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Article

Promoting effects of Fe_2O_3 to Pt electrocatalysts toward methanol oxidation reaction in alkaline electrolyte

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ABSTRACT

Fe_2O_3 nanorods and hexagonal nanoplates were synthesized and used as the promoters for Pt electrocatalysts toward the methanol oxidation reaction (MOR) in an alkaline electrolyte. The catalysts were characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, cyclic voltammetry and chronoamperometry. The results show that the presence of Fe_2O_3 in the electrocatalysts can promote the kinetic processes of MOR on Pt, and this promoting effect is related to the morphology of the Fe_2O_3 promoter. The catalyst with Fe_2O_3 nanorods as the promoter (Pt- Fe_2O_3 /C-R) exhibits much higher catalytic activity and stability than that with Fe_2O_3 nanoplates as the promoter (Pt- Fe_2O_3 /C-P). The mass activity and specific activity of Pt in a Pt- Fe_2O_3 /C-R catalyst are 5.32 A/mg_{Pt} and 162.7 A/m²_{Pt}, respectively, which are approximately 1.67 and 2.04 times those of the Pt- Fe_2O_3 /C-P catalyst, and 4.19 and 6.16 times those of a commercial PtRu/C catalyst, respectively. Synergistic effects between Fe_2O_3 and Pt and the high content of Pt oxides in the catalysts are responsible for the improvement. These findings contribute not only to our understanding of the MOR mechanism but also to the development of advanced electrocatalysts with high catalytic properties for direct methanol fuel cells.

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1. Introduction

Direct methanol fuel cells (DMFCs) show great potential as future power sources for automobile power and portable electronic devices owing to a number of advantages, such as the low operating temperature (< 100 °C), high energy efficiency, convenient transportation, low environmental pollution and fast start-up time [1]. To date, the noble metal Pt is still the most active catalyst material both for the anodic and cathodic reactions of DMFCs and cannot be completely replaced by other base metals. Owing to the high cost of Pt, the commercial application of DMFCs has been limited. In addition, Pt is easily

poisoned by the CO-like intermediates in the process of the methanol electro-oxidation reaction (MOR). The intermediates adsorb on the surface of Pt atoms, resulting in a significant decrease in the catalytic performance of Pt, which further increases the cost of DMFCs.

Over the past decades, a number of studies have focused on the investigation of Pt-free electrocatalysts or the modification of Pt catalysts [2,3]. The traditional modification was accomplished through the addition of other components or promoters. The components themselves exhibit no catalytic activity toward the reactions but can promote the activity of Pt during catalysis. It is well known that the addition of Ru to Pt catalysts

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can increase the CO tolerance and catalytic activities of Pt owing to a synergistic effect or bifunctional mechanism, which has been reported by many groups [3]. The promoter Ru can activate water at lower potentials than Pt to yield adsorbed OH species. The OH species can oxidize the -CO species adsorbed on the surface of the neighboring Pt atoms to CO_2 and, thus, increase the CO tolerance of Pt. Besides the metal promoters, metal oxides, such as SnO_2 and CeO_2 , have also been used as effective promoters for Pt catalysts owing to the low cost and easily tunable surface properties by straightforward synthesis procedures [4–6]. Xing et al. [4] reported that Sb-doped SnO_2 could not only act as an effective promoter but also act as a favorable support for Pt catalysts owing to the high electrical conductivity. Shen et al. [5] reported that the addition of CeO_2 to Pt catalysts could remarkably improve the catalytic properties and poisoning resistance of Pt toward alcohol electro-oxidation owing to the synergistic effect. In our previous work, we found that composite metal oxides, In_mSnO_2 , could be used as effective promoters and functionalized supports for a Pt catalyst toward MOR [7]. Changes in the Pt electronic structure arising from the interaction between Pt and the promoter were vital for an improvement of the catalytic properties of Pt. Among other low-cost oxides, Fe_2O_3 nanocrystals may be used as a promoter or support material for a Pt catalyst owing to their excellent physicochemical properties, such as high surface and sizable surface defects. It is reported that Fe_2O_3 can act as an effective promoter of Pt or Pd catalysts for the methanol, ethanol and formic acid electro-oxidation reactions [8–10].

The morphologies of Pt are known to play a crucial role in the electrocatalytic behavior [11,12], while the morphology effects of the promoters have not attracted much attention. Owing to the close affinity between the promoters and Pt, different morphologies of the promoters may induce different promoting effects to Pt. Therefore, we intend to determine whether Fe_2O_3 with different morphologies can exhibit different promoting effects. In the present work, Fe_2O_3 nanorods and nanoplates are prepared and used as the promoters for Pt electrocatalysts toward MOR. It is reported that MOR in an alkaline electrolyte is more facile than in an acid media [13], and the concerning progressive carbonation of the alkaline electrolyte can be addressed by application of alkaline anion exchange membranes, which have been developed in recent years [14]. Therefore, we chose an alkaline electrolyte (0.5 mol/L KOH) as the environment for the MOR. Electrochemical characterizations of the catalysts showed that the metal oxides Fe_2O_3 could exhibit a significant promoting effect to Pt, and the promoting effects are strongly dependent on the morphologies of Fe_2O_3 . The catalyst with Fe_2O_3 nanorods as the promoter facilitated a much higher catalytic activity and stability of Pt as compared with that including Fe_2O_3 nanoplates as the promoter.

