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Nanoparticulate TiO2-promoted PtRu/C catalyst for methanol oxidation: TiO2 nanoparticles promoted PtRu/C catalyst for MOR

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Abstract

To improve the electrocatalytic properties of PtRu/C in methanol electrooxidation, nanoparticulate TiO_2-promoted PtRu/C catalysts were prepared by directly mixing TiO_2 nanoparticles with PtRu/C. Using cyclic voltammetry, it was found that the addition of 10 wt% TiO_2 nanoparticles can effectively improve the electrocatalytic activity and stability of the catalyst during methanol electro-oxidation. The value of the apparent activation energy (E_a) for TiO_2-PtRu/C was lower than that for pure PtRu/C at a potential range from 0.45 to 0.60 V. A synergistic effect between PtRu and TiO_2 nanoparticles is likely to facilitate the removal of CO-like intermediates from the surface of PtRu catalyst and reduce the poisoning of the PtRu catalysts during methanol electrooxidation. Therefore, we conclude that the direct introduction of TiO_2 nanoparticles into PtRu/ C catalysts offers an improved facile method to enhance the electrocatalytic performance of PtRu/C catalyst in methanol electrooxidation.

Introduction

Carbon-supported PtRu catalyst, PtRu/C, offers a state-of-the-art anode electrocatalyst for direct methanol fuel cells (DMFCs) due to its high activity toward methanol electro-oxidation and tolerance to carbon monoxide poisoning [1–5]. Alloying Pt with Ru promotes the formation of oxygenated species at a lower temperature than Pt particles and promotes oxidation of CO to CO_2. However, despite promising progress in the development of PtRu/C, the durability and activity of the PtRu/C anode still cannot meet the demands for practical DMFCs applications.

Various metal oxides such as IrO_2, V_2O_5, WO_3, CeO_2, MoO_3, Nd_2O_3, RuO_2, and TiO_2 can enhance the catalytic activity of Pt-based electrocatalysts for methanol oxidation reaction (MOR) [6–15]. Among them, TiO_2 is the most promising promoter of PtRu/C due to its natural abundance, low cost, and stability in acidic environments [15–21]. The addition of TiO_2 to Pt-based catalysts can lower the adsorption energy of CO on the surface of Pt-based nanoparticles because TiO_2 is reduced to Ti^{+3}, which results in a higher electronic density on Pt-based nanoparticles and in turn changes its chemisorption properties and weakens the bond between Pt and CO [16]. Various studies have introduced TiO_2 into Pt-

based electrocatalysts via hydrolysis of organic Ti sources, such as $Ti(OBu)_4$ [15, 16, 18, 19]. However, the methods are quite complicated and unsuitable for large-scale production and furthermore do not allow for easy manipulation of the TiO_2 content and structure in the catalyst.

In this study, a facile way to prepare TiO_2-modified PtRu/ C (TiO_2-PtRu/C) has been successfully developed by directly introducing commercial TiO_2 nanoparticles into the preparation process of PtRu/C electrocatalysts. The electrocatalytic properties of TiO_2-modified PtRu/C for MOR were evaluated by cyclic voltammetry and chronoamperometry, and the effect of temperature on MOR was also investigated. E_a calculated to evaluate the effects and mechanism of TiO2 in the electrocatalytic activity of TiO2-PtRu/C in MOR.

Experimental

TiO_2-PtRu/C catalysts were synthesized by a modified organic colloid method in an ethylene glycol (EG) solution. H_2PtCl_6 and $RuCl_3$ (atomic ratio of Pt to Ru is 1:1) were dissolved in 50 ml of EG in a flask. The pH of above solution was adjusted to 9 by 5 wt% of KOH/EG solution. Pretreated carbon black Vulcan® XG72R was added to the mixture with stirring and ultrasonicated for 1 h (PtRu/C040:60). The mixture was transferred into a flask and heated at 160 °C for 6 h. Specific amounts of commercial TiO_2 (99.8 %, 5–10 nm, Aladdin Chemistry Co. Ltd) (ratios of PtRu to TiO_2 were 90:10, 80:20, 70:30, and 60:40) were introduced into the same above mixtures and ultrasonicated for 0.5 h. The synthesized TiO_2-PtRu/C catalysts were collected by filtration and washed with deionized water to remove chloride anions from the filtrate. The products were dried in air at 60 °C for 12 h.

Electrochemical studies on the catalysts used an Autolab electrochemical workstation (PGSTAT128N). A common three-electrode electrochemical cell was used for the measurements. The counter and reference electrodes were a platinum wire and an Ag/AgCl (3 M KCl) electrode, respectively. The working electrode was a 5-mm diameter glassy carbon disk. The thin film electrode was prepared as follows: 5 mg of catalyst was dispersed ultrasonically in 1 mL Nafion/ethanol (0.25 % Nafion) for 15 min. Eight microliters of the dispersion was transferred onto the glassy carbon disk using a pipette and then dried in the air. The catalysts were characterized by cyclic voltammetry (CV) and chronoamperometry tests at room temperature. Before each measurement, the solution was purged with high purity N_2 gas for at least 30 min to ensure O_2 Results and discussion The electrocatalytic activities of PtRu/C and TiO_2-PtRu/C catalysts toward MOR were investigated by cyclic voltammetry in CH_3OH 0.5 M+H_2SO_4 0.5 M solution. The mass activity of precious metal for MOR is a critical parameter in terms of its practical applications. The activity measurement results based on the total PtRu mass are shown in Fig. 1. The mass activity of the TiO_2-PtRu/C (10 %) and TiO_2-PtRu/C (5 %) catalyst was 0.20 and 0.19 Amg^{-1} PtRu, respectively, which was higher than that of PtRu/C catalyst (0.18 Amg^{-1} PtRu). Additionally, the onset potential for the TiO_2-PtRu/C (10 %) and TiO_2-PtRu/C (5 %) catalyst was also lower than that of PtRu/C.

Therefore, MOR activity of PtRu/C is promoted by introducing TiO_2 nanoparticles into PtRu/C. The proposed reason for this improvement is that on TiO_2-PtRu/ C, OH species can easily form on the surface of TiO_2 during the MOR process, which facilitates the conversion of the poisonous CO into CO_2 [22].

The amount of TiO_2 nanoparticles in the PtRu/C catalyst had a significant effect on the activity towards MOR. Further increase of TiO_2 content (20, 30, and 40 %) resulted in the reduction of current value. This phenomenon can be explained by a percolation effect, which is also observed when Fe_2O_3 nanoparticles are introduced into PtRu/C catalysts [14]; too much TiO_2 can block the path of electron transportation to the PtRu catalyst. Additionally, when the TiO_2 nanoparticles content increases, the oxophilicity also increases which leads to a decrease in the activity because the OH groups on these particles can effectively block the active sites required for the adsorption of CH_3OH [23].

Since the MOR activity of PtRu/C was improved by mixing certain amount of TiO_2 nanoparticles (10 wt%), the property of the TiO_2-PtRu/C (10 wt%) catalyst was further investigated and compared with the PtRu/C catalyst. Figure 2 shows the cyclic voltammetric curves in N_2-purged 0.5 M H_2SO_4 electrolyte, recorded on PtRu/C and TiO_2-PtRu/C (10 wt%) catalysts from −0.2 to 1 V (vs. Ag/AgCl). Both catalysts had the characteristic features of polycrystalline Pt, i.e., hydrogen adsorption/desorption peaks in low potential region, oxide formation/stripping wave/peak in high potential region, and a flat double layer in between. Compared with the CV curves of PtRu/C and TiO_2-PtRu/C, the double layer regions of TiO_2-PtRu/C are thicker than that of PtRu/C catalyst, which may be caused by the OH species absorbed on the surface of TiO_2 nanoparticles.

The electrochemically active specific area (S_{EAS}) was also obtained from CO-stripping voltammetry carried out in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} at room temperature.

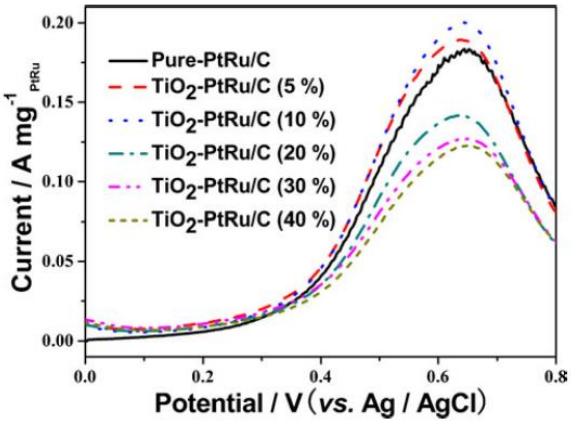


Fig. 1 Cyclic voltammograms of the PtRu/C and TiO_2-PtRu/C catalyst with various amounts of TiO_2 in 0.5 M CH_3OH+0.5 M H_2SO_4 solution under N_2 atmosphere. Scan rate, 50 mV s^{-1}; at room temperature. Rotation speed, 300 rpm

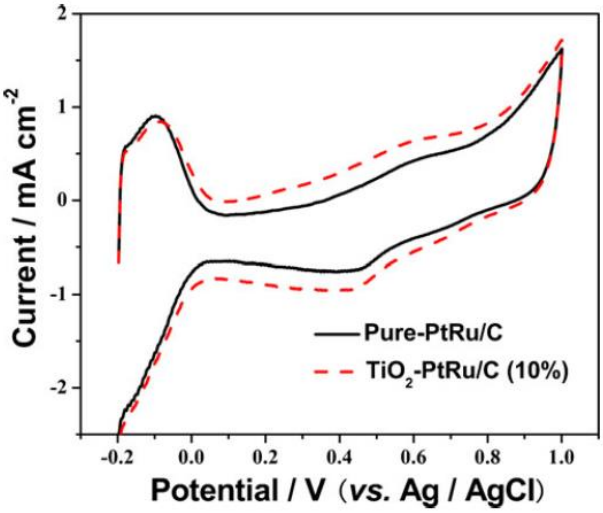


Fig. 2 Cyclic voltammograms of PtRu/C and TiO_2-PtRu/C (10 %) catalysts in 0.5 M H_2SO_4 under N_2 atmosphere; scan rate, 50 mV s^{-1}, at room temperature. Rotation speed, 300 rpm

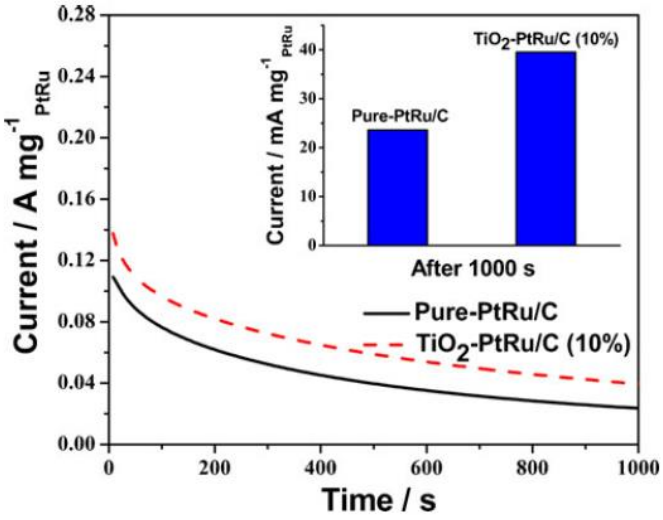


Fig. 3 The chronoamperometric curves of 0.5 M CH_3OH+0.5 M H_2SO_4 solution on PtRu/C and TiO_2-PtRu/C (10 %) catalysts for 1,000 s at room temperature. Fixed potential, 0.6 V; rotation speed, 300 rpm. *Inset*: the current of catalysts after 1,000 s

The S_{EAS} of the catalysts was calculated by using the equation [24], $S_{EAS} = Q_{CO}=420\delta\mu C\ cm^{-2}Þ=w$, where S_{EAS} is the electrochemically active specific area of different catalysts; Q_{CO} is the charge for CO desorption electrooxidation in microcoulomb (μC); 420 is the charge required to oxidize a monolayer of CO on the catalyst in microcoulomb per square centimeter, and w is the Pt loading. The S_{EAS} of the PtRu/C and TiO_2-PtRu/C (10 %) catalysts is 75.70 and 80.08 $m^2\ g^{-1}$ Pt, respectively, similar to the literature [25]. The S_{EAS} of TiO_2-PtRu/C is slightly larger than that of PtRu/C, which may be due to the formation of new sites at the interface between the platinum and the oxide materials. The chronoamperometry measurement provides further information about the electroactivity and stability of the catalysts for MOR. Chronoamperograms in 0.5 M H_2SO_4 +0.5 M CH_3OH are shown in Fig. 3, in which the mass is also based on the total PtRu mass. In the initial stage, all potentiostatic currents decreased rapidly, corresponding to the formation of intermediate species such as CO_{ads}, CH_3OH_{ads}, and CHO_{ads} during the methanol oxidation reaction [26]. Figure 3 shows that the current density of TiO_2-PtRu/C (10 %) is higher than that of PtRu/C. The current on PtRu/C and TiO_2-PtRu/C (10–1wt%) catalysts after 1,000 s was 23.6 and 39.7 mA mg_{PtRu}, respectively. A cooperative effect of Pt with TiO_2 nanoparticles can accelerate the oxidation of absorbed CO-like intermediate species [27], which in turn improve the stability of the TiO_2-PtRu/C (10 wt%) catalyst for MOR. Ru is known to be dissolved or dealloyed from PtRu alloy particles, which will result in the activity loss. It was reported that the presence of TiO_2 can restrain the Ru loss. The dissolved Ru species may be trapped on the surface of TiO_2 nanoparticles, preventing dissolved Ru from diffusion into the electrolyte, which should be beneficial to the stability of the TiO_2-PtRu/C (10 %) catalyst [15].

Figure 4a shows a typical linear sweep with a scan rate of 5 mV s^{-1}, which is close to a steady-state polarization curve of the MOR on PtRu/C and TiO_2-PtRu/C (10 wt%). Excellent linear correlations are found in both Tafel plots of PtRu/C and TiO_2-PtRu/C (10 wt%). In the low potential region, the current densities increased very slowly with increasing polarization potential and two curves are almost overlapped. In the relatively high potential region (above 0.45 V vs. Ag/AgCl), the polarization current increases sharply with polarization potential and the current density of the TiO_2-PtRu/C (10 %) catalyst is larger than those of PtRu/C catalysts. There is a limit current at about 0.6 V in Fig. 4a, which can be attributed to the blocking of active catalytic sites by the adsorbed intermediate species [28, 29].

Figure 4b shows the corresponding Tafel plot of the MOR, calculated from the quasi-steady-state curve in Fig. 4a. Each plot can be fitted and divided into two linear regions according to the change of Tafel slopes. The first fitted Tafel slopes fall within the scope of 138–160 mV dec^{-1} at low overpotentials (<0.45 V vs. Ag/AgCl), while the second slopes are in the range of 226–291 mV dec at high overpotentials (0.45 to 0.50 V vs. Ag/AgCl). With increasing potential, the adsorbed CO-like residues are gradually oxidized, and thus, the active sites on platinum are cleaned up for the subsequent methanol dehydrogenation

reaction. So, the increase of the second Tafel slope is caused by the decreased coverage of the poisonous intermediate species [29]. The second slopes are almost twice higher than the first slopes, indicating a possible change of reaction mechanism or at least a transformation of rate-determining step at different potential range [29].

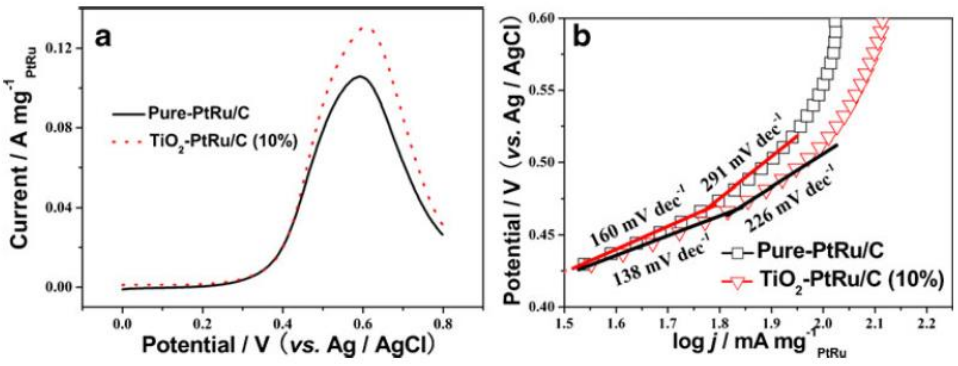


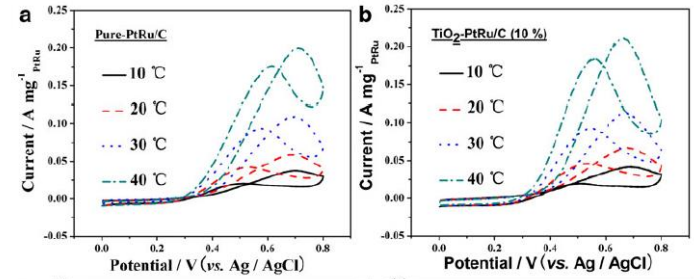
Fig. 4 Tafel plots of MOR on the PtRu/C and TiO_2-PtRu/C (10 %) in 0.5 M CH_3OH+ 0.5 M H_2SO_4 solution under N_2 atmosphere at room temperature. Scan rate, 5 mV s^{-1}

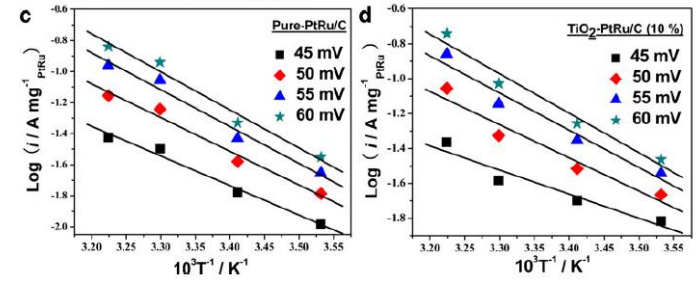
MOR on PtRu/C (Fig. 5a) and TiO_2-PtRu/C (10 wt%) (Fig. 5b) electrocatalyst were carried out at different temperatures between 10 and 40 °C in 0.5 M H_2SO_4 +0.5 M CH_3OH solution. The corresponding cyclic voltammograms displayed an increasing oxidation current with rising temperature. As expected, the process of MOR is thermally activated. With temperature increasing, the current peak becomes stronger and the onset potentials shift to a lower position. The enhanced reaction rate occurs because the elevated temperature not only activates the C–H bond scission process but also accelerates the oxidation reaction of CO-like residues [29].

In many of these temperature-dependent MOR studies, apparent activation energies have been calculated. The apparent activation energies for MOR on the PtRu/C and TiO_2-PtRu/C (10 wt%) catalysts were obtained at different potentials by linear regression of the Arrhenius plots presented in Fig. 5c, d. Arrhenius plots for the two catalysts at different overpotentials are obtained by constructing diagrams of log i vs. reciprocal T, where i is the current density at controlled potentials and T is the applied temperature. The activation energies were calculated using the following equation [30]: log i ¼ const: $-E_a=RT$, (where i is the current at a specific potential, R is the gas constant, T is the temperature in Kelvin, and E_a is the apparent activation energy at a specific potential) at a given potential.

Parameters, such as surface adsorption and poisoning, have a significant effect on the E_a value. Comparison of E_a values is an efficient way to evaluate the difference between two catalysts. The values of the activation energy are plotted vs. the potential in Fig. 6. E_a is potential dependent because a number of different surface processes and adsorption processes that affect the current values are potential dependent [30].

Fig. 5 Cyclic voltammetry of PtRu/C (a) and TiO_2-PtRu/C (10 %) (b) catalysts in 0.5 M CH_3OH+0.5 M H_2SO_4 solution under N_2 atmosphere within the temperature range of 10–40 °C; scan rate, 50 mV s^{-1}. Arrhenius plots of MOR on PtRu/C (c) and TiO_2-PtRu/C (10 %) catalysts (d)





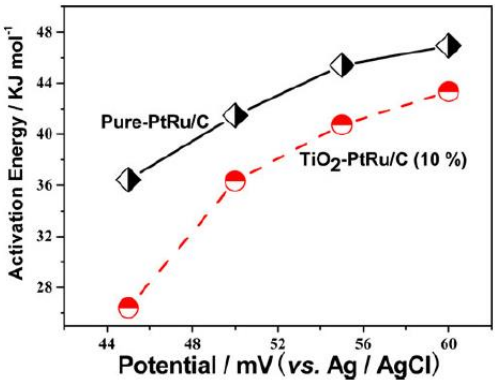


Fig. 6 Apparent activation energy vs. potentials

The activation energy values obtained on PtRu/C and TiO_2-PtRu/C (10 wt%) catalysts under potential from 0.45 to 0.60 V range from 36.4 to 46.9 kJ mol^{-1} and 26.4 to 43.3 kJ mol^{-1}, respectively. This correlates with previously reported values for MOR on PtRu catalysts varying from 29 to 70 kJ mol^{-1} sharing both a similar preparation method and working conditions [29]. The value of apparent activation energy of TiO_2-PtRu/C (10 wt%) is lower than that of PtRu/C over the whole potential range, which results from the synergistic effect of PtRu and TiO_2 nanoparticles. Similar to Pt catalyst, the OH species, which are present on the surface of TiO_2 in aqueous solutions, cause a greater shift in the surface oxidation of Pt (Pt–OH formation). Therefore, the presence of TiO_2 facilitates the removal of CO-like intermediates from the surface of PtRu catalyst and reduces the poisoning of the PtRu catalysts during MOR [22].

Conclusions

TiO_2-modified PtRu/C catalysts with various TiO_2 contents were successfully prepared via a facile method of directly adding TiO_2 nanoparticles into PtRu/C catalysts. The results show that this method of adding TiO_2 in PtRu/C catalysts can improve the

electrocatalytic performance in MOR. The value of the apparent activation energy of TiO_2-PtRu/C (10 wt%) is lower than that of PtRu/C over the whole potential range due to the synergistic effect between PtRu and TiO_2 nanoparticles, which facilitates the removal of CO-like intermediates from the surface of PtRu catalyst and reduces poisoning of the PtRu catalysts during MOR. Therefore, we conclude that directly introducing TiO_2 nanoparticles into PtRu/C catalysts offers an improved facile method for improving the electrocatalytic performance of PtRu/C catalyst in MOR.

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