Investigation on the role of hydrous ruthenium oxide in PtRu/C catalyst for methanol electrooxidation

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PtRu/Vulcan XC-72 catalyst with high catalytic performance has been synthesized by microwave-assisted polyol process, heat-treated, and characterized by X-ray diffraction, X-ray photoelectron spectra, transmission electron microscopy, thermogravimetric analysis, and differential scanning calorimetry. Their electrochemical performance has been tested by cyclic voltammetry, chronamperometry curves, and CO-stripping techniques. The effect of annealing treatment on performance of the PtRu/C catalyst has been investigated. The results show that prior to the annealing treatment the as-prepared PtRu/C catalyst has a small particle size and has a relatively high amount of Pt and Ru in their metallic state, along with some amount of hydrous ruthenium oxides (RuO\textsubscript{x}H\textsubscript{y}), all of which contribute to the higher activity of catalyst. On the other hand, the anhydrous ruthenium oxide, which exist after the catalyst is annealed at 300 \degree C for 1 h, is found to be less active for methanol electrooxidation.

Keywords: Catalysts, Direct methanol fuel cell PtRu/C electrocatalysts, Annealing treatment, Anode catalyst, Electrooxidation, Methanol electrooxidation

Direct methanol fuel cells (DMFCs) possess great potentials as future portable power sources, electric vehicles, and mobile applications\textsuperscript{1,3}. Considerable efforts have been devoted to developing Pt-based alloy catalysts for methanol electrooxidation\textsuperscript{4,7}. Among the various investigated catalysts, the state-art-of PtRu supported on carbon support exhibits the most prominent catalytic activity due to the neighboring Ru atoms producing oxygenated species to afford Pt atoms at lower potentials compared with pure Pt\textsuperscript{8}, which is likely to be absorbed on Pt surface to promote the oxidation of poisonous intermediate species.

In recent times, much attention has been focused on the study of the relationship between the structure, dispersivity, and morphology of the catalyst and its catalytic performance. However, there is no consensus on whether the PtRu alloy or hydrous ruthenium oxide improves its catalytic activity for methanol electrooxidation. The PtRu binary system is reported to be the best CO-tolerant catalyst for electrooxidation of hydrogen and/or methanol\textsuperscript{9,11}. Nevertheless, Ge and co-workers\textsuperscript{12} opine that the PtRu alloy structure makes no contribution to its performance. Gao and co-workers\textsuperscript{13} highlighted the importance of hydrous ruthenium oxides since the RuO\textsubscript{2}·xH\textsubscript{2}O in nanoscale PtRu/CNTs catalyst showed both higher electron and proton conductivities, resulting in a much higher activity of the catalyst for methanol electrooxidation. Rolison and co-workers\textsuperscript{14,15} also supported the same viewpoint that a hydrous ruthenium oxide is necessary and important for methanol electrooxidation. However, there is no direct evidence of the catalytic function of hydrous ruthenium oxides at present. In the present study, the results of physical and electrochemical characteristics show that both metallic state of amorphous Ru as well as the hydrous ruthenium oxides in PtRu/C catalyst promote the catalytic activity for methanol electrooxidation\textsuperscript{16}. The former is identified as the bifunctional mechanism, in which Ru provides oxygenated species at low potentials that converts the CO\textsubscript{ads} on neighboring Pt atoms to CO\textsubscript{2}. The latter also may afford oxygen-containing species close to the poisoned Pt sites, and along with its higher electron and proton conductivities donate hydroxide species more easily to Pt sites to assist CO\textsubscript{ads} oxidation, which may be more beneficial for catalytic activity\textsuperscript{13}.
Materials and Methods

Preparation of PtRu/C catalyst by microwave-assisted polyol process

PtRu/C catalyst (20 wt.%) with a Pt-to-Ru atomic ratio of 1:1 was prepared by microwave-assisted polyol process in ethylene glycol (EG) solution. Briefly, Vulcan XC-72 carbon black (50 mg) was dispersed into the mixed solution of EG and isopropyl alcohol (30 mL v/v = 4:1) in a 100 mL beaker under ultrasonic treatment for 1 h to form uniform carbon ink. Then the H2PtCl6 and RuCl3 precursor solutions were added with the subsequent mixing for 3 h. The pH value of the ink was adjusted to 8 with 1 mol L−1 NaOH-EG solution, drop-by-drop, which was monitored with a pHs-32 meter. The beaker was placed at the center of a microwave oven (2450 MHz, 800 W) and argon gas was fed into the ink for 15 min to expel oxygen, then heated for 50 s to fix Pt and Ru nanoparticles on the carbon support. The solution was allowed to cool down to room temperature with continuous stirring, and then 0.1 mol L−1 HNO3 solution was added into the cooled mixture to adjust its pH value to about 4. The mixture was stirred for 12 h and then the product was washed repeatedly with ultrapure water (18.2 MΩ cm) until no Cl− ions were detected. The thus prepared PtRu/C catalyst was dried for 3 h at 80 °C in a vacuum oven and then stored in a vacuum vessel. All chemicals used were of analytical grade.

