

Platinum-macrocycle co-catalysts for electro-oxidation of formic acid

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Received 21 December 2007; accepted 7 January 2008

Available online 20 January 2008

Abstract

In this paper, it was found that the electrocatalytic activity of a Pt electrode for the electro-oxidation of formic acid could be dramatically enhanced with the modification of macrocycle compounds, such as iron-tetrasulfophthalocyanine (FeTSPc). The electro-oxidation of formic acid on a modified Pt electrode with FeTSPc occurs mainly through a direct pathway. A series of macrocycle compounds were also investigated as modifiers and exhibited a promotion effect similar to the Pt electrode. Therefore, platinum-macrocycle co-catalysts can promote the electro-oxidation of formic acid through a highly effective route, and are potential catalyst materials for a direct formic acid fuel cell (DFAFC).

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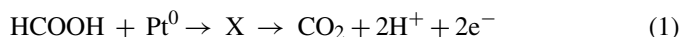
Keywords: Formic acid; Macrocycle compound; Iron-tetrasulfophthalocyanine; Platinum electrode; Fuel cell

1. Introduction

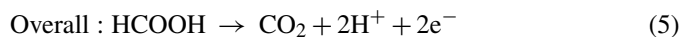
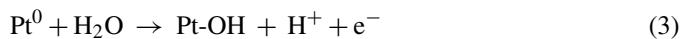
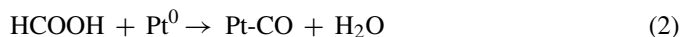
Recently, great attention has been focused on formic acid because it is a good candidate for methanol as fuel in fuel cells. Therefore, a direct formic acid fuel cell (DFAFC) is being gradually recognized as a promising power source due to its advantages [1–9]. The electrochemical activity of formic acid is much higher than that of methanol. Unlike methanol, formic acid is non-toxic and non-flammable, and is also a strong electrolyte that is able to facilitate the proton transport within the anode catalyst layer [2]. Additionally, its crossover flux through a Nafion® membrane is two orders of magnitude lower than that of methanol [1], which makes it possible for DFAFC to work at concentrations as high as 15 M formic acid [3,4]. Thus, the practical power density of DFAFC could be higher than that of direct methanol fuel cells (DMFC) despite the specific energy density of formic acid being lower than methanol. Although the commercial price of formic acid is a little higher than that of methanol, it is still acceptable in portable applications due to its unique merits.

It was reported that the electro-oxidation of formic acid on a catalyst Pt surface could occur through two parallel pathways

[5–12], the so-called “direct pathway” and the “CO pathway”. In the “direct pathway”, the formic acid is oxidized directly and rapidly to CO₂:



where X is an active intermediate. However, the formic acid is oxidized slowly in the “CO pathway”, because a poisoning intermediate CO_{ad} will be formed before the end product O₂ is yielded.



Obviously, the “CO pathway” is not welcomed because the CO_{ad} intermediate can be strongly adsorbed on the surface of the Pt, thereby poisoning the catalyst. Therefore, an ideal catalyst should lead the electro-oxidation process completely through the direct pathway [5–12]. Unfortunately, recent studies indicate that the electro-oxidation on common Pt catalysts occurs mainly through the CO pathway [5–8]. In order to lead the reaction to the desired “direct pathway”, the Pt-based composite catalysts, such as PtSn [13–15], PtGe [13,15], PtPb [15], PtAs [15], PtBi [15–18], PtRu [19–21], PtSe [21], PtTe [22], PtSb [23],

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were redesigned and tested. It was found that the performance of composite catalysts is much better than that of pure Pt catalysts [13–23]. In addition, the interactions between unlike surface anions and increases in the rate of electrochemical reactions were studied [24–28]. The rate can be increased by replacing a small fraction of the original anions in solution with more inhibiting ones [25].

In the present research, it was discovered that the electro-oxidation of formic acid would occur directly on the modified Pt electrode and Pt catalysts with some macrocycle compounds. The electrocatalytic activities of the modified Pt electrode and Pt/C catalysts with iron-tetrakisulfophthalocyanine (FeTSPc) were enhanced dramatically. This discovery may present a novel route to overcoming the CO poisoning barrier for DFAFC electro-oxidation.

2. Experimental

An EG&G PAR Model 273 Potentiostat/galvanostat with Powersuit Software and a three-electrode cell were used in the electrochemical measurements. An Ag/AgCl/sat KCl electrode was used as the reference electrode. All the potentials are quoted with respect to the reference electrode. A Pt foil was used as the auxiliary electrode. The bare Pt electrode and the modified Pt electrode with FeTSPc (Aldrich Co.) as shown in Fig. 1 or Bi were used as the working electrodes, respectively. All the modified electrodes with FeTSPc will be described as the modified electrode in the paper. The bare Pt electrode was obtained by polishing the Pt electrode with the slurry of 0.05- μm alumina powders and was sonicated in triple-distilled water. After the bare Pt electrode was placed into 0.1 mg mL⁻¹

FeTSPc solution or 1×10^{-4} mg mL⁻¹ BiCl₃ for 1 min, the electrode was washed with triple-distilled water and dried in air. Thus, the modified Pt electrodes were obtained. The solutions used for the electrochemical measurements were 0.5 M H₂SO₄ or 1.0 M HCOOH + 0.5 M H₂SO₄ solution, respectively. Oxygen was purged from the solution by bubbling with N₂ (99.99%) for 30 min prior to the electrochemical measurements. Usually, the electrochemical measurements were carried out at 25 ± 1 °C.