2. Experimental

2.1. Chemicals

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, NaCl, Na_2CO_3 , sodium citrate and ethanol were purchased from Jinan Chemical Reagent Company. PEG, sodium

acetate and K_2PtCl_4 were purchased from Sinopharm Chemical Reagent Co. Ltd. Vulcan XC-72 carbon (BET: $237 \text{ m}^2/\text{g}$) and NaBH_4 were purchased from Carbot (USA) and Merck (Schuchardt, Germany), respectively. All of the chemicals were of analytical grade and were used as received without further purification. Deionized water was used throughout.

2.2. Preparation of Fe_2O_3 nanorods and hexagonal nanoplates

The Fe_2O_3 nanorods were synthesized through an aqueous precipitation method [15]. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.38 g) and NaCl (11.60 g) were dissolved in deionized water (190 mL) containing PEG (10 mL) under vigorous magnetic stirring. A Na_2CO_3 aqueous solution (200 mL, 0.2 mol/L) was then added at a rate of 5.5 mL/min through a syringe pump. The mixture was then maintained at 120°C for 1 h. The precipitate was washed with ethanol and distilled water, and finally dried in a vacuum oven at 50°C for 6 h. The product was calcinated at 500°C for 5 h to obtain Fe_2O_3 nanorods. The Fe_2O_3 hexagonal nanoplates were prepared through a hydrothermal procedure [16]. In a typical experiment, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.273 g, 1.0 mmol) was dissolved in ethanol (10.0 mL) containing water (0.7 mL) under vigorous magnetic stirring. After complete dissolution, sodium acetate (0.8 g) was added to the solution with stirring. The mixture was then transferred into a Teflon-lined stainless steel autoclave (25 mL) and heated at 180°C for 12 h. After being allowed to cool naturally down to room temperature, the resulting solid products were separated by filtration, washed with ethanol and distilled water several times, and finally dried in a vacuum oven at 60°C for approximately 10 h to obtain the Fe_2O_3 hexagonal nanoplates.

2.3. Preparation of the Pt- $\text{Fe}_2\text{O}_3/\text{C}$ samples

Pt colloids were prepared according to the methods previously reported by our laboratory [17]. K_2PtCl_4 (8 mL, 9.64 mmol/L) and sodium citrate solution (6.4 mL, 60 mmol/L) were added into deionized water (135 mL) containing Fe_2O_3 nanorods (30 mg) and Vulcan XC-72 carbon (37.5 mg). After stirring for 2 h, NaBH_4 solution (5 mL, 7.69 mmol/L) was added dropwise under vigorous stirring to produce Pt nanoparticles and was stirred for another 3–4 h. The resultant sample was filtrated and washed several times with deionized water. Then, the filter cake was dried at 60°C for 12 h to obtain the Pt- $\text{Fe}_2\text{O}_3/\text{C-R}$ sample. The Pt- $\text{Fe}_2\text{O}_3/\text{C-P}$ sample with Fe_2O_3 nanoplates as the promoter was prepared with an identical procedure. For the two catalysts, the nominal loading of Pt was approximately 20 wt%. The commercial PtRu catalyst was purchased from Johnson-Matthey and the loadings of Pt and Ru were 20 and 10 wt%, respectively.

2.4. Physico-chemical characterizations of the Pt- $\text{Fe}_2\text{O}_3/\text{C}$ samples

The morphologies of the as-prepared samples were investigated using a field-emission scanning electron microscope (SEM, JSM 7401F, JEOL, Tokyo, Japan) at an operating voltage of

3.0 kV and a transmission electron microscope (TEM, JEM-2010) operating at 120 kV. X-ray diffraction (XRD) patterns were obtained on a MiniFlex 600 X-ray diffractometer with a scan rate of $4^\circ/\text{min}$ ($20^\circ < 2\theta < 80^\circ$) and the wavelength of the incident radiation was 0.15406 nm ($\text{Cu K}\alpha$). X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo ESCALAB 250 instrument equipped with Al $K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$). The actual loading amounts of Pt in the as-prepared samples were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima-4300DV Spectrometer). For the Pt- $\text{Fe}_2\text{O}_3/\text{C-R}$ and Pt- $\text{Fe}_2\text{O}_3/\text{C-P}$ samples, the real Pt contents in the catalysts were 14.2 and 14.5 wt%, respectively, slightly lower than those of the nominal loadings (20 wt%) probably arising from the losses of Pt during the preparation.

2.5. Electrochemical characterizations

A glassy carbon electrode with a diameter of 5 mm was used as the working electrode and polished with 0.2–0.5 and 0.02–0.05 μm alumina slurries prior to each use. The catalyst (5.0 mg) was added to isopropanol (1.0 mL) to produce the catalyst ink. After a proper amount of the suspension was dropped onto the glassy carbon disk electrode, the electrode was dried by a lamp irradiation. Then, 0.05 wt% Nafion solution (10 μL , Dupont) was pipetted onto the electrode to immobilize the catalyst layer and then air-dried.

A conventional three-electrode cell was used for the electrochemical measurements, which were carried out on a CHI 760E electrochemical workstation (Shanghai Chenhua Apparatus, China). A saturated calomel electrode (SCE) and a platinum electrode ($1.0 \text{ cm} \times 1.0 \text{ cm}$) were used as the reference and counter electrodes, respectively. All of the potentials mentioned in this work are referenced to RHE. Electrochemical tests, including cyclic voltammetry (CV) and chronoamperometry (CA), were performed in 0.5 mol/L KOH + 2.0 mol/L CH_3OH solution. Before the electrochemical tests, the electrolyte was initially purged with high-purity dry nitrogen to remove the dissolved oxygen. The CO stripping test was performed in 0.5 mol/L KOH. Adsorption of CO on the electrode catalyst was conducted by bubbling high-purity CO through the electrolyte for 15 min, followed by purging with N_2 for 20 min to expel the residual CO out of the solution. The CA tests were performed under a constant potential of 0.62 V versus RHE.

3. Results and discussion

3.1. Characterization of the Pt- $\text{Fe}_2\text{O}_3/\text{C}$ samples

Fig. 1 shows the morphologies of the Pt- $\text{Fe}_2\text{O}_3/\text{C-R}$ and Pt- $\text{Fe}_2\text{O}_3/\text{C-P}$ samples. From the SEM images in Fig. 1(a) and (b), we can observe that the Fe_2O_3 nanorods have a diameter of approximately 70 nm and a length of approximately 420 nm. Fig. 1(e) and (f) shows the hexagonal nanoplate structures with

Fig. 1. Representative SEM images of Fe_2O_3 nanorods (a and b) and nanoplates (e and f). TEM images of the Pt- $\text{Fe}_2\text{O}_3/\text{C-R}$ (c, i, j) and Pt- $\text{Fe}_2\text{O}_3/\text{C-P}$ (g, k, l) samples. The insets show the HRTEM images and the corresponding FFT patterns of Pt nanoparticles supported on Fe_2O_3 nanorods or nanoplates. The size histograms for the metal particles supported on Pt- $\text{Fe}_2\text{O}_3/\text{C-R}$ (d) and Pt- $\text{Fe}_2\text{O}_3/\text{C-P}$ (h) samples.

a width of approximately 200 nm and a thickness of approximately 10 nm. From the HRTEM images of Pt particles on the Fe_2O_3 nanorods Fig. 1(i) and nanoplates Fig. 1(e), the fringes of 0.224 nm assigned to Pt(111) can be clearly observed by electron diffraction. The corresponding Fourier transform patterns are shown in the inset of the figures. The mean sizes of the Pt nanoparticles were calculated from an ensemble of at least 200 particles in a randomly chosen area of the TEM images. For the Pt- Fe_2O_3 /C-R sample, the metal particle size was 4.57 ± 0.38 nm and the particles were well dispersed on the support without obvious aggregation. For the Pt- Fe_2O_3 /C-P sample, the spherical morphology was the same as that in the Pt- Fe_2O_3 /C-R sample while the size of the particles became slightly smaller (4.19 ± 0.63 nm), suggesting that the morphology of the support has little effect on the dispersion state of the nanoparticles and the interaction between the supports and Pt nanoparticles. Fig. 1(d) and (h) show the size histograms for the metal particles in Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples, respectively.

Fig. 2 shows the XRD patterns of the as-prepared Pt- Fe_2O_3 /C samples. The results of the reference Fe_2O_3 nanorods and nanoplates samples are also shown for comparison. The strong diffraction peaks marked with stars and dots correspond to the signals of Fe_2O_3 and Pt, respectively. For the Fe_2O_3 nanorods and nanoplates samples, the positions of the diffraction peaks were almost at the same position, which suggested that the crystalline structure of the Fe_2O_3 samples with different morphologies did not show a difference. For the two Pt- Fe_2O_3 /C samples, the diffraction peak positions and profiles corresponding to the signals of Fe_2O_3 were almost the same as those of the Fe_2O_3 nanorods and nanoplates. The well-defined peaks at 2θ positions of 33.2° , 35.5° , 49.5° and 54.1° could be assigned to the (1014), (1120), (0224) and (1126) crystal faces of α - Fe_2O_3 (PDF #33-0664), respectively. The other peaks at 24.1° , 40.7° , 62.4° and 64.0° are associated with the (0112), (1123),

Fig. 2. XRD patterns of the Pt- Fe_2O_3 /C-R, Pt- Fe_2O_3 /C-P, Fe_2O_3 nanorods and Fe_2O_3 nanoplates samples. The peaks marked with stars and dots are the signals from Fe_2O_3 and Pt, respectively.

(2134) and (3030) crystal faces, respectively. All of the peaks were in good agreement with the results reported in the literature [16], suggesting that the Fe species in the as-prepared Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples was characteristic of Fe_2O_3 . In addition, the peaks at around 39.6° and 46.2° were from the diffractions at the (111) and (200) planes of Pt (PDF #04-0802), respectively.

The chemical states of Pt and Fe in the as-prepared Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples were characterized using XPS (Fig. 3). All of the Pt $4f_{7/2}$ and $4f_{5/2}$ signals were deconvoluted into three doublets, among which the most intense doublet with relatively lower binding energies (BEs) was assigned to Pt(0), and the other two doublets at relatively higher BEs were signatures of Pt(II) and Pt(IV) [18]. For the two Pt- Fe_2O_3 /C samples, the profiles of the doublets were similar to

Fig. 3. Pt 4f (a, b, c) and Fe 2p (d) XPS spectra of the Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples; (e) The entire XPS spectra of the samples.

those in the Pt/C catalyst, and the BE positions showed a weak negative BE shift (~ 0.2 eV). The shift toward lower BEs suggested that there was a weak electronic interaction between Pt and the Fe_2O_3 promoters, which would be beneficial for weakening the adsorption strengths of the intermediates ($-\text{CO}_{\text{ads}}$) formed in the process of methanol electro-oxidation and would have the possibility to improve the catalytic properties [19]. For the Fe 2p spectra in Fig. 3(d), the two peaks at 711.2 and 724.7 eV correspond to the Fe $2p_{3/2}$ and Fe $2p_{1/2}$ peaks of Fe^{3+} in Fe_2O_3 , respectively. No lower peaks were observed for the two samples, suggesting that Fe_2O_3 , rather than Fe_3O_4 or FeO , is present in the samples. Fig. 3(e) shows the entire XPS spectra of the Pt- Fe_2O_3 /C-R, Pt- Fe_2O_3 /C-P and Pt/C samples. It can be seen that the peaks at approximately 711 and 724 eV were evident for the Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples, while they were absent for the Pt/C sample. These results are consistent with the XRD results.

3.2. Cyclic voltammetry of Pt- Fe_2O_3 /C and PtRu/C samples in KOH

Fig. 4 shows the cyclic voltammograms of the Pt- Fe_2O_3 /C and PtRu/C samples in N_2 -saturated KOH solution (0.5 mol/L) without methanol. For the two Pt- Fe_2O_3 /C samples, the profiles of the CV curves were similar. The pronounced cathodic peaks at approximately 0.64 V could be assigned to the reduction of Pt oxides formed in the forward scan. The typical cathodic and anodic peaks in the low potential region of 0.08 to 0.42 V were ascribed to the adsorption and desorption of hydrogen on the surface of Pt. These peaks were associated with the three low index crystal faces of Pt(110), (100) and (111), and could be used to calculate the electrochemically active surface area (EAS) of Pt in the two Pt- Fe_2O_3 /C samples based on the following equation [20–24]:

$$\text{EAS (m}^2/\text{g}_{\text{Pt}}) = Q_{\text{H}} / (0.21 \times W_{\text{Pt}})$$

where, Q_{H} is the charge consumed for the desorption and adsorption process of hydrogen on the surfaces of Pt nanoparti-

Fig. 4. CV curves of the Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P samples in N_2 -saturated 0.5 mol/L KOH electrolyte (free of methanol). Results of the commercial PtRu/C catalyst are also provided in the figure for comparison. The loadings of Pt on the electrode were 3.56, 3.62 and 10 μg for the Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P and PtRu/C catalysts, respectively (scan rate 50 mV/s).

Table 1

Electrochemical parameters and activities for MOR on Pt- Fe_2O_3 /C-R, Pt- Fe_2O_3 /C-P and commercial PtRu/C catalysts.

Catalysts	EAS ^a (m ² /g)	E_{o} ^b (V)	E_{p} ^c (V)	I_{p} ^d (A/mg)	Mass activity ^e (A/mg)	Specific activity ^f (A/m ²)
Pt- Fe_2O_3 /C-R	32.7	0.37	0.80	5.32	5.32	162.7
Pt- Fe_2O_3 /C-P	39.9	0.39	0.88	3.87	3.18	79.7
PtRu/C	48.1	0.42	0.88	1.42	1.27	26.4

^a Electrochemically active surface area of Pt.

^b Onset potential for MOR.

^c Peak potential for MOR.

^d Peak current for MOR.

^e Measured at 0.80 V vs. RHE for MOR.

^f Measured at 0.80 V vs. RHE for MOR.

cles, corresponding to the integrated peak area of the hydrogen-desorption (or anode hydrogen peak) in the positive scanning curve, W_{Pt} is the Pt loading on the working electrodes, and 0.21 is the theoretical quantity of the electric charge (mC/cm^2) for the surface of the Pt electrode, supposing that the Pt atoms are covered with monolayer hydrogen and the surface density of Pt is 1.3×10^{15} atoms/ cm^2 [24]. The EAS of Pt- Fe_2O_3 /C-R and Pt- Fe_2O_3 /C-P catalysts are 32.7 and 39.9 $\text{m}^2/\text{g}_{\text{Pt}}$, respectively. Since the presence of Ru would distort the profile of the hydrogen adsorption-desorption peaks, the EAS of Pt in the commercial PtRu/C sample was calculated from the CO stripping voltammogram rather than the hydrogen adsorption/desorption peaks. The CO stripping voltammograms are shown in the next part of this work and the EAS was calculated assuming a monolayer of linearly adsorbed CO and the coulombic charge necessary for oxidation was 0.42 mC/cm^2 [25,26]. All of the EAS values of Pt in the two Pt- Fe_2O_3 /C samples and PtRu/C samples are listed in Table 1. The EAS values of Pt- Fe_2O_3 /C-R is lower than that of the Pt- Fe_2O_3 /C-P catalyst probably owing to the slightly larger size of the Pt metal nanoparticles in the Pt- Fe_2O_3 /C-R catalyst.

3.3. Electrocatalytic performance for methanol oxidation on Pt- Fe_2O_3 /C catalysts

The electrocatalytic activities of the Pt- Fe_2O_3 /C catalysts for the methanol oxidation reaction were investigated by CV in an aqueous solution of 0.5 mol/L KOH electrolyte with 2.0 mol/L CH_3OH at a scan rate of 50 mV/s. The results of the reference PtRu/C catalyst are also shown in Fig. 5 for comparison. The currents of MOR have been normalized to the actual loading of Pt on the surface of the electrode, which was measured by ICP. All of the curves contain a strong methanol oxidation peak during the forward scan and a weak anodic peak during the backward scan, which present the typical cyclic voltammetric characteristics of the methanol oxidation reaction on Pt-based catalysts in an alkaline electrolyte [27].

For the evaluation of the activities of the catalysts, both the potentials and currents of MOR on the catalysts were always used to compare the catalytic performance of the catalysts. The onset or peak potential of MOR during the forward scan was an effective indicator. The data are listed in Table 1. For the

Fig. 5. CV curves of the Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P catalysts in 0.5 mol/L KOH + 2.0 mol/L CH₃OH (scan rate 50 mV/s). The currents have been normalized to the mass of Pt on the electrodes.

Pt-Fe₂O₃/C-R catalyst, the onset and peak potentials were 0.37 and 0.80 V, respectively, which were more negative than those of the Pt-Fe₂O₃/C-P catalyst (0.39 and 0.88 V), and also much lower than those of the reference PtRu/C catalyst (0.42 and 0.88 V). Pt-Fe₂O₃/C-R catalyst presented an approximately 80 mV more negative peak potential for methanol oxidation compared with the PtRu/C catalyst, showing a much higher catalytic performance. Besides the onset or peak potential, the peak current of MOR or the current at a fixed potential is always used as another indicator for comparison of the catalytic activities of the catalysts [28–30]. The peak currents normalized to the mass of Pt on the electrode were 5.32 and 3.87 A/mg_{Pt} for the Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P catalysts, respectively, which were much higher than that of the PtRu/C catalyst (1.42 A/mg_{Pt}). This result suggested that the Fe₂O₃ exhibited promoting effects to the Pt catalyst toward MOR. However, since the peak potentials of MOR on the catalysts are different, the currents at a fixed potential should be more reasonable for comparing the catalytic activities. In this work, we chose the most negative peak potential (0.80 V) as the fixed potential and the corresponding mass activities of the catalysts are listed in Table 1. The mass activity of Pt in Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P was 5.32 and 3.18 A/mg_{Pt}, which was approximately 4.19 and 2.50 times that of the PtRu/C (1.27 A/mg_{Pt}) catalyst, respectively. The specific activities at 0.80 V calculated by normalizing the mass activity data to the EAS of Pt are also provided in Table 1. It can be observed that the two Fe₂O₃-promoted catalysts also showed much higher specific activities. The specific activities of Pt in the Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P catalysts were 162.7 and 79.7 A/m²_{Pt}, which were approximately 6.16 and 3.02 times that of PtRu/C (26.4 A/m²_{Pt}), respectively.

The enhanced catalytic performance of Pt in the two Pt-Fe₂O₃/C catalysts may arise from the promoting effect of Fe₂O₃, and this promoting effect to Pt was strongly dependent on the morphology of the promoter. For the two Fe₂O₃-promoted catalysts, Fe₂O₃ nanorods presented a higher promoting effect to the Pt catalyst toward MOR as compared

with the Fe₂O₃ nanoplates. The electronic effect and synergistic effect are the common reasons for the enhancement of the catalytic properties for oxides-promoted Pt-based catalysts. In the above XPS results, the BEs of Pt 4f in the Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P catalysts showed a slight shift to more negative values as compared with those in the pure Pt/C catalyst. These findings indicated that there was an electronic interaction between Fe₂O₃ and Pt and the change in the electronic structure of Pt may be responsible for the improvement of the catalytic activities. However, by carefully observing the XPS peaks, we found that the shift in the BEs was so small (~0.2 eV) that it might not induce such a high promoting effect. Therefore, we propose that there must be other effects that improve the catalytic properties of Pt. For the oxides-promoted Pt-based catalysts, it has been confirmed that the catalytic properties are closely related to the synergistic effect or bifunctional mechanism [31–33]. Just as the Ru species in PtRu bimetallic electrocatalysts, the oxides have also been confirmed as the active sites for the formation of oxygen-containing species, which could oxidize the CO-like poisons on the surface of the noble metal and thus release the active sites for further electrochemical reaction [18,31–33]. A possible mechanism of MOR on the Fe₂O₃-promoted catalysts will be discussed in more detail in the next sections.

Additionally, the ratio of I_f (the anodic peak current during the forward scan) to I_b (the anodic peak current during the backward scan) is always regarded as an essential factor to evaluate the CO tolerance of the catalysts [23,34]. It is generally considered that the anodic peak during the forward scan comes from the oxidation of methanol and the peak during the backward scan is associated with the oxidation of CO formed in the forward scan. Therefore, a higher ratio of I_f to I_b suggests a higher CO tolerance of the catalyst [35–37]. However, recent findings reported by Hofstead-Duffy et al. [38], using an *in-situ* IR technique, indicated that both the anodic peaks in the forward and backward scans were associated with the oxidation of methanol, and the ratio of I_f to I_b was not appropriate to evaluate the CO tolerance of the catalysts. Therefore, we used the CO stripping cyclic voltammograms rather than the ratio of I_f to I_b to evaluate the CO resistance of the catalysts.

Fig. 6 shows the CO stripping cyclic voltammograms of the catalysts in 0.5 mol/L KOH electrolyte. The profiles of the CO stripping voltammograms on the two Fe₂O₃-promoted catalysts were almost the same and three anodic peaks in the positive-direction scans, corresponding to the CO oxidation, were observed. This phenomenon was similar to the results previously reported by Jiang et al. [39] and our group [8]. Taking the Pt-Fe₂O₃/C-R catalyst as an example, the voltammogram of CO oxidation first exhibited a fast-rising current with the onset potential at around 0.24 V, then a current plateau region from 0.40 to 0.46 V followed by another fast-rising current. After a shoulder peak with the peak potential at approximately 0.57 V, the current showed a dramatic increase until a current peak was found at 0.66 V. The vertical dashed lines in Fig. 6 represented the onset potentials (E_o) for CO oxidation on the catalysts and the peak potential on Pt-Fe₂O₃/C-R. By carefully comparing the positions of E_o , it can be seen that the E_o posi-

Fig. 6. CO stripping voltammograms of Pt-Fe₂O₃/C-R, Pt-Fe₂O₃/C-P and PtRu/C catalysts in 0.5 mol/L KOH (scan rate 50 mV/s).

tions for the catalysts were different. The onset potentials of the Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P catalysts were 0.24 and 0.30 V, respectively. Both potentials are more negative than that of the commercial PtRu/C catalyst (0.42 V), suggesting that the presence of Fe₂O₃ in the catalysts enhances the CO tolerance of the Pt catalyst. The enhancement of the CO tolerance of Pt probably arises from the synergistic effects or bifunctional mechanism [23,40,41], which was similar to that in the oxide-promoted Pt catalysts toward the electro-oxidation reaction [28,42]. In an alkaline electrolyte, the OH⁻ anions could be adsorbed on the catalysts to form OH_{ads} species, and this process would become easier when the oxides exist in the catalysts [31]. The formation of OH_{ads} species could oxidize the CO-like poisoning species on the surface of Pt, releasing the active sites on the Pt surface for a further catalytic process. Specific mechanisms are given as follows [43,44]:

Apart from the bifunctional mechanism, it is reported that the CO can also be oxidized through the formate pathway in the alkaline electrolyte. That is, CO firstly reacts with bulk OH⁻ to form a soluble formate intermediate [8,39,45]:

then, the soluble formate is electro-oxidized to CO₂:

For the MOR process, the presence of the promoter can not only lower the onset potential of MOR, but also increase the MOR current densities on the Pt catalyst (Fig. 5). The data of “mass activity” (A/mg_{Pt}) equals the product of the “specific activity” (A/m²_{Pt}) and EAS (m²/g_{Pt}) [46–48]. That is, the higher “mass activities” of Pt in the Pt-Fe₂O₃/C catalysts comes not only from the higher EAS of Pt but also from the higher “specific activity”. A timely removal of the CO-like poisoning intermedi-

ate species on the surface of Pt would release the active sites and enhance the intrinsic activity (specific activity) of the Fe₂O₃-promoted catalysts. In addition, we also found that the well-known PtRu/C catalyst with high catalytic properties for MOR in an acidic electrolyte [49] did not show superior catalytic properties in an alkaline electrolyte, which is similar to the results reported by Tripković and co-workers [43,50].

The synergistic effect between Fe₂O₃ and Pt may contribute to the enhancement of the catalytic properties of Pt. However, the question remains as to why the Fe₂O₃ nanorods show a higher promoting effect to Pt compared with Fe₂O₃ nanoplates. By a semi-quantitative analysis of the Pt 4f peaks, based on the integration areas of Pt in different valence states in Fig. 3(a) and (b), we determined that the Pt species in the two Pt-Fe₂O₃/C samples are different. For Pt-Fe₂O₃/C-R, about 57% of Pt was in its high valence states (II and IV). For Pt-Fe₂O₃/C-P, only 36% of Pt was from Pt(II and IV). It is generally accepted that Pt(0) is the active center for the catalysis. A high content of PtO or PtO₂ would depress the catalytic performance of Pt. Recently, Li et al. [51] reported that the highly oxidized Pt species could promote the interaction between the reactant and the Pt nanoparticles, and thus increased the catalytic performance. In the Pt-Fe₂O₃/C-R catalyst, a high content of Pt oxides (ca. 57%) may show the same effect. The Pt oxides increase the interaction between the nanoparticles and methanol molecules, which is beneficial for the first step of methanol oxidation on the surface of Pt, that is, the adsorption of methanol molecules on Pt becomes easier. As a result, the kinetics of the methanol oxidation reaction would be accelerated. In addition, the different morphologies of Fe₂O₃ signifies that the surfaces of the nanocrystals are enclosed by definite facets, such as (110) crystal plane for nanorod and (1120) for nanoplate-structured Fe₂O₃. These different lattice fringes can induce different interactions between Fe₂O₃ and Pt owing to the close affinity between them. The catalytic kinetics of methanol oxidation would then be affected by the different interfacial properties [44,52,53]. However, owing to the restriction of the current experimental facilities, we cannot provide the detailed relationship between the exposed crystal planes of Fe₂O₃ and the catalytic properties of Pt. More work is needed to further uncover the structural details that govern the catalytic properties of the catalysts.

3.4. Stabilities of the Pt-Fe₂O₃/C catalysts

A standard test of the catalysts for the tolerance to CO poisoning during continuous fuel cell operation can be based on the evaluation of their medium term activity under constant potential conditions. CA measurements have always been used to evaluate the stabilities. Fig. 7 shows the results of the two Fe₂O₃-promoted Pt catalysts and the commercial PtRu/C catalyst in 0.5 mol/L KOH + 2.0 mol/L CH₃OH solution for 3600 s at the fixed potential of 0.62 V. The current density retentions of the Pt-Fe₂O₃/C-R, Pt-Fe₂O₃/C-P and PtRu/C catalysts are approximately 34%, 38% and 43%, respectively. The two Fe₂O₃-promoted catalysts showed comparable stabilities, which are slightly lower than the PtRu/C catalyst. Even so, both the initial and final currents of Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P

Fig. 7. Chronoamperograms of the Pt-Fe₂O₃/C-R, Pt-Fe₂O₃/C-P and PtRu/C catalysts in 0.5 mol/L KOH + 2.0 mol/L CH₃OH at 0.62 V.

are much higher than the PtRu/C catalyst. The initial currents of Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P are 1.72 and 0.95 A/mg_{Pt}, respectively, which are 3.24 and 1.79 times that of the commercial PtRu/C catalyst (0.53 A/mg_{Pt}). These results are consistent with the above CV measurements and further demonstrate the improved catalytic activity of the Pt-Fe₂O₃/C catalysts. After 3600 s of running time, the currents of Pt-Fe₂O₃/C-R and Pt-Fe₂O₃/C-P decreased to 0.59 and 0.36 A/mg_{Pt}, respectively, which are still higher than that of the PtRu/C catalyst (0.23 A/mg_{Pt}). Although Pt-Fe₂O₃/C-R shows the highest catalytic activity among the catalysts, it is worth mentioning that the long-term stability of the Fe₂O₃-promoted catalysts needs to be further improved since both the activity and stability of the catalyst are crucial for practical applications. Future work is needed to further investigate the catalytic mechanism and improve the long-term stability of the Fe₂O₃-promoted Pt catalysts.

4. Conclusions

Fe₂O₃ nanorods and nanoplates were prepared through the precipitation or hydrothermal methods and used as the promoters for Pt catalysts toward the electro-oxidation of methanol. Results showed that both the Fe₂O₃-promoted Pt catalysts exhibited a much higher catalytic performance than the com-

mercial PtRu/C catalyst and the catalytic properties of the two Fe₂O₃-promoted Pt catalysts were strongly dependent on the morphology of the Fe₂O₃ promoter. The catalyst with Fe₂O₃ nanorods as the promoter showed a much higher catalytic activity than that with Fe₂O₃ nanoplates as the promoter. Synergistic effects between Fe₂O₃ and Pt and the highly oxidized Pt species play an important role in the enhancement of the catalytic properties of Pt. These findings have potential applications for understanding the catalytic mechanism and the designed preparation of Pt-based electrocatalysts for alkaline fuel cells.

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Graphical Abstract

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Promoting effects of Fe₂O₃ to Pt electrocatalysts toward methanol oxidation reaction in alkaline electrolyte

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The presence of Fe₂O₃ can promote the kinetic processes of MOR on Pt, and the promoting effect is related to the morphology of Fe₂O₃ promoter. The Fe₂O₃ nanorods show higher promoting effects than Fe₂O₃ nanoplates.

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氧化铁对铂在碱性介质中催化氧化甲醇的促进作用

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摘要: Pt催化剂是电催化领域用途最为广泛的贵金属催化剂。Pt资源稀缺, 价格昂贵, 同时它的物理化学特性又决定了其在多种催化反应中难以被替代。在质子交换膜燃料电池的小分子醇类电氧化过程中, 难免存在Pt的毒化现象, 其催化性能有待进一步提升。因此, 围绕着Pt催化剂纳米结构的设计、抗毒性及反应机理的探索一直是电催化研究面临的重要课题。

目前, 已被广泛认可的提高Pt催化性能的方法之一是引入第二种金属, 通过金属间协同效应(双功能机理)、张力效应或电子效应等对Pt的催化行为进行改性。对于由双/多金属组成的纳米结构催化剂, 无论是协同效应还是电子效应, 催化活性的提高都需要金属间有丰富的接触界面和恰当的邻近状态。通过调变两组元的种类、原子比和接触状态等可以实现对金属-金属界面的调控, 进而调变催化性能。除金属助剂外, 金属氧化物对Pt催化剂的助催化作用也引起广泛关注。由于金属氧化物与Pt之间的密切接触作用, 氧化物的形貌特点对Pt的催化性能可产生重要影响。

到目前为止, 有关催化剂形貌效应的研究主要集中于贵金属纳米颗粒上(Pt, Au, Pd等), 但关于金属氧化物载体/助剂的形貌对贵金属催化性能影响的研究尚不多。具有明确形貌的金属氧化物载体/助剂, 暴露的晶面不同, 表面原子的配位状态也不同, 从而造成与之密切接触的Pt的性质发生改变。因此, 金属氧化物的表面性质以及Pt-金属氧化物的界面性质将对电催化性能产生重要影响, 深入阐释贵金属-金属氧化物的表/界面性质以及建立有效的构效关系, 对设计和制备高效电催化剂具有一定的指导意义。

为了提高Pt基催化剂活性、抗CO中毒能力以及稳定性, 本文采用共沉淀法和水热法分别制备了纳米棒和六边形纳米片状的Fe₂O₃作为Pt催化剂的助剂, 考察了助剂形貌对Pt催化剂在碱性介质中催化氧化甲醇的促进作用。通过X射线衍射、扫

描电子显微镜、透射电子显微镜、X射线光电子能谱以及电化学技术对催化剂进行了表征。结果显示, Fe_2O_3 的存在能显著提高Pt催化剂在碱性介质中对甲醇氧化的电催化性能, 而且以 Fe_2O_3 纳米棒为助剂制备的Pt- Fe_2O_3 /C-R催化剂催化活性以及稳定性比 Fe_2O_3 纳米片为助剂制备的Pt- Fe_2O_3 /C-P催化剂更高。这种促进效应可能与助剂 Fe_2O_3 的形态有关。Pt- Fe_2O_3 /C-R催化剂中Pt的质量比活性为5.32 A/mg_{Pt}, 本征活性为162.7 A/m²_{Pt}, 分别是Pt- Fe_2O_3 /C-P催化剂的1.67和2.04倍, 是商业PtRu/C样品的4.19和6.16倍。协同效应和电子效应是Pt催化性能提升的主要原因。此外, Pt- Fe_2O_3 /C-R样品中高价态Pt的含量较高, 可能也是加速甲醇氧化反应动力学的原因之一。高价态的Pt可能会增强甲醇分子在Pt表面的吸附强度, 促进Pt上甲醇氧化反应初始步。这些发现不仅可对甲醇电催化氧化机理有了更深的理解, 而且对设计和制备高性能甲醇氧化电催化剂也具有一定的指导意义。

关键词: 铂; 氧化铁; 助催化作用; 甲醇电氧化反应; 碱性电解质

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