Pt 的氧化状态对甲醇氧化活性的影响

曾建皇, 舒婷, 廖世军, 梁振兴

华南理工大学化学与化工学院, 广东广州 510641

摘要: 采用NaBH₄还原法制备了XC-72碳黑负载的Pt电催化剂,并在化学还原后用H₂O₂处理部分催化剂以改变Pt的氧化状态,以期改善Pt活性中心上水的离解而提高催化活性。X射线光电子能谱结果表明,经H₂O₂处理的催化剂含有较多的氧化态Pt。通过循环伏安法和计时电流法考察了经处理和未经处理的催化剂在酸性条件下的甲醇氧化的催化活性。结果表明,经氧化法产生的含有较多氧化态Pt的催化剂并不能提供活性状态的氧以去除阻碍反应的CO中间体,含有较多金属状态Pt的催化剂活性反而更高,抗CO性能更佳。

关键词: 铂; 催化活性; 氧化态; 甲醇氧化

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Effect of Pt Oxidation State on Methanol Oxidation Activity

ZENG Jianhuang, SHU Ting, LIAO Shijun, LIANG Zhenxing*

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, Guangdong, China

Abstract: Pt catalysts supported on Vulcan XC-72 carbon were prepared by the NaBH₄ reduction of H₂PtCl₆ in the presence of a carbon support. One of the catalysts was deliberately treated with H₂O₂ after chemical reduction to alter the oxidation state of Pt and to promote methanol oxidation through more efficient water dissociation on the Pt sites. X-ray photoelectron spectroscopy confirmed that H₂O₂ treatment resulted in a more oxidized Pt catalyst. The electrooxidation of methanol over treated and untreated Pt catalysts in acidic solutions at room temperature was investigated by cyclic voltammetry and chronoamperometry. Despite their design, the more oxidized Pt catalysts could not supply active oxygen capable of removing the reaction-inhibiting CO-like reaction intermediates. As a result the catalytic activity was still largely dependent on the Pt oxidation state with the more “metallic” catalyst showing higher methanol oxidation activity and more CO tolerance.

Key words: platinum; catalytic activity; oxidation state; methanol oxidation

In direct methanol fuel cells (DMFCs), methanol is oxidized at the anode through successive dehydrogenation. Pt is the standard catalyst for the oxidation of small organic molecules including methanol and it is active during methanol dehydrogenation but is readily deactivated at room temperature by CO-like intermediates that are generated during the dehydrogenation reactions [1–4]. It has been established that the dehydrogenation of methanol consists of the following sequence [5–10]:

In the presence of active surface oxygen species, which are represented here as either Pt-O or Pt-OH, the reaction goes to completion and the active Pt surface is regenerated:

Pt-(CHO)_{ads} can also rearrange into more stubborn forms of the adsorbed species resulting in a gradual but permanent loss of the active Pt surface area [11]:

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*Corresponding author. Tel/Fax: +86-20-87113586; E-mail: zliang@scut.edu.cn

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The timely supply of active surface oxygen species in the required quantities and in a form that promotes the regeneration of Pt active sites by reaction (4) is, therefore, important for catalyst activity. For example, the higher CO tolerance of the bimetallic Pt-Ru catalyst is due to the presence of oxygen species on oxophilic metal sites [7]. Ru modified Pt catalysts are equally effective and interestingly this method of construction also leads to a concurrent increase in surface Pt-O species [4]. In this work the Pt catalyst was deliberately treated in an oxidizing solution to obtain a higher oxidation state than that of a common Pt catalyst [12]. The effectiveness of this approach to increase the supply of active surface oxygen species was evaluated.

1 Experimental

1.1 Preparation of catalysts

Chloroplatinic acid (H_2PtCl_6) was obtained from Aldrich. Sodium boron hydride (NaBH_4), H_2O_2 solution (30%), sulfuric acid (95%–97%), and methanol were obtained from Merck. Vulcan XC-72 carbon (BET surface area of $250 \text{ m}^2/\text{g}$ and average particle size of 40–50 nm) was obtained from Cabot. All chemicals were used as received. Deionized water was used throughout the study.

1.1.1 Preparation of Pt-1/C

In a N_2 filled glove box, Vulcan XC-72 carbon was added to a beaker containing distilled water and stirred vigorously. A calculated amount of 0.05 mol/L chloroplatinic acid solution was added slowly to the carbon suspension. The deposition of Pt nanoparticles from the aqueous solution occurred when a stoichiometric excess of 0.5 mol/L NaBH_4 solution was slowly added to the carbon suspension. Stirring was continued for a further 12 h. The solid phase was filtered, washed with a copious amount of distilled water, and recovered by high-speed centrifugation at 15000 r/min. The catalyst obtained after vacuum drying at room temperature overnight was labeled Pt-1/C.

1.1.2 Preparation of Pt-2/C

The preparation of Pt-2/C was carried out under a normal laboratory atmosphere. The dispersion of XC-72 carbon and the addition of H_2PtCl_6 and NaBH_4 solutions was the same as that for the preparation of Pt-1/C. Ten minutes after the end of NaBH_4 addition, a 30% H_2O_2 solution was introduced to the carbon suspension. Stirring was continued for 12 h. The catalyst was recovered in the same way as Pt-1/C and was dried at 80°C overnight in a common laboratory oven.

1.2 Characterization of catalysts

The X-ray powder diffraction (XRD) patterns of catalysts were recorded with a Rigaku D/Max-3B diffractometer (Shimadzu) using $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The 2θ angles were scanned from 20° to 85° at $2^\circ/\text{min}$. The diffraction data was curve fitted using a least square program supplied by the equipment manufacturer. Elemental compositions and Pt loadings in particular were determined using an EDX analyzer that was attached to a JEOL MP5600LV scanning electron microscope (SEM) operating at 15 kV. Information on the particle size, shape, and size distribution was obtained with a JEOL JEM2010 transmission electron microscope (TEM) operating at 200 kV. X-ray photoelectron spectra (XPS) were obtained with an ESCALAB MKII spectrometer (VG Scientific) using $\text{Al } K_\alpha$ radiation (1486.71 eV). Spectral correction was based on graphite's C 1s level at 284.3 eV. The vendor-supplied software XPSPEAK (version 4.1) was used to deconvolute the XPS data based on the fixed half widths and the fixed spin orbit splitting from the first trials.

1.3 Evaluation of catalysts

A conventional three-compartment electrochemical cell and an Autolab PGSTAT30 potentiostat/galvanostat were used to evaluate the catalysts by cyclic voltammetry and chronoamperometry. The working electrode was fabricated by casting Nafion-impregnated catalyst ink onto a 4 mm diameter glassy carbon disk electrode with a Pt loading of $13 \mu\text{g}$. A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and the reference electrodes, respectively, while 2 mol/L CH_3OH in 1 mol/L H_2SO_4 was the electrolyte. All the reported potentials were referenced to the SCE. The catalysts were cycled between 0 V and 1 V at 50 mV/s until a stable response was obtained before the cyclic voltammograms and chronoamperograms were recorded.

2 Results and discussion

2.1 Characterization of catalyst microstructures

The Pt loadings in Pt-1/C and Pt-2/C were about 20% as determined by EDX. The XRD patterns of the catalysts are shown in Fig. 1. The broad reflection centered at $2\theta = 26^\circ$ is a graphite (002) diffraction from the carbon support [13–15]. For both catalysts, the strong diffraction peaks at Bragg angles of 39.8° , 46.3° , 67.5° , and 81.3° can be indexed to the (111), (200), (220), and (311) planes of face centered cubic (fcc) platinum [16]. A volume-averaged particle size can be calculated from Scherrer's equation ($L =$

Fig. 1. XRD patterns for Pt-1/C (1) and Pt-2/C (2).

$0.9\lambda_{\text{K}\alpha 1}/B_{2\theta}\cos\theta_{\text{max}}$) using the Pt(220) peak.

In this equation, L is the average Pt particle size, $\lambda_{\text{K}\alpha 1}$ is the wavelength of the incident X-ray ($\text{Cu } K_{\alpha 1} = 0.15406 \text{ nm}$), $2\theta_{\text{max}}$ is the Bragg angle for the peak maximum and $B_{2\theta}$ is the half width at peak maximum [17,18]. The average calculated Pt particle sizes for Pt-1/C and Pt-2/C were 4.4 and 5.2 nm, respectively.

The morphology, size, and size distribution of the Pt particles were examined by TEM and no significant difference between Pt-1/C and Pt-2/C was found. A TEM image of Pt-1/C and the corresponding histogram of the particle size distribution are shown in Fig. 2 as an example. This figure

Fig. 2. Typical TEM image (a) and particle size distribution (b) of Pt-1/C (mean diameter = 4.6 nm, standard deviation = 1.2 nm).

shows the high dispersion of nanosized Pt particles in the carbon matrix. The number-averaged particle size from counting hundreds of particles in the TEM image (mean = 4.6 nm, standard deviation = 1.2 nm) is in good agreement with the volume-averaged particle size from the XRD measurements.

The Pt 4f spectrum of Pt-1/C in Fig. 3(a) was deconvoluted into two pairs of doublets. In the spectral deconvolution it was assumed that the $4f_{5/2}$ and $4f_{7/2}$ lines have the same half widths and the same spin orbit splitting as pure Pt. The more intense doublet at 71.44 and 74.74 eV is a signature of metallic Pt (Pt^0). The less intense doublet at 72.84 and 76.04 eV is often assigned to oxidized Pt in divalent states such as PtO and $\text{Pt}(\text{OH})_2$ [19–21]. The Pt 4f spectrum of Pt-2/C (Fig. 3(b)) was similarly deconvoluted with the doublet at 71.61 and 74.81 eV assigned to Pt^0 and the doublet at 73.01 and 76.21 eV assigned to Pt^{2+} . The slight shift in the Pt^0 peak to higher binding energies (BEs) relative to standard Pt arises from the metal-support interaction and/or small cluster-size effects [22].

Fig. 3. Pt 4f XPS spectra of Pt-1/C (a) and Pt-2/C (b).

The BEs of the Pt 4f components and the percentages of Pt^0 and Pt^{2+} in the catalysts calculated from the respective integrated area intensities are summarized in Table 1. The results in Table 1 clearly indicate that Pt was more reduced in Pt-1/C (78%) than in Pt-2/C (54%). The higher Pt^{2+} content in Pt-2/C may be present as an X-ray amorphous PtO phase, as is generally believed [23]. From literature the majority of Pt catalysts for fuel cell applications contain 70%–85% Pt^0 irrespective of the preparation method [15,20,24]. Hence Pt-2/C would qualify as an “unusual”

Table 1 Binding energies and relative integrated area intensities of the component species deconvoluted from the Pt 4f XPS spectra

Catalyst	Species	Binding energy (eV)	Relative intensity (%)
Pt-1/C	1	71.44	43
	2	74.74	35
	3	72.84	13
	4	76.04	9
Pt-2/C	1	71.61	25
	2	74.81	29
	3	73.01	18
	4	76.21	28

Pt/C catalyst. The high Pt²⁺ content is the result of the deliberate addition of the strong oxidizing agent H₂O₂ during catalyst preparation.

The O 1s regions in the XPS spectra shown in Fig. 4(a) and Fig. 4(b) can be deconvoluted into three component species for Pt-1/C and two component species for Pt-2/C. The BEs of these components and their relative intensities are shown in Table 2.

The O 1s spectra show the strong presence of -CO species from the carbon-support at around 532 eV [13,15]

Fig. 4. O 1s XPS spectra of Pt-1/C (a) and Pt-2/C (b).**Table 2** Binding energies and relative integrated area intensities of the component species deconvoluted from the O 1s XPS spectra

Catalyst	Species	Binding energy (eV)	Relative intensity (%)
Pt-1/C	1	531.25	48
	2	532.55	43
	3	533.55	9
Pt-2/C	1	531.42	70
	2	532.72	30

(43% for Pt-1/C and 30% for Pt-2/C). The component peak with a BE of about 531 eV can be assigned to oxidized metal such as a Pt-O like species [22]. The intensity of this peak is stronger in Pt-2/C (70%) than in Pt-1/C (48%), corroborating the Pt 4f spectral data which shows more oxidized Pt in Pt-2/C (46%) than in Pt-1/C (22%).

The small peak at a BE of 533.55 eV for Pt-1/C could be oxygen associated with the carbon functional groups [25]. The corresponding C 1s spectra of the catalysts are given in Fig. 5 and the binding energies and the relative intensities are summarized in Table 3. The C 1s spectra consist of contributions from graphitic carbon (284.3 eV) and -C=O like species (285.6 eV for Pt-1/C and 285.5 eV for Pt-2/C) [13,25]. The contribution from the carbon support is very strong (85% for Pt-1/C and 73% for Pt-2/C) and this is similar to the predominant presence of the C(002) peak in the XRD (Fig. 1).

Fig. 5. C 1s XPS spectra of Pt-1/C (a) and Pt-2/C (b).**Table 3** Binding energies and relative integrated area intensities of the component species deconvoluted from the C 1s XPS spectra

Catalyst	Species	Binding energy (eV)	Relative intensity (%)
Pt-1/C	1	284.3	85
	2	285.6	15
Pt-2/C	1	284.3	73
	2	285.5	27

2.2 Electrochemical properties

Catalytic activity can be expressed in terms of specific mass activity (current per unit mass of catalyst) or specific activity wherein the electrochemically active surface area

(ECSA) is used to normalize the current [26]. The former reflects the effectiveness of catalyst preparation with respect to metal utilization, whereas the latter is more indicative of the intrinsic activity of the Pt sites. The ECSA of a Pt catalyst can be estimated from the charge associated with hydrogen adsorption on Pt (the hatched area in Fig. 6) [26–29]. 1 mol/L H_2SO_4 was used as the electrolyte for the measurements. High purity Ar was used before and during the measurement to deaerate the electrolyte. The baseline for the measured current was extended from the double-layer region of the cyclic voltammogram. The electrochemical surface area in m^2/g was calculated assuming a correspondence value of $0.21 \text{ mC}/\text{cm}^2 \text{ Pt}$ [13].

Compared to the voltammogram of Pt-1/C, the voltammogram of Pt-2/C shows a very thick double layer region suggesting a higher oxide content in the surface layer [15]. This agrees well with the higher Pt-O content in Pt-2/C as measured by XPS. While the hydrogen adsorption/desorption region (-0.2 to 0 V) of Pt-1/C is characterized by two adsorption peaks and three desorption peaks [30], only two adsorption peaks and a non-descript hydrogen desorption peak were found for Pt-2/C. This can be used to indicate the presence of well developed Pt crystal facets in Pt-1/C. For example the peak at -0.03 V for Pt-1/C corresponds well to the reported measurements for Pt(110) single crystals [31]. Additionally, the more positive hydrogen adsorption peaks correlate with Pt(100) sites. The almost featureless hydrogen adsorption/desorption region from Pt-2/C is most likely a result of its highly amorphous Pt-O content.

Fig. 6. Hydrogen electroadsorption voltammograms of the catalysts in 1 mol/L H_2SO_4 obtained at 50 mV/s and at room temperature. The hatched area represents the charge of electroadsorption for hydrogen on Pt.

Figure 7 shows the specific activity for room temperature methanol oxidation as evaluated by cyclic voltammetry in 2 mol/L CH_3OH + 1 mol/L H_2SO_4 and measured at a scan rate of 50 mV/s. The voltammetric features agree well with

Fig. 7. Cyclic voltammograms of methanol electrooxidation in 2 mol/L CH_3OH + 1 mol/L H_2SO_4 measured at 50 mV/s and at room temperature. (1) Pt-1/C; (2) Pt-2/C.

those reported in the literature [21]. The current increases significantly at about 0.2 V for both catalysts. There are two oxidation peaks, one at about 0.69 V in the forward scan and the other at about 0.47 V in the reverse scan. The specific activity of Pt-2/C is lower than that of Pt-1/C. While both voltammograms have a similar general appearance, the ratio of the forward oxidation peak current to the reverse oxidation peak current (R) is quite different for the two catalysts. R is smaller than unity for Pt-1/C but is greater than unity for Pt-2/C. While the $R = 1$ demarcation is highly reproducible there were noticeable fluctuations in the individual R values measured experimentally, even for the same catalyst.

The chronoamperograms (change of current with time) in Fig. 8 show the fractional decrease in initial current with time. The slower rate of decay for Pt-1/C (from $1.94 \text{ mA}/\text{cm}^2$ to $0.89 \text{ mA}/\text{cm}^2$) indicates that it has better CO tolerance than Pt-2/C (from $1.15 \text{ mA}/\text{cm}^2$ to $0.31 \text{ mA}/\text{cm}^2$).

Since both catalysts have the same Pt loading and a

Fig. 8. Chronoamperograms (change of current with time) of the catalysts in 2 mol/L CH_3OH + 1 mol/L H_2SO_4 at 0.30 V.

comparable particle size, the difference in specific activity between them as determined by comparative voltammetric and chronoamperometric measurements is due to their different Pt oxidation states. During methanol electrooxidation the reaction begins upon the adsorption of methanol onto the Pt surface (reaction (2)). A number of successive dehydrogenation reactions then ensue ending with a Pt-(CHO)_{ads} intermediate. In the presence of an active surface oxygen species, Pt-(CHO)_{ads} is removable and the Pt active sites are regenerated as per reaction (4). However, Pt-(CHO)_{ads} can easily rearrange into bridge CO_{ads} species and finally into the more stubborn linearly bound CO_{ads}. The linear form of CO_{ads} is slowly removed at room temperature and this is the principal cause of catalyst deactivation [32,33]. Pt-2/C contains more oxidized Pt than Pt-1/C and yet it is more susceptible to catalyst poisoning (Fig. 8). This is contrary to our initial expectation that a deliberate presence of excess oxide on the Pt surface would promote reaction (4). It is apparent that the oxidized sites on Pt-2/C are not of the “active” type. Long-term activity in the chronoamperogram (e.g. at 3600 s in Fig. 8) depends on the supply of active surface oxygen species to remove the strongly held CO_{ads}. The decomposition of water on Pt could be a source of oxygen species:

Reaction (6) is only promoted by Pt⁰ and this could explain the better sustained activity of the more “metallic” Pt-1/C catalyst. The overall catalytic activity is, therefore, determined primarily by the effectiveness of Pt⁰ in methanol and by water activation reactions. Water activation often lags behind methanol activation resulting in the observed catalyst deactivation.

The evaluation of Pt catalysts for methanol electrooxidation in acidic solutions by cyclic voltammetry often leads to the detection of two oxidation peaks. One peak is detected in the anodic scan and the other in the cathodic scan. There are ongoing discussions on the interpretation of these oxidation peaks particularly for the peak found in the cathodic scan. According to Manoharan et al. [11], the forward oxidation peak is associated with linear Pt-CO species while the reverse oxidation peak is associated with the more removable bridged CO species. The anodic peak in the cathodic scan has also been attributed to the re-oxidation of methanol on more reduced Pt active sites [34]. Additionally, others consider the two oxidation peaks to be caused by the hysteresis in surface site blocking [35]. Since methanol electrooxidation is a structure sensitive reaction, catalysts with inherently different Pt oxidation states are expected to respond differently in the anodic and cathodic scans and may be characterized as such (the “R” value). A more “metallic” Pt catalyst should have a larger number of vacant Pt

sites neighboring the linearly bound CO_{ads} and this would allow the latter to rearrange into a more easily removable bridge CO_{ads} [11,33]. A prominent oxidation peak would be expected in the reverse scan (Fig. 7). The difference in R values between Pt-1/C and Pt-2/C can be understood on this basis. For the Pt-2/C catalyst, approximately half of the surface (54%, Table 1) is metallic Pt and, therefore, a transformation from the linear to the bridge form could be rate limited by the availability of vacant Pt sites.

3 Conclusions

Pt catalysts were produced and were designed to have different oxidation states. The addition of a strong oxidizing agent H₂O₂ after the reduction of H₂PtCl₆ by NaBH₄ resulted in the formation of an overall more oxidized Pt catalyst. The activities of the treated and untreated catalysts during room temperature methanol oxidation in acid solutions were evaluated by cyclic voltammetry and chronoamperometry. Catalyst performance was found to correlate well with the Pt⁰ content in the catalyst. The more oxidized catalyst could not supply active oxygen by water dissociation to remove the linear CO_{ads} species, despite being designed for this purpose. This was reflected by the higher proportion of linear to bridge species, which was greater than unity for the forward to reverse oxidation current for the more “oxidized” catalyst.

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