CO was bubbled into the solution for 10 min and fully adsorbed on the electrode before the electrochemical measurement of the adsorbed CO. Thereafter, N₂ was bubbled for 10 min to remove CO dissolved in the solution. Then, the potential scan was carried out for two circles with a scan rate of 20 mV s⁻¹.

The preparation procedure for the membrane–electrode assembly (MEA) for DFAFC is described below. Both the anodic and cathodic catalysts were the carbon-supported Pt catalyst with 20 wt% Pt (E-TEK Co.) for a single DFAFC. For another single DFAFC, the anodic catalyst was the modified Pt/C catalyst with FeTSPc, which was prepared by 2-h cyclic pumping 4 $\mu\text{g mL}^{-1}$ FeTSPc into anode channels with the Pt/C catalyst and then sequentially washed with 0.5 M H₂SO₄ and triple-distilled water. The anodic and cathodic Pt/C (20 wt.% Pt) powders were suspended, respectively, in 10% PTFE solution under ultrasonic conditions until their homogeneous inks were formed. The inks were sprayed onto 20% PTFE wet-proofed carbon paper and cured at 340 °C in a nitrogen-filled vacuum oven for 1 h. The Pt loadings in the anodic and cathodic catalyst layers were controlled at around 0.5 mg cm⁻² and 1.5 mg cm⁻², respectively. The sandwich MEA was fabricated by hot-pressing the anode and cathode onto the both

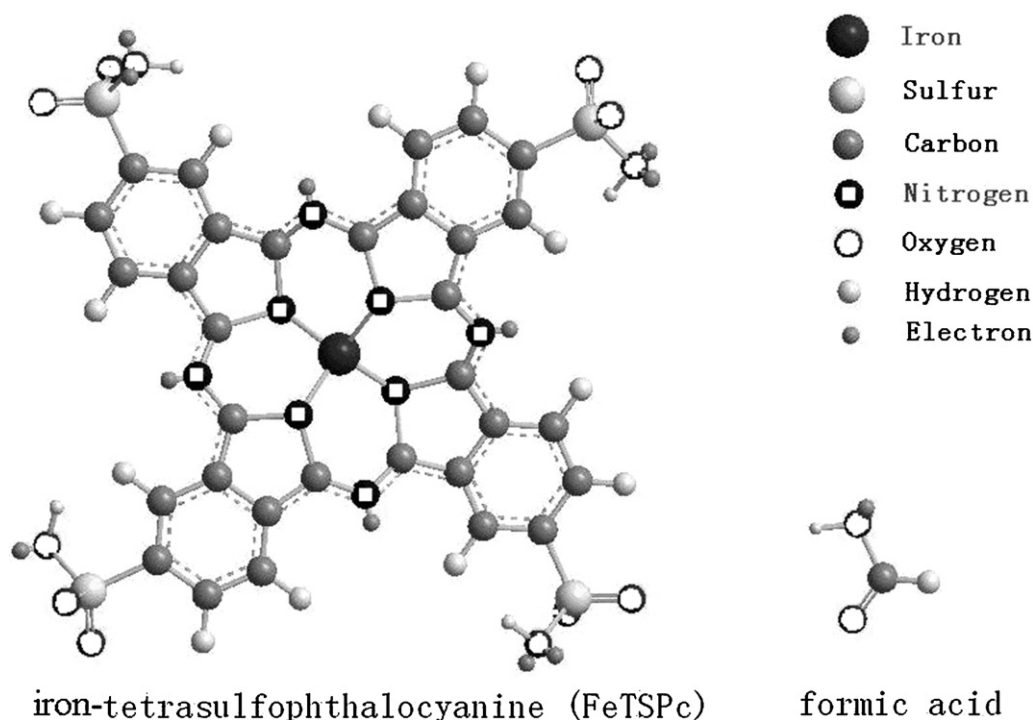


Fig. 1. The structure scheme of FeTSPc and formic acid.

sides of 117 Nafion membrane (Dupont Co.) at 130 °C and 100 kgf cm⁻¹ for 3 min. A 2.5 cm × 2.5 cm single cell was manufactured with the above-described MEA. The single cell was operated at the atmospheric pressure and 60 °C with the flow rates of the fuel and oxygen 1.0 mL min⁻¹ and 100 mL min⁻¹, respectively. The concentration of formic acid as the fuel was 6.0 M.

The double potential step chronoamperometry was performed according to the literature [29] by keeping the potential at 0.80 V (vs. Ag/AgCl/sat KCl) for 1.0 s to remove surface CO poison completely, followed by keeping the hydrogen evolution potential at -0.15 V (vs. Ag/AgCl/sat KCl) for 3.0 s. Then, the potential was kept at a certain value for 1.0 s. The temperature of the electrochemical reaction system was controlled by using an ultra-precise thermostat bath (Shanghai Instrument, China) that can guarantee a deviation of temperature from a given value within ±0.1 °C.

The X-ray photoelectron spectroscopy (XPS) measurements were performed with an ESCALAB MKII photoelectron spectrometer (VG Scientific Ltd., England) using the standard Mg K α radiation with the mean energy of 1253.6 eV and a 150 mm hemispherical electron energy analyzer. The binding energy was calibrated with respect to C_{1s} at 284.6 eV with ±0.2 eV accuracy. The energy resolution of the spectrometer was ~0.8 eV.

