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ORIGINAL PAPER

Nickel phthalocyanine-tetrasulfonic acid as a promoter of methanol electro-oxidation on Pt/C catalyst

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Abstract This paper describes an investigation of the role of nickel phthalocyanine-tetrasulfonic acid (NiPcTs) for methanol electro-oxidation on a Pt/C catalyst. Cyclic voltammetry (CV) revealed that NiPcTs has no catalytic activity in methanol or CO electro-oxidation. However, methanol electro-oxidation occurs faster on a Pt/C catalyst modified with NiPcTs than on the original Pt/C catalyst. CO stripping results demonstrated that NiPcTs promotes electro-oxidation of adsorbed CO (CO_{ads}) on the Pt/C catalyst, which is likely to be responsible for the enhancement of the methanol electro-oxidation rate. The promotion effect of NiPcTs is attributable to its ability to modify the electron density of the Pt surface. The electron deficiency of Pt^0 in the NiPcTs-Pt/C catalyst is shown by the shift of the Pt^0 *4f* peak to higher binding energies in the X-ray photoelectron spectrum.

Keywords Fuel cell · NiPcTs · Methanol · Carbon monoxide · Electro-oxidation

1 Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable research effort in recent years, focused particularly on the development of highly efficient electrocatalysts for methanol oxidation [1–3]. A series of reactions takes place on the Pt surface during methanol oxidation. The main drawback of Pt-based catalysts is that CO chemisorbs strongly on the Pt surface. Even traces of CO lead to severe poisoning of Pt catalysts [4]. The main approach to overcome this limitation is to use a bimetallic catalyst. Ru is well known as a second metal in the Pt-based bimetallic catalysts which promotes methanol electro-oxidation. The bifunctional mechanism, defined by Watanabe and Motoo [5], suggests that Ru acts as an oxygen supplying promoter ($Ru–OH_{ads}$) at more negative potentials than bare Pt. Moreover, Ru weakens CO adsorption on Pt by decreasing the Pt–CO bond strength, thereby increasing the CO electro-oxidation rate [6]. Although the Pt–Ru catalyst has exhibited high methanol electro-oxidation activity, much improvement is still required in order: (1) to further enhance the catalytic activity in methanol electro-oxidation; and (2) to replace expensive noble metals, Pt or Ru [7]. Various efforts have been expended to reach these goals, and many other bimetallic or even ternary catalysts have been being investigated [8–10].

A promising approach to further enhance the catalytic activity in methanol electro-oxidation is to apply macrocycles containing non-noble transition metals in combination with platinum as anodic catalysts. Various transition metal phthalocyanines have been studied as co-catalysts, and the enhancement of methanol oxidation rate was found when Pt was used together with Sn phthalocyanine or Ni phthalocyanine [11–13]. In particular, after heating at 700 °C in nitrogen atmosphere, nickel phthalocyanine-tetrasulfonic acid (NiPcTs) used together with Pt/C as the anode catalyst for DMFCs shows improved cell performance as compared to the Pt/C catalyst, whereas the catalytic activity of NiPcTs-Pt/C is only slightly lower than that of the bimetallic Pt–Ru catalyst [13].

However, in these previous studies the catalytic activity of Pt/C modified with phthalocyanine in methanol

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electro-oxidation was evaluated in single fuel cell testing. Therefore, these studies lacked the evidence from electrochemical experiments, such as cyclic voltammogram (CV). Moreover, methanol electro-oxidation on Pt/C co-catalyzed with phthalocyanine has not been studied in detail, and the role of the phthalocyanine compound as a co-catalyst is not yet fully understood. It is not clear whether phthalocyanine weakens CO adsorption by decreasing the Pt–CO bond strength or acts as an oxygen supplying promoter.

The aim of the present study is to investigate the role of the phthalocyanine co-catalyst in enhancing the rate of methanol electro-oxidation. Since NiPcTs is considered to be the most active co-catalyst, our study focused on Pt/C co-catalyzed with NiPcTs [12, 13]. The electro-catalytic activity of the NiPcTs-Pt/C was evaluated first in electrochemical experiments, such as CV, rather than a cell performance test employed in previous studies [11–13], for detailed characterization of methanol electro-oxidation on NiPcTs-Pt/C. Subsequently, CO stripping voltammetry was carried out for the first time for the NiPcTs-Pt/C catalyst, because the knowledge of CO electro-oxidation behavior on NiPcTs-Pt/C is critical for establishing the role of NiPcTs as a co-catalyst during methanol electro-oxidation., Finally, the effect of NiPcTs on the Pt^0 electron density was characterized by X-ray photoelectron spectroscopy (XPS), since the surface electron density of Pt^0 affects CO electro-oxidation.

2 Experimental

2.1 Materials

Commercial Pt/C catalyst (20 wt.% Pt) was obtained from Johnson Matthey. NiPcTs was obtained from Aldrich. Ethanol was obtained from Shanghai Medicines Co. All reagents were AR grade. Nafion (5 wt.% isopropyl alcohol solution) with average MW of 4×10^5–5×10^5 was received from Dupont Co. Vulcan XC-72 (Cabot Corp.), which is a carbon black with relatively large surface area of 220 $m^2\ g^{-1}$ was used as a support for NiPcTs. Glass containers were dipped in aqua regia for 2 h and rinsed in deionized water.

2.2 Preparation of composite NiPcTs-Pt/C electrocatalyst

The preparation of NiPcTs-Pt/C was similar to that described elsewhere [12, 13]. The commercial Pt/C catalyst was dispersed in ethanol by sonication and NiTsPc was then added to the suspended solution containing a 4:1 weight ratio of Pt to NiTsPc. The mixture was stirred and refluxed at 84 °C for 12 h. After thorough mixing, the suspended solution was filtered and the residue was rinsed three times with deionized water. The residue was dried at 120 °C and ground to fine powder.

2.3 Characterization of catalyst and electrochemical measurements

The NiTsPc-Pt/C catalysts were characterized by transmission electron microscopy (TEM) using a JEM-2010FEF microscope operated at 200 kV. The sample was prepared for TEM by placing a catalyst suspension in acetone after sonication for 1 h on a 3 mm Cu grid, followed by drying under ambient condition. The XPS binding energy analysis was carried out with a VG ESCALAB MKII instrument using an MgK_α X-ray source. The samples for XPS were prepared by depositing the suspended solution onto a polished graphite surface followed by drying. The $C_{1s} = 284.6$ eV peak was used for charge calibration.

The electrochemical measurements were run using a conventional three-electrode system on PGSTAT30/GPES potentiostat/galvanostat Autolab of Eco Chemie Inc., the Netherlands. The working electrode was prepared by the thin film electrode method. It consisted of a mirror polished Glassy Carbon (GC) (dia. 3 mm.) rod coated with catalysts. A catalyst ink which contained 20 mg Pt/C (20 wt.% Pt) or 25 mg NiTsPc-Pt/C, 20 μl 5 wt.% Nafion solution, 0.6 mL water and 1.38 mL ethanol was prepared. An appropriate volume of ink was pipetted onto the GC. Finally, it was dried at room temperature and then heated to 150 °C in N_2 atmosphere for 1 h. A platinum sheet served as the counter electrode, an $Hg|Hg_2SO_4|K_2SO_4$ (sat) as the reference electrode. A Luggin capillary faced the working electrode at a close distance of 2 mm. All electrode potentials in this study refer to the RHE scale. All electrochemical measurements were conducted at 25 °C.

3 Results and discussion

The TEM micrograph of the NiTsPc-Pt/C is shown in Fig. 1a. The large light gray particles correspond to the carbon support, while the scattered black spots are the Pt particles. The size distribution of the Pt particles was obtained by measuring the sizes of at least 150 particles selected at random using image analysis technology. The results shown in Fig. 1b indicated that the platinum particles have a narrow size distribution with an average diameter of ca. 4.1 nm. The diameter of platinum particles is slightly larger than that of commercial Pt/C [14]. Some Pt particle coarsening was likely caused by a heat effect during preparation at elevated temperatures for 12 h.

The electrochemically active surface area (ESA) of Pt/C and NiPcTs-Pt/C catalysts was measured by a CV test in a

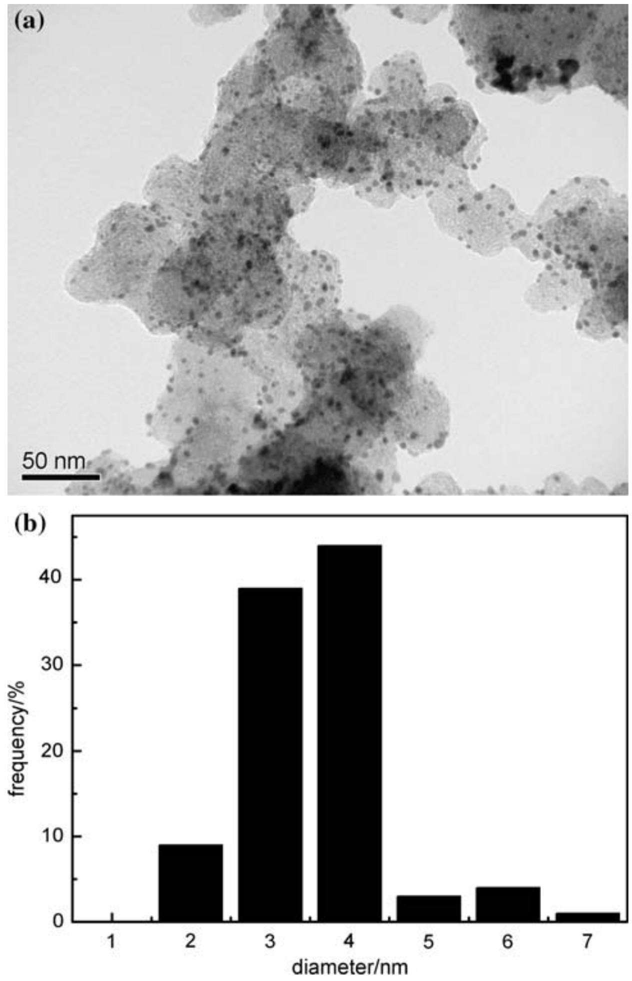

Fig. 1 (**a**) Bright field TEM image of NiPcTs-Pt/C and (**b**) Pt particle size distribution

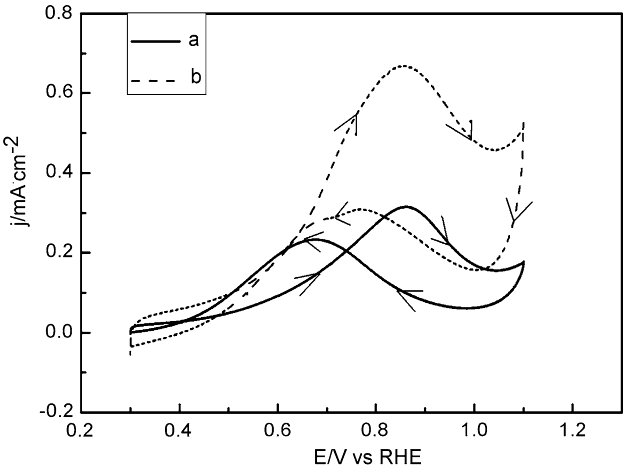

Fig. 2 Tenth sweep cyclic voltammetries of (**a**) commercial Pt/C catalyst and (**b**) NiTsPc-Pt/C in 0.5 M CH_3OH + 1 M H_2SO_4, 25 °C, 50 mV s^{-1}

1 M H_2SO_4 solution at a sweep rate of 50 mV s^{-1}. The methanol electro-oxidation activity on Pt/C and NiPcTs-Pt/C catalysts was measured in a 0.5 M H_2SO_4 + 1 M CH_3OH solution at a sweep rate of 50 mV s^{-1}. The current density refers to ESA. Figure 2a shows a CV curve of a commercial Pt/C catalyst which displays a forward oxidation peak with current density (j_f) of 0.31 mA cm^{-2} at ~860 mV vs. RHE and a backward oxidation peak with a peak current density (j_b) of 0.23 mA cm^{-2}. Figure 2b shows a CV curve of NiPcTs-Pt/C. In the forward sweep, an oxidation peak with current density (j_f) of 0.67 mA cm^{-2} appeared at ~850 mV vs. RHE. In the backward sweep, a second oxidation peak with a peak current density (j_b) of 0.31 mA cm^{-2} was obtained. Table 1 lists the electrochemical parameters of methanol oxidation on Pt/C and NiPcTs-Pt/C.

The forward anode peak current density of the NiPcTs-Pt/C catalyst, which is an important parameter characterizing the methanol electro-oxidation activity [15], is twice the value for the Pt/C catalyst (0.67 mA cm^{-2} vs. 0.31 mA cm^{-2}). This indicates that the NiPcTs-Pt/C catalyst promotes methanol electro-oxidation activity. Bett et al. [11] reported that Sn phthalocyanine (SnPc) promoted methanol oxidation on platinum based on the electroactive area and the total weight of platinum. Goetz and Wendt [13] studied the performance of single methanol fuel cell operated at ambient pressure at 95 °C with NiPcTs-Pt/C after it was pyrolyzed at 700 °C as the anode catalyst. The pyrolyzed NiPcTs-Pt/C co-catalyst showed remarkable effect on methanol oxidation and current density twice the value for Pt/C at 0.4 V, which is consistent with our CV results.

It was proposed that the backward oxidation peak is caused by the adsorbed surface intermediates [16, 17], which are unfavorable for methanol oxidation. The ratio of the backward anode peak current density to forward anode peak current density (j_b to j_f) reveals the extent of self-poisoning of the electro-catalysts [18]. The smaller the j_b to j_f ratio, the better the electro-catalyst is for methanol oxidation. It is observed that this ratio for the NiPcTs-Pt/C catalyst is approximately half of that for the Pt/C catalyst (0.46 vs. 0.74), which indicates that NiPcTs-Pt/C is more tolerant to poisoning than Pt/C.

CO is one of the main poisonous intermediates during methanol oxidation over Pt-based electro-catalysts [19, 20]. Therefore, CO stripping voltammetry of Pt/C and NiPcTs-Pt/C in 1 M H_2SO_4 solution with purged CO was investigated. Prior to the CO stripping voltammetry measurements, CO was passed through the cell for 45 min to allow complete adsorption of CO onto the electro-catalysts while maintaining a constant voltage of 300 mV vs. RHE [21]. Excess CO dissolved in the electrolyte was removed by purging with N_2 for at least 40 min. As shown in Fig. 3a, a peak current density of CO_{ads} oxidation of 0.40 mA cm^{-2}

Table 1 The comparison of cyclic voltammetry parameters for Pt/C and NiPcTs-Pt/C, 50 mV s^{-1}, in 0.5 M CH_3OH + 1 M H_2SO_4, 25 °C

Catalyst	The forward peak		The backward peak		j_b/j_f
	Current density j_f (mA cm^{-2})	Potential E_b (V)	Current density j_b (mA cm^{-2})	Potential E_b (V)	
Pt/C	0.31	0.86	0.23	0.68	0.74
NiPcTs-Pt/C	0.67	0.85	0.31	0.77	0.46

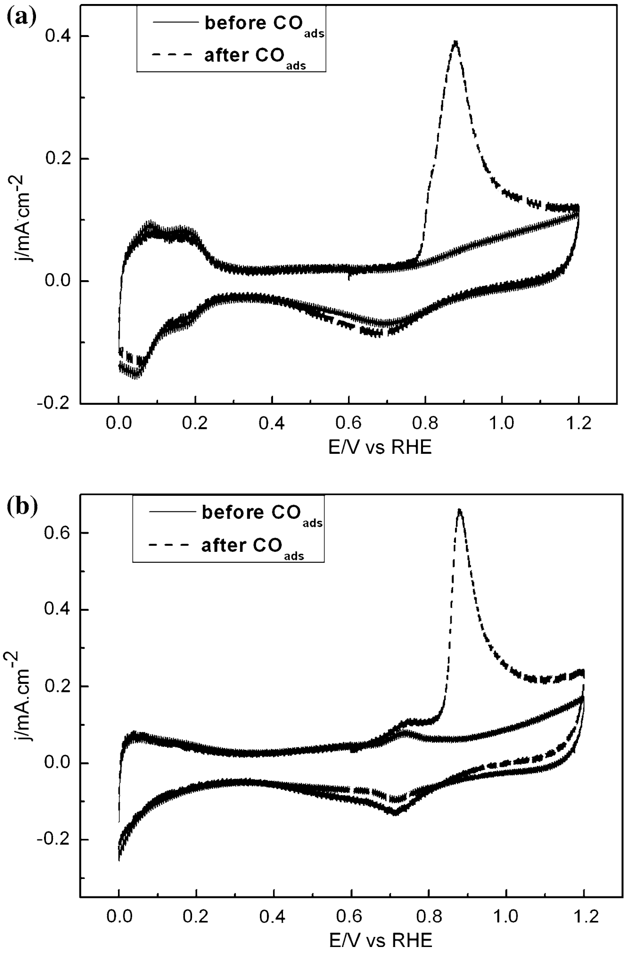

Fig. 3 Cyclic voltammetries of Pt/C (**a**) and NiPcTs-Pt/C (**b**) before and after CO_{ads}, in 1 M H_2SO_4, 25 °C, 50 mV s^{-1}. Gaseous CO was purged into the cell for 45 min to allow complete adsorption of CO onto the electrocatalysts while maintaining a constant voltage of 300 mV vs. RHE

at the 0.88 mV potential was observed on Pt/C. A peak current density of CO_{ads} oxidation for NiPcTs-Pt/C was surprisingly high: 0.67 mA cm^{-2} at 0.88 mV potential (Fig. