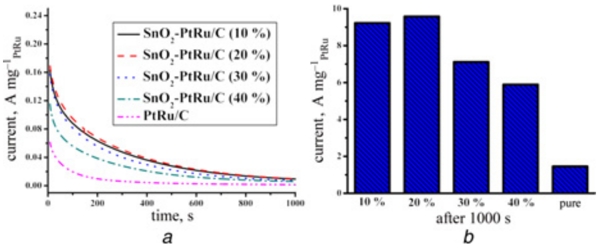

Figure 3 *Chronoamperometry curves of pure PtRu/C, 10, 20, 30 and 40 SnO_2–PtRu/C composite catalysts for methanol oxidation, fixed potential: 0.6 V (Fig. 3a); corresponding current histogram after 1000 s (Fig. 3b)*

The high durability of the power sources is one of the main requirements for practical applications. As known, the accumulation of intermediate species on the catalyst surface, which leads to 'catalyst poisoning', is the major deficiency of all Pt-based catalysts used for methanol oxidation [14]. Fig. 3*a* shows the chronoamperometric studies of the SnO_2–PtRu/C composite catalysts. It can be observed that the current of the SnO_2–PtRu/C composite catalysts at 1000 s are 9.2, 9.6, 7.1, 5.8 mA/mg PtRu for different contents of SnO_2 nanoparticles (10, 20, 30 and 40%, respectively) in the SnO_2–PtRu/C system (Fig. 3*b*). However, the chronoamperometry current of pure PtRu/C is just 1.5 mA/mg PtRu after 1000 s. The tolerance performance of PtRu/C was improved by directly mixing SnO_2 nanoparticles, and the SnO_2–PtRu/C (20%) catalyst shows the best stability.

In summary, the SnO_2–PtRu/C composite catalyst can act as an efficient electrocatalyst for methanol oxidation in DMFCs. It is generally thought that the role of SnO_2 was relaxing the strong CO adsorption on Pt, which originates from the modification of the electronic band structure of Pt and the interaction between Pt and SnO_2 [15]. The property of the SnO_2–PtRu/C (20%) catalyst was further investigated by TEM morphology characterisation, Tafel slopes, CO-stripping and the effect of a temperature on methanol oxidation study.

For characterising the morphologies, Fig. 4 presents the TEM images of the composite catalysts. The TEM image of pure commercial PtRu/C (Fig. 4*a*) and SnO_2–PtRu/C (40%) catalysts (Fig. 4*d*) were also observed for comparison. It can be observed

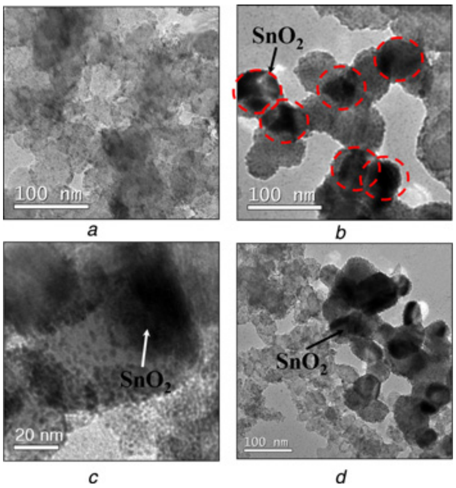

Figure 4 *TEM images*
a Pure commercial PtRu/C catalyst
b 20% SnO_2–PtRu/C composite catalyst
c Magnification of the 20% SnO_2–PtRu/C catalyst
d 40% SnO_2–PtRu/C composite catalyst

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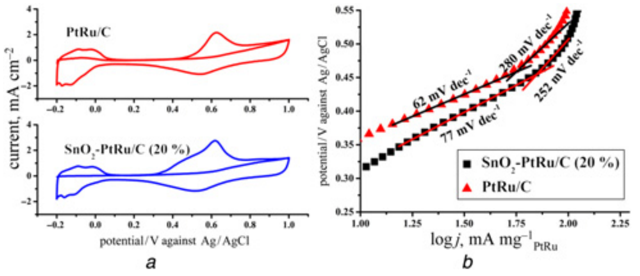