3. Results and discussion

3.1. XPS measurement

Fig. 2a and b shows the Fe(2p) and N(1s) XPS spectrum, respectively, of the bare Pt electrode and the modified Pt electrode with FeTSPc. The peaks of Fe(2p) and N(1s) of the modified Pt electrode illustrate that FeTSPc has been adsorbed onto the Pt surface. Before the XPS test, the samples were immersed in triple-distilled water for 60 min to wash away the FeTSPc that was not adsorbed on the Pt surface. Despite a 1-h wash, there was still some FeTSPc detected in XPS test. Therefore, it can be deduced that some FeTSPc can be steadily adsorbed on the Pt surface.

Fig. 2c and d shows the Pt 4f XPS spectrum of a bare Pt electrode and modified Pt electrode, respectively. The spectrum could be deconvoluted into three components (Table 1), which were Pt(0), Pt(II) and Pt(IV), respectively. The sum of the relative intensities in Pt 4f_{7/2} decreased after the modification, which means that FeTSPc has covered only part of the surface of the Pt electrode. The relative intensities in Pt 4f_{7/2} of Pt(0) and Pt(IV) decreased, while the relative intensities of Pt(II) increased after the modification. Furthermore, the binding energies of Pt(0), Pt(II) and Pt(IV) decreased. These variations of Pt 4f caused by the modification show that FeTSPc has a great interaction with

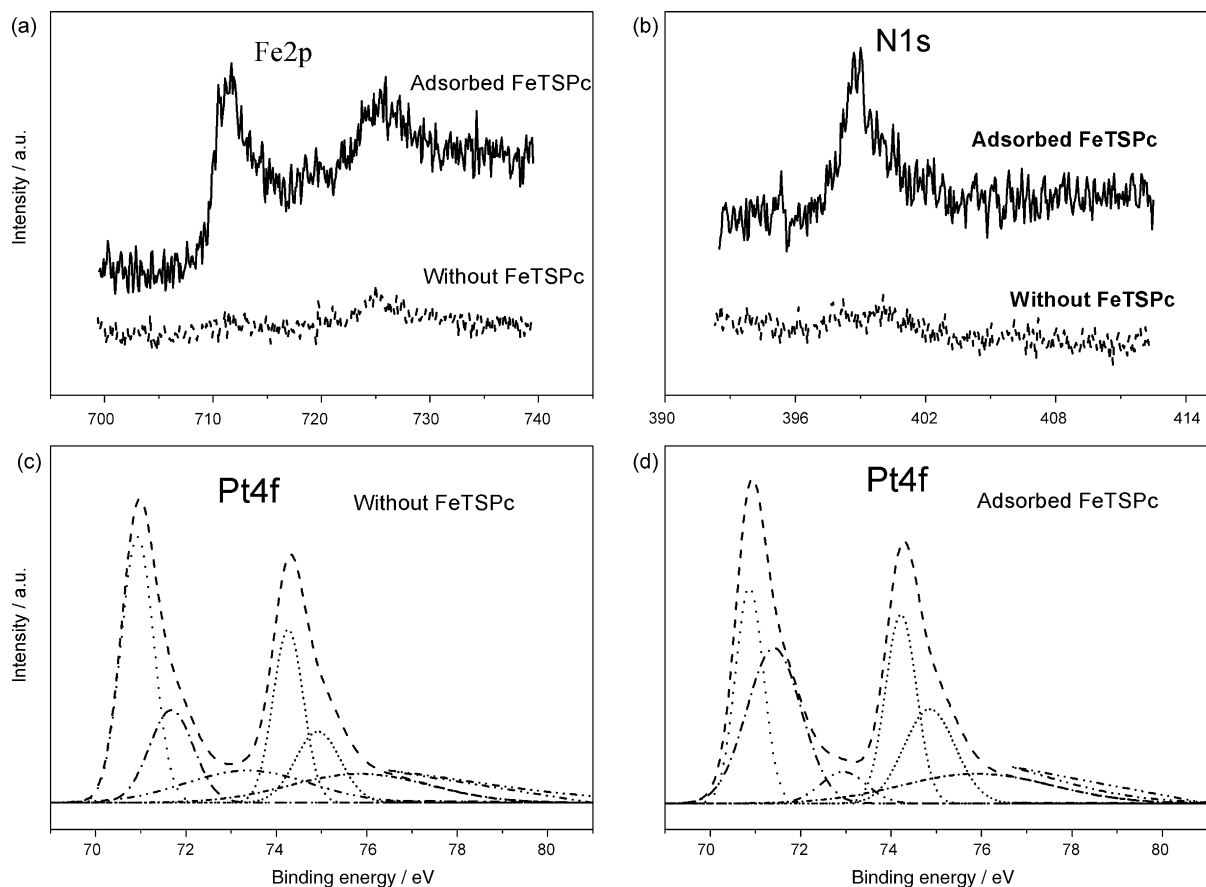


Fig. 2. The XPS spectra of the bare Pt electrode and FeTSPc-modified Pt electrode for (a) Fe(2p), (b) N(1s), (c) Pt(4f) without FeTSPc and (d) Pt(4f) adsorbed FeTSPc.

Table 1
The binding energies and relative intensities of the bare Pt electrode and modified electrode as observed from Fig. 2

	4f _{7/2}			Total	4f _{5/2}		
	Pt(0)	Pt(II)	Pt(IV)		Pt(0)	Pt(II)	Pt(IV)
BE _b ^a	70.93	71.68	73.37		74.26	74.92	75.85
BE _m ^b	70.87	71.41	72.94		74.22	74.85	75.89
A _b ^c	29,855	10,396	3606	43,857	19,483	7990	3236
A _m ^d	16,660	11,951	2439	31,050	14,577	7258	2287
A _b /43857	0.681	0.237	0.082	1			
A _m /31050	0.537	0.385	0.079	1			
A _m – A _b	–13,195	1555	–1167	–12,807			
(A _m – A _b)/12807	1.030	–0.121	0.091	1			

^a Binding energy of bare Pt electrode.

^b Binding energy of FeTSPc-modified Pt electrode.

^c Relative intensity of bare Pt electrode.

^d Relative intensity of FeTSPc-modified Pt electrode.

the Pt surface, which implies that it is a chemical adsorption of FeTSPc on the Pt surface.

3.2. Promotion effect of FeTSPc modification on the electro-oxidation of formic acid

Fig. 3 shows the cyclic voltammograms (CV) on the bare Pt electrode, the modified glass carbon electrode, and the modified Pt electrode in 1.0 M HCOOH + 0.5 M H₂SO₄ solution as well as on the bare Pt electrode in the same solution with 0.1 mg mL^{–1} FeTSPc, respectively. The dashed dotted line shows that there is no peak for formic acid electro-oxidation on the FeTSPc-modified carbon glassy electrode, which means that the FeTSPc compound itself has no electrocatalytic activity for the electro-oxidation of formic acid. The CV on the bare Pt electrode as shown with the dotted line has two classic electro-oxidation current peaks [5–12] for the positive scan at 0.397 V with 2.62 mA cm^{–2} and at 0.74 V with 5.58 mA cm^{–2}, respectively. The current density peaks at 0.397 V and 0.74 V were attributed

to the electro-oxidation of formic acid through the “direct pathway” and “CO pathway”, respectively [5]. The ratio between the current densities under 0.397 V and 0.740 V is 0.46, which indicates the electro-oxidation of formic acid, occurs mainly through the “CO pathway” on a common Pt surface. The high ratio represents the direct oxidative pathway. The CV curve of the modified Pt electrode shows a big current density peak reaching 21.95 mA cm^{–2} at 0.404 V and a small shoulder peak of 9.0 mA cm^{–2} at 0.740 V. The ratio of the two peaks is 2.43, which is much higher than the 0.46 of the bare Pt electrode. The higher ratio implies that the modification of FeTSPc can promote the electro-oxidation of formic acid through the direct pathway. Furthermore, the current density of the modified electrode at 0.397 V is 8.38 times larger than that of the bare Pt electrode, which illustrates that the modification of FeTSPc could dramatically enhance the electrocatalytic activity of the Pt catalyst for the electro-oxidation of formic acid. After treatment of the bare Pt electrode in 1.0 M HCOOH + 0.5 M H₂SO₄ solution with 0.1 mg mL^{–1} FeTSPc, as shown with a dashed line in Fig. 3, only one anodic peak at 0.405 V was observed. The current density of the anodic peak is even larger than that for the modified Pt electrode in 1.0 M HCOOH + 0.5 M H₂SO₄ solution (Fig. 3, solid line). The above results demonstrate that the promotion effect of FeTSPc in the solution is better than that of FeTSPc adsorbed on the Pt electrode surface. The reason might be that solid FeTSPc could not completely cover the surface of the modified electrode, resulting in limited reactivity, while in the liquid solution, the ionic FeTSPc is more efficient and active around the electrode.

Fig. 4a shows the chronoamperometric curves of 0.01 M HCOOH + 0.5 M H₂SO₄ solution on the bare and the modified Pt electrodes at 0.2 V for 7200 s, respectively. It is observed that the current densities on the bare Pt electrode and the modified Pt electrode at 7200 s are 0.303 and 1.879 mA cm^{–2}, respectively. Compared to the untreated electrode, the chronoamperometric performance of the modified Pt electrode decreased, but its electrocatalytic activity was still higher. This suggests that the adsorption strength of FeTSPc molecules on the Pt electrode is not uniform at the anodic reaction potential, then some FeTSPc compounds have desorbed from the Pt surface during the chronoamperometric operation. The normalized result shown in

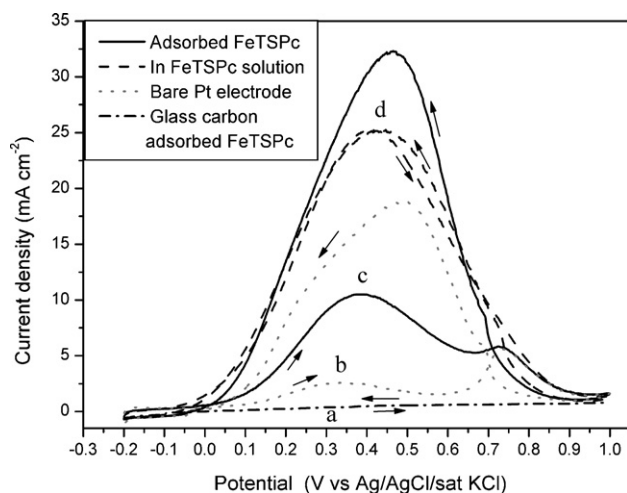


Fig. 3. The cyclic voltammograms of 1.0 M HCOOH at (a) the FeTSPc-modified glass carbon electrode, (b) the bare Pt electrode, (c) the FeTSPc-modified Pt electrode in 0.5 M H₂SO₄ solution and (d) on the bare Pt electrode in 0.5 M H₂SO₄ solution with 0.1 mg mL^{–1} FeTSPc. Scan rate: 100 mV s^{–1}.

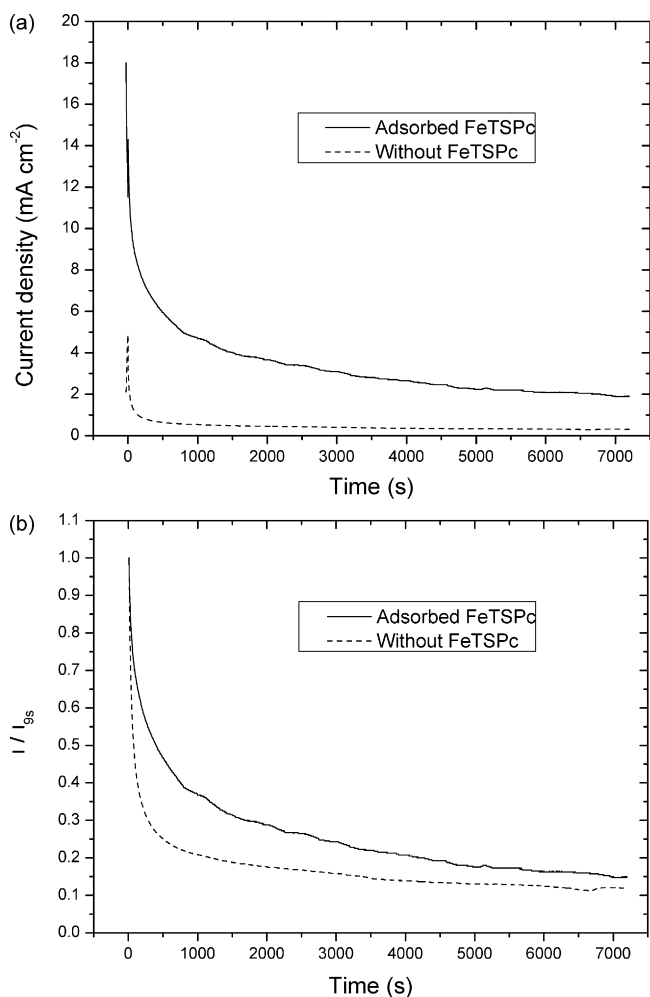


Fig. 4. (a) The chronoamperometric curves of 0.01 M HCOOH + 0.5 M H₂SO₄ solution on the bare Pt electrode and the modified Pt electrode at 0.2 V for 7200 s. (b) The normalized result was obtained by dividing the current density, i , during the test by the current density at the 9th second, i_9 , in (a).

Fig. 4b is achieved by dividing the current density, i , during the test by the current density at the 9th second, i_9 , in Fig. 4a. The relative value of the decrease for the modified Pt electrode is relatively lower than that of the bare Pt, which means the FeTSPc modification can help the electrode work longer.

Fig. 5 displays the double potential step chronoamperometric curves of a 0.01 M HCOOH + 0.5 M H₂SO₄ solution on the bare Pt electrode and the modified Pt electrode at the different potential. Fig. 6 illustrates the plots of the current density at 0.2 s versus the potential of the bare Pt electrode and the modified Pt electrode, respectively, which was obtained from Fig. 5 according to the referenced procedure [29]. It was observed that the current densities for the electro-oxidation of formic acid on the modified Pt electrode in the 0.2–0.8 V potential range were higher than those on the bare Pt electrode. In accordance with the CV results, this conclusion also indicates that FeTSPc modification of the electrode can greatly promote the electro-oxidation capability of formic acid.

Fig. 7 shows the stripping voltammograms of CO adsorbed on the bare Pt electrode and the modified electrode in 0.5 M H₂SO₄. The peak potentials for the CO electro-oxidation on

the bare Pt electrode and the modified Pt electrode appeared at 0.73 V and 0.61 V, respectively. The negative shift in the peak potential for the CO electro-oxidation implies that CO can be easily oxidized on the modified Pt electrode. In addition, the current density for the modified electrode was much smaller than that for the bare Pt electrode, which indicates that the CO_{ad} amount on the modified Pt electrode was decreased. Both the results of the peak current and peak potential confirm that the adsorption strength of CO on the surface of the modified Pt electrode had been weakened largely for the FeTSPc modification. Therefore, the reason for the promotion effect of FeTSPc modification on the electro-oxidation of formic acid is highly relevant to the weakened adsorption strength of CO.