Electrode preparation and electrochemical measurement

The ultrasonically re-dispersed catalyst suspension (5 μL) was spread by pipette onto the glassy carbon disk substrate. The subsequent evaporation of solvent led to the formation of the deposited catalyst layer (28 μgmetal cm−2), onto which 5 μL of a dilute aqueous Nafion® solution (5 wt.% solution in a mixture of lower aliphatic alcohols and DuPont water) was applied. The resulting Nafion® film with a thickness less than 0.2 μm had the sufficient strength to keep carbon particles permanently on the glassy carbon electrode without producing significant film diffusion resistances. The glassy carbon working electrode with 3 mm diameter and 0.0706 cm² electrode area was polished with 0.05 μm alumina to a mirror finish before being used as the substrate for carbon-supported catalyst.

Electrochemical measurements were carried out in a conventional sealed three-electrode electrochemical cell at 25 °C, with the glassy carbon disk electrode prepared vide Supra as the working electrode and Pt foil (1 sq cm) as the counter electrode. The reference electrode was a reversible hydrogen electrode (RHE) with its solution connected to the working electrode chamber by a Luggin capillary whose tip was placed appropriately close to the working electrode. All chemicals used were of analytical grade, and solutions were prepared with ultrapure water (MilliQ, Millipore, 18.2 MΩ cm). The solution of 0.5 mol L−1 H2SO4 containing 0.5 mol L−1 CH3OH was kept on constantly stirring and purging with ultrapure argon gas. The cyclic voltammograms (CV) were recorded within a potential of 0.05 V−1.2 V. The chronoamperometry curves were plotted with CHI650D electrochemical analysis instrument controlled by an IBM PC. In order to remove the possible contaminations caused by Nafion® film, the working electrode was treated by continuously cycling at 0.05 V s−1 until a stable response was obtained before the CV curves were recorded. Fresh electrolyte solution was used for each electrochemical measurement in order to ensure reproducible results. For CO-stripping measurements, pre-adsorption of CO on the catalyst surface was carried out by bubbling CO through 0.5 mol L−1 H2SO4 electrolyte for 30 min, followed by purging with argon for 30 min to expel any residual CO in the solution. The potential was scanned at a rate of 0.02 V s−1 between 0.05 and 1.2 V. All potentials are reported versus RHE herein.

Characterization

XRD analysis of catalyst was carried out with a D/max-rB diffractometer (Japan) using a Cu Kα X-ray source operating at 45 kV and 100 mA, scanning at a rate of 4 min−1 with an angular resolution of 20–0.05°. X-ray photoelectron spectroscopy (XPS) analysis was performed with a Physical Electronics PHI (model 5700) instrument to determine the chemical state of Pt and Ru. The Al X-ray source operated at 250 W and sample-to-analyzer take off angle was 45°. Survey spectra were collected at pass energy (PE) of 187.85 eV over a binding energy range of 0 eV to 1300 eV. High binding energy resolution multiplex data for the individual elements were collected at a PE of 29.55 eV. The C 1s electron binding energy was referenced at 284.6 eV, and a nonlinear least-squares curve-fitting program was employed with a Gaussian-Lorentzian production function. During the XPS experiments, the pressure inside the vacuum system was maintained at 1×10−7 Torr. Before analysis, all the samples were dried under vacuum at 80 °C overnight.
TEM for the catalyst samples were recorded on a JEOLJEM-2010EX transmission electron microscope (Japan) with a spatial resolution of 1 nm. Before recording the electron micrographs, the catalyst samples were finely ground and ultrasonically dispersed in isopropyl alcohol, and a drop of the resultant dispersion was deposited and dried on a standard copper grid coated with a polymer film. The applied voltage was 100 kV.

Thermogravimetric (TG) analysis and differential scanning calorimetry (DSC) were carried out with NETZSCH STA 449F3 instrument. The as-prepared composites (about 15 mg) were heated in the temperature range of 25−800 °C in argon flow at a heating rate of 10 °C min\(^{-1}\).

**Results and Discussion**

**Role of hydrous ruthenium oxide for methanol oxidation**

Figure 1 shows the CV curves of methanol electrooxidation on the hydrous ruthenium oxide in an Ar-saturated solution of 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) with or without 0.5 mol L\(^{-1}\) CH\(_3\)OH at a scanning rate of 50 mV s\(^{-1}\) at 25 °C. It can be observed from Fig. 1 that the two profiles are similar without methanol oxidation peak, indicating hydrous ruthenium oxide itself does not have catalytic ability for methanol electrooxidation, and the role of hydrous ruthenium oxide with good proton and electron conductivities is only as co-catalyst by bifunctional mechanism.

**Characterization of PtRu/C catalysts**

XRD patterns of the PtRu/C catalysts prepared at the pH 8, before and after annealing treatment at 300 °C for 1 h is shown in Fig. 2. After annealing treatment at 300 °C, the new diffraction peaks at the 20 positions of 28.1°, 35.1° and 54.3° are noticeable. These are ascribed to Ru(110), Ru(101), and Ru(211) characteristic diffraction peaks, respectively, which are typically associated with the presence of anhydrous Ru oxides rather than the Pt oxides that could not be formed by annealing treatment below 400 °C\(^{15}\). This indicates that the hydrous RuO\(_x\)H\(_y\) in the PtRu/C catalyst tends to dehydrate and become anhydrous RuO\(_2\) by self-dehydration\(^{20}\). In addition, the degree of alloying of PtRu increases to some extent after annealing treatment according to the calculated values of the lattice parameters (\(a_{fcc}\)) (0.3897 and 0.3891 nm) of the strongest the Pt (111) peak according to Vegard’s law\(^{21,22}\) for the catalysts before and after annealing treatment at 300 °C, respectively, showing that the annealing treatment increases its degree of alloying. The Ru atomic fraction in the alloy (\(\chi_{Ru}\)) can be estimated by using the formula proposed by Antolini and coworkers\(^{23}\), which is also an effective parameter to present the degree of alloying of PtRu/C catalyst. The \(\chi_{Ru}\) value increases from 7.1% to 11.9%, indicating again that the degree of alloying after annealing treatment is enhanced.

TEM results and particle size distribution histograms are presented in Fig. 3. It can be seen that the PtRu nanoparticles increase in size and agglomerate after annealing treatment. The average particle size increases from 2.2 nm to 3.5 nm after the annealing treatment.

The XPS spectra of the synthesized PtRu/C catalysts before and after annealing treatment at 300 °C are shown in Fig. 4. The C 1s electron binding energy was
Fig. 3 – TEM images and particle size distribution histograms of the PtRu/C catalysts (a, a') before and (b, b') after annealing treatment at 300 °C.

Fig. 4 – XPS core level spectra of the PtRu/C catalysts before (a, b) and after (c, d) annealing treatment at 300 °C.
referenced at 284.6 eV, and a nonlinear least-squares curve-fitting program was employed with a Gaussian-Lorentzian function. The results obtained by the deconvolution of the XPS spectra are listed in Table 1. The Pt 4f spectra (Fig. 4 a and c) consist of three couples of peaks with the low bonding energies at 71.8, 73.3, and 74.7 eV, which can be assigned to Pt(0), Pt(II), and Pt(IV) species in the PtRu/C catalysts, respectively. It can be seen that the peak area of Pt(0) is much larger than those of Pt(II) and Pt(IV), illustrating that Pt(0) is the predominant species in the PtRu/C catalyst. To avoid interference from the C1s signals, Ru3p spectrum was used to analyze the surface compositions of Ru element (Fig. 4b). It consists of three peaks with the low bonding energies at 462.2, 463.9 and 466.2 eV, which are attributed to metallic Ru (Ru0), anhydrous Ru oxide (RuO2), and hydrous Ru oxides (RuOxH_y), respectively24,25. Since RuO3 is thermodynamically unstable, the component with the highest binding energy (466.2 eV) is ascribed to the hydrous RuOxH_y species26, which is reported to have a higher binding energy than anhydrous RuO2 species26,14. The percentage of Ru(0) and hydrous RuOxH_y in the catalyst surface decreases while the Ru(IV) oxide increases after annealing treatment (Fig. 4d and Table 1) probably due to loss of water in hydrous RuOxH_y, changing it to anhydrous RuO2, while the presence of hydrous RuOxH_y may give the catalytic property required for methanol electrooxidation.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the as-prepared PtRu/C catalyst prepared at pH 8 are shown in Fig. 5. From the TGA results, the loss of about 4.85 wt% between room temperature and 280 °C under flowing Ar atmosphere is considered as the loss of water of the hydrous RuOxH_y in synthesized PtRu/C catalyst, accompanied with phase transition from amorphous hydrous ruthenium oxide to crystalline RuO2 with the exothermic peaks at 200 °C in the DSC curve27,28. The

![Fig. 5 − TGA and DSC of the as-prepared PtRu/C catalyst prepared at pH 8.](image)

Table 1 – Binding energies and surface compositions from deconvolution of XPS spectra for catalysts before and after annealing treatment at 300 °C

<table>
<thead>
<tr>
<th>PtRu/C</th>
<th>Species</th>
<th>Orbital spin</th>
<th>Binding energy (eV)</th>
<th>Peak half width (eV)</th>
<th>Assignment</th>
<th>Rel. conc.(%) a</th>
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<tr>
<td>Before annealing</td>
<td>Pt 4f</td>
<td>4f_{7/2}</td>
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aRelative concentrations are equal to the corresponding, deconvoluted peak areas divided by the total XPS area extracted from the experimental XPS core level regions of either Pt 4f or Ru 3p.
TGA and DSC curves are consistent with the results obtained from XRD and XPS above, which confirm the presence of RuO$_2$·xH$_2$O and crystalline transition on annealing treatment$^{29-31}$. The further weight loss between 300 and 800 °C may be ascribed to the decomposition of PtO$_x$H$_y$ to Pt metal$^{27}$.

**Electrochemical characterization of PtRu/C catalysts**

Figure 6 shows CO adsorption-oxidation curves on the PtRu/C catalyst before and after annealing treatment at 300 °C for 1 h in an Ar-saturated solution of 0.5 mol L$^{-1}$ H$_2$SO$_4$ at a scanning rate of 20 mV s$^{-1}$ at 25 °C. It is clear that the CO$_{ads}$ oxidation peak shift to positive direction after annealing treatment, which may be an indication of composition variation after annealing treatment. This is also proved by the XPS analysis which shows that the amounts of Pt and hydrous RuO$_x$H$_y$ decrease after annealing treatment and also the results of XRD, TG, and DSC above.

The CV curves of methanol electrooxidation on the PtRu/C catalysts before and after annealing treatment at 300 °C for 1 h in an Ar-saturated solution of 0.5 mol L$^{-1}$ H$_2$SO$_4$ containing 0.5 mol L$^{-1}$ CH$_3$OH at a scanning rate of 50 mV s$^{-1}$ at 25 °C is shown in Fig. 7. It can be observed from Fig. 7 that the PtRu/C catalyst before annealing treatment exhibits higher current density (17.6 mA cm$^{-2}$) at the peak potential of 0.88 V. This as compared to the catalyst after annealing, indicates the better catalytic activity for methanol electrooxidation of the catalyst before annealing than the sample after annealing treatment. This is because the particles increase in size and agglomerate after annealing treatment as shown in Fig. 3. This also shows that the hydrous Ru oxide promotes the catalytic activity of the PtRu/C catalyst by providing active oxygen, which is necessarily required for methanol electrooxidation$^{15}$.

The chronoamperometry curves at a constant potential 0.6 V are shown in Fig. 8. The un-annealed PtRu/C catalyst exhibits not only higher initial current density but also the final current density at 1000 s, which is about 1.4 times that after annealing treatment, demonstrating further that suitable particle size, as well as participation of oxygenated species formed on the catalyst surface served by hydrous RuO$_x$H$_y$ may promote methanol electrooxidation. The better stability of unannealed PtRu/C catalyst is
also related to the more stable RuO\textsubscript{x}H\textsubscript{y} species that undergo slower dissolution and agglomeration than the smaller Ru islands.\textsuperscript{32}

**Conclusions**

In summary, PtRu/C catalyst had been prepared by the microwave-assisted polyol process. Its characteristics before and after the annealing treatment at 300 °C are presented. The non-annealed catalyst shows better catalytic activity for methanol electrooxidation due to its small and uniform particle size and enrichment of hydrous ruthenium oxides that have high oxygen buffer capacity. They also act as a co-catalyst with good proton and electron conductivities, providing activated oxygen-containing species for removing strongly adsorbed CO. On the other hand, the anhydrous ruthenium oxides produced after annealing treatment were inactive.

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**References**