Figure 5 *CO-stripping; scan rate: 10 mV/s, and Tafel plots; scan rate: 5 mV/s*
a Co-stripping
b Tafel plots

that the PtRu nanoparticles are dispersed uniformly on the surface of the carbon support in the Fig. 4*a*. It is believed that the boundaries (between SnO_2 and PtRu nanoparticles) provide the enhanced active site towards complete methanol oxidation [16]. The SnO_2–PtRu/C (20%) shows that the SnO_2 nanoparticles (black regions are SnO_2 nanoparticles) are dispersed on the surface of the carbon support (see Fig. 4*b*). As shown in the magnified image (Fig. 4*c*), the PtRu nanoparticles in close contact with the surface of the SnO_2 nanoparticles, could significantly favour the electrocatalytic activity towards methanol oxidation. The TEM image of SnO_2–PtRu/C (40%) shown in Fig. 4*d* is similar that of SnO_2–PtRu/C (20%), the other 10 and 30% samples (not shown here) also show similar results.

Fig. 5*a* shows CO adsorption–oxidation curves in anodes on the SnO_2–PtRu/C (20%) and commercial PtRu/C catalysts. Hydrogen adsorption/oxidation is completely suppressed after CO adsorption on the SnO_2–PtRu/C (20%) and PtRu/C catalysts at the first scan, suggesting the catalytic particles are covered by a saturated CO adlayer. A single oxidation peak occurs, whereas no CO oxidation was observed in the second scan, confirming the complete removal of the adsorbed CO_{ad} species. When composite with SnO_2 nanoparticles, the CO oxidation peak was observed at the same potential as that of commercial PtRu/C. The onset potential for CO oxidation on SnO_2–PtRu/C (20%) catalyst (0.26 V) is about 130 mV, which is lower than that on commercial PtRu/C (0.39 V) indicating the CO electrooxidation is significantly affected by the SnO_2 nanoparticles. In comparison with commercial PtRu/C, the SnO_2–PtRu/C (20%) composite catalyst is much more effective in promoting CO oxidation at low potential.

Fig. 5*b* displays the Tafel plots of the anode polarisation of the SnO_2–PtRu/C (20%) and commercial PtRu/C catalysts. Each plot can be fitted and divided into two linear regions according to the change of Tafel slopes. The first fitted Tafel slopes come within the scope of 62–77 mV/dec at low overpotentials (<0.45 V), whereas the second slopes are in the range of 252–280 mV/dec at high overpotentials (0.45–0.55 V). According to the literature, the first region indicates that the unit reaction involving the splitting of the first C–H bond of methanol molecules and the first electron transfer is the rate-determining step in low potentials [17]. The increase of second Tafel slopes is caused by the decreased coverage of the poisonous intermediate species, which reveals that at higher potential the rate-determining step shifts from methanol dehydrogenation to CO_{ads} oxidation [18].

The SnO_2–PtRu/C (20%) catalyst offers an excellent performance for the methanol oxidation. The mechanism of SnO_2–PtRu/C catalyst for methanol oxidation can be simplified into the step of the decomposition of methanol to adsorbed CO over active Pt sites (Step 1) and the active Pt sites release (Step 2).

$$\text{Step 1: } Pt + CH_3OH \rightarrow Pt - (CO)_{ads} + H^+ + e^- \quad (1)$$

$$\text{Step 2: } Pt - (CO)_{ads} \rightarrow CO_2 + Pt + 2e^- \quad (2)$$

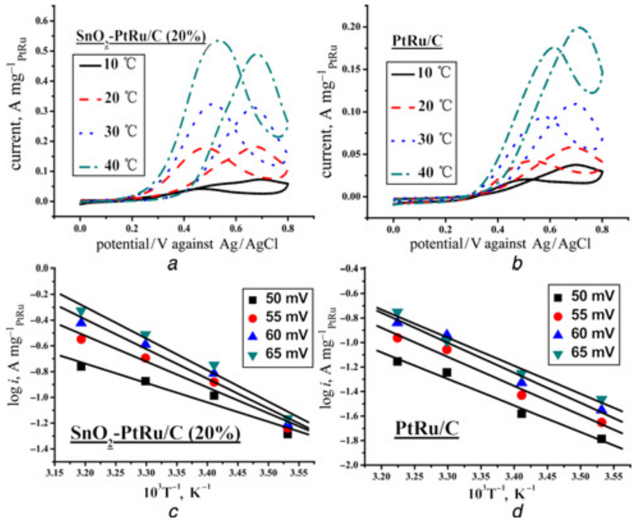

Figure 6 *Methanol electrooxidation in different temperature; scan rate: 50 mV/s (Figs. 6a and b); Arrhenius plots (Figs. 6c and d)*

Similar to the Ru species, Sn sites predominantly adsorb OH_{ads} and H_2O_{ads} (3) and (4) [19]. As the removal of CO_{ads} on Pt sites proceeded via its reaction with OH_{ads} on metal species, the additive SnO_2 promotes the water activation as well as Ru, which generates more species of $-OH_{ads}$ to oxidise CO-like intermediates and release more active reaction sites of Pt. Therefore similar to the literature [13], the addition of SnO_2 with PtRu provides an additional route for OH_{ads} formation [20]. Both Ru and SnO_2 with platinum minimise the poisoning effect of CO_{ads} on Pt active sites in step 2 and accelerates methanol oxidation (5).

$$Pt + SnO_2 + H_2O \rightarrow Pt - H_{ads} + SnO_2 - (OH)_{ads} \quad (3)$$

$$Pt + Ru + H_2O \rightarrow Pt - H_{ads} + Ru - (OH)_{ads} \quad (4)$$

$$\begin{aligned} &Pt - (CO)_{ads} + SnO_2 - (OH)_{ads} + Ru - (OH)_{ads} \\ &\rightarrow CO_2 + H^+ + Pt + SnO_2 + Ru + 2e^- \end{aligned} \quad (5)$$

The effect of temperature on methanol oxidation was also investigated. Methanol oxidation experiments on the SnO_2–PtRu/C (20%) and PtRu/C electrocatalyst were performed at different temperatures between 10 and 40°C by employing 0.5 M H_2SO_4 + 0.5 M CH_3OH solution as the working electrolyte. The apparent activation energies (E_a) for methanol oxidation on the PtRu/C and SnO_2–PtRu/C (20%) catalysts were obtained at different potentials by linear regression of the Arrhenius plots presented in Fig. 6. The activation energies were calculated using the following equation [21]

$$\log i = \text{const.} - E_a/RT$$

where i is the current at a specific potential, R is the gas constant, T is the temperature in K and E_a is the apparent activation energy.

The activation energy values of PtRu/C and SnO_2–PtRu/C (20%) catalysts are 44.4 and 39.8 kJ/mol, respectively. It is obvious that the E_a value of the SnO_2–PtRu/C (20%) catalyst is lower than that of the PtRu/C catalyst. It confirms an intrinsic prominent performance of the SnO_2–PtRu/C (20%) catalysts and the decrease of apparent activation energy for SnO_2–PtRu/C (20%) catalysts can be attributed to the synergy effect of Sn and Ru [21].

4. Conclusion: In summary, the electrocatalytic behaviour of commercial PtRu/C is enhanced by mixing SnO_2 nanoparticles. The electrochemical results demonstrate that the amount of SnO_2 nanoparticles had a significant effect on the performance of PtRu/C for methanol oxidation. Among all the SnO_2–PtRu/C catalysts, the SnO_2–PtRu/C (20%) catalyst shows the best performance. The studies shed light on the simple and economic way for reducing PtRu loading and the prepared catalyst has excellent electrocatalyst activities for DMFCs.

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