3.3. Comparison of promotion effects of FeTSPc and Bi for the electro-oxidation of formic acid

It was reported that a Bi atom can also promote the electro-oxidation of formic acid on the Pt catalysts [30–34]. Herein, the promotion effects of FeTSPc and Bi for the electro-oxidation of formic acid on the Pt electrode have been compared. Fig. 8 displays the CVs on the bare Pt electrode, the FeTSPc-modified Pt electrode and the Bi-modified Pt electrode in 1.0 M + HCOOH 0.5 M H₂SO₄. Both the peak current densities and the peak potentials on the FeTSPc-modified Pt electrode are similar to that on the Bi-modified Pt electrode, which suggests that FeTSPc exhibits similar promotion effects on the electro-oxidation of formic acid as Bi. However, when compared to the disadvantages of heavy metal Bi, such as ease of desorption from the Pt surface at the highly positive potential and being environmentally hazardous, FeTSPc is the more promising catalyst in DFAFC applications.

3.4. Mechanism analysis for the promotion effect

Due to the complexity of the structure of FeTSPc as shown in Fig. 1, there are many factors affecting the promotion effect. According to the special structure of FeTSPc and the electrochemical process, we suggest the possible mechanism of the promotion effect as follows.

First, in the XPS test, the relative intensities in Pt 4f_{7/2} of Pt(0) decreased greatly after FeTSPc modification, while the variations of Pt(II) and Pt(IV) were much smaller than that of Pt(0). At the mean time, the electrochemical activity of Pt electrode increased greatly with the decrease of Pt(0). This result means that Pt(0) plays a key role in the dehydration reaction (2), which leads formic acid to be electro-oxidized through the CO pathway. Therefore, when FeTSPc covers parts of Pt(0) on the Pt surface, the dehydration reaction (2) is inhibited, which makes the direct pathway become the main reaction.

Secondly, tetrasulfophthalocyanine (TSPc) is a special surface anion that might speed up the rate of the electrochemical reaction of formic acid. It was found by Schell and co-workers that the rate of the electrochemical reaction of formic acid could be promoted by replacing a small fraction of the original anions with more inhibiting ones in solution [24–28]. The TSPc group might act as a substitute of the anion of SO₄²⁻ since it can

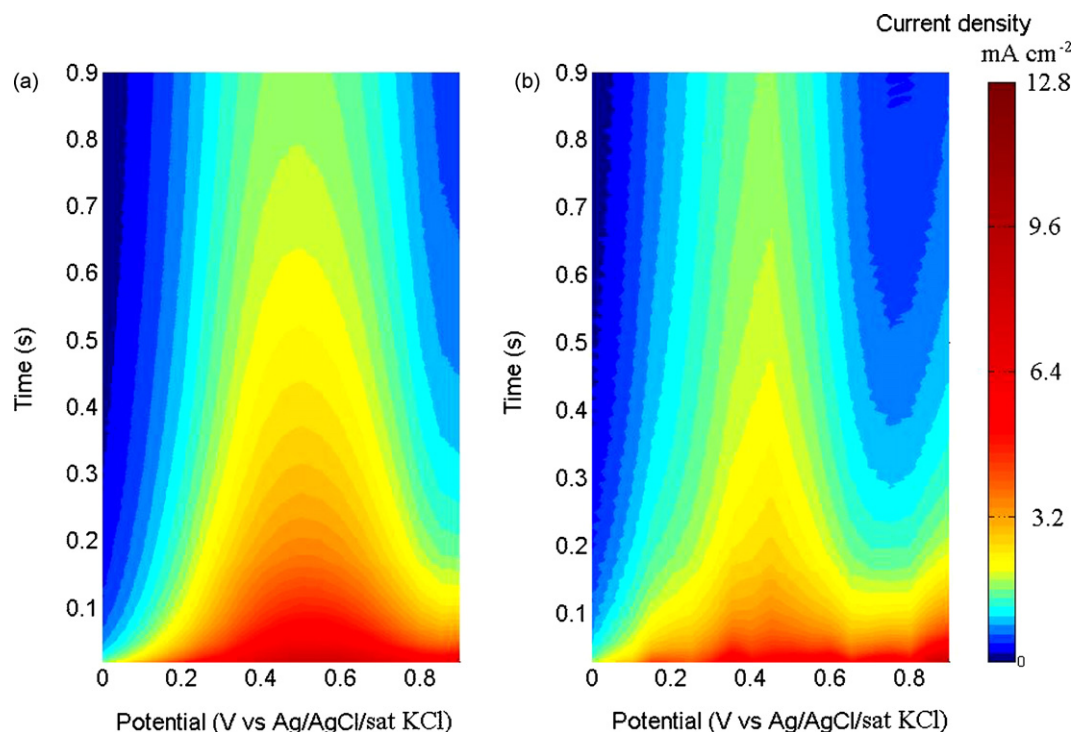


Fig. 5. The chronoamperometric curves of 0.01 M HCOOH in 0.5 M H₂SO₄ solution on (a) the FeTSPc-modified Pt electrode and (b) the bare Pt electrode at the different potential.

adsorb onto the Pt surface strongly, which can be seen in XPS and chronoamperometric tests. It is reasonable to attribute the promotion effect of FeTSPc partly to the inhibiting effect.

Thirdly, the steric hindrance of FeTSPc may be an important source for the promotion effect, because FeTSPc with specific macrocycle structure might greatly affect the Pt surface microstructure. The XPS test has revealed that some parts of the Pt surface have been covered by FeTSPc. The Pt surface is consequently divided into a lot of small regions by FeTSPc. In the small region, the relative intensities of Pt(0) are much less than those on a bare Pt surface. Iwasita and Clavilier et al. suggested

that the dehydration reaction (2) in the CO pathway, which generates the poison intermediate CO_{ad}, is strongly dependent on the Pt surface microstructure [35,36]. FeTSPc might modify the surface microstructure and block some sites of Pt(0), which is active in the dehydration reaction (2), and consequently inhibit the formation of CO_{ad}. Therefore, the CO pathway is inhibited and the direct pathway becomes possible.

Finally, the abundant electrons of FeTSPc may generate an electronic effect, which benefits the electro-oxidation of formic acid [33]. From Table 1, it can be seen that Pt(II) increased after the modification, though some parts of the Pt surface

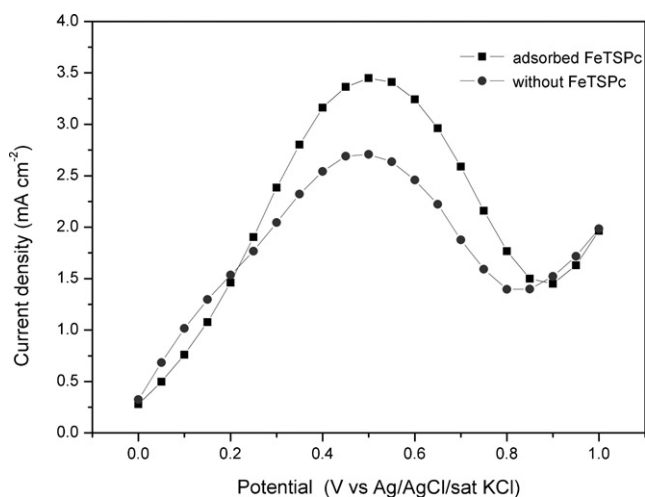


Fig. 6. The plots of the current density sampled at 0.2 s vs. the potential for the bare Pt electrode and the FeTSPc-modified Pt electrode. The data were obtained from Fig. 5.

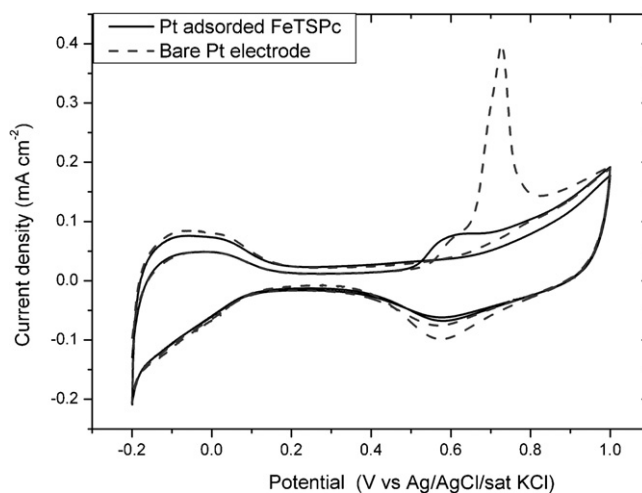


Fig. 7. The cyclic voltammograms of the adsorbed CO on (dash line) the bare Pt electrode and (solid line) the FeTSPc-modified Pt electrode. Scan rate: 20 mV s⁻¹.

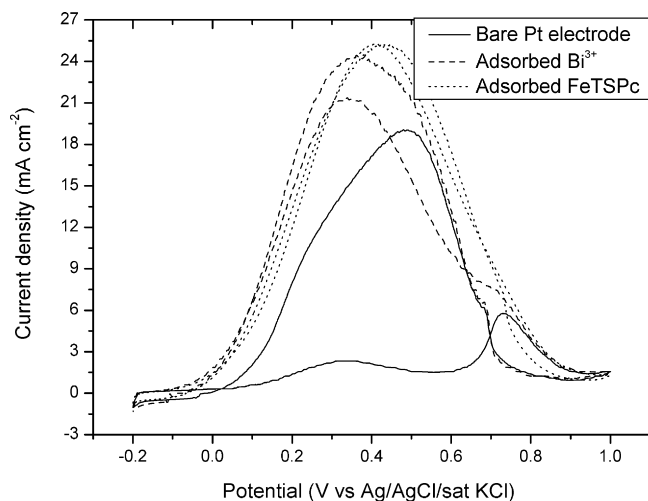


Fig. 8. The cyclic voltammograms of 1.0 M HCOOH in 0.5 M H₂SO₄ solution on the bare Pt electrode (solid line), the Bi-modified Pt electrode (dash line) and the FeTSPc-modified Pt electrode (dot line). Scan rate: 100 mV s⁻¹.

were covered. This indicates that FeTSPc can affect the electrons on the Pt surface and transfer some Pt(0) to Pt(II). That is to say that FeTSPc can change the electron distribution on the Pt surface, and therefore might change the reaction pathway.

With the elicitation of FeTSPc, a series of macrocycles, such as 5,10,15,20-tetraphenyl-21*H*,23*H*-porphyrin (TAPP) and Pd-5,10,15,20-tetraphenyl porphyrin (Pd-TAPP), were investigated as promoters for the electro-oxidation of formic acid on the Pt electrode, which is shown in Fig. 9. It was discovered that all of the macrocycle compounds could promote the electro-oxidation of formic acid on Pt electrode to some degree. The capabilities of the promotion effect are exhibited in the order FeTSPc > Pd-TAPP > TAPP. The reason for this phenomenon may be the different structures of macrocycle compounds. It

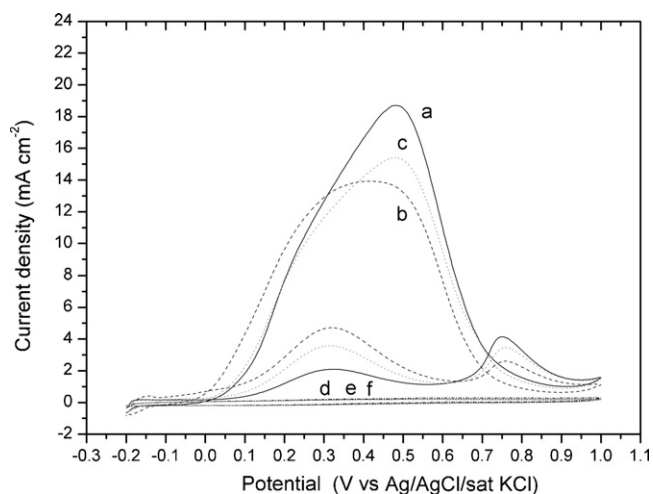


Fig. 9. The cyclic voltammograms of different electrodes in 0.5 M H₂SO₄ and 1.0 M HCOOH with scanning rate 100 mV s⁻¹ at 25 °C: (a) bare Pt electrode; (b) Pt adsorbed Pd-TAPP; (c) Pt adsorbed TAPP; (d) bare glassy carbon electrode; (e) glassy carbon electrode adsorbed Pd-TAPP; (f) glassy carbon electrode adsorbed TAPP.

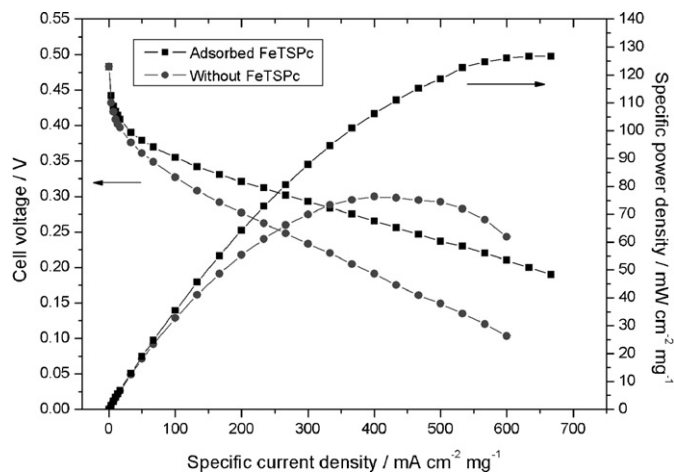


Fig. 10. The plots of the specific current density vs. the cell voltage and the specific power density for DFAFC with the anodes of the bare Pt/C catalyst and the FeTSPc-modified Pt/C catalyst. Cell potentials are not compensated for series resistance. Specific current density equals current density/Pt loading.

also can be seen from the order that the cations in macrocycle compounds have a more significant promotion effect.

3.5. Performances of single cells with different anodic catalysts

Fig. 10 shows the working polarization plots and the power density of a single DFAFC with the different anodic catalysts. With the FeTSPc-Pt/C composite catalyst, the single cell exhibited an obviously higher discharge performance as compared with the Pt/C catalyst (E-TEK Co.). The enhancement of voltages for the two tested single cells with the above two catalysts was two times (0.2 V/0.1 V) at the specific current density of 600 mA/(cm² mg-Pt). In the working case, the single DFAFC with the FeTSPc-Pt/C composite catalyst could work constantly while performance of another cell obviously dropped with enlarged over-potential. The largest power density of the single DFAFC with the FeTSPc-Pt/C composite catalyst can reach 130 mW/(cm² mg-Pt), which is 1.6 times higher than the cell with the Pt/C catalyst (80 mW/(cm² mg-Pt)).

4. Conclusions

Novel Pt composite electrodes modified with macrocycle compounds and composite FeTSPc-Pt/C catalysts were prepared successfully for the enhancement of the electro-oxidation of formic acid. The modifications can greatly enhance the electrocatalytic activities of both a Pt electrode and a Pt/C catalyst in DFAFC performance studies. The promotion effect is due to three factors: (1) the inhibiting factor of TSPc as a welcomed surface anion, (2) the steric hindrance to the formation of poisoning species (CO_{ad}) and (3) weakening the adsorption strength of CO_{ad}. The modification of macrocycle compounds on the Pt surface leads formic acid oxidation through the direct pathway. These studies present a novel route to prepare highly effective and environmental-friendly catalytic materials for DFAFC.

Acknowledgments

The authors are grateful for the financial sponsors of the State Key Fundamental Research Program of China (973 Program, G2000026408), the State Key High Technology Research Program of China (863 Program, 2001AA323060, 2003AA517062, 2006AA05Z137), and the Nature Science Foundation of China (20373068, 20433060). The authors are also grateful for the help from Huazhi Li, Dongmei Wang, Xinzhong Xue, Weilin Xu, Xinglin Li, Wenbing Xie, Jingwei Xu, Guangfu Zeng, Xianglin Liao, Yawen Tang, and Yan Xiang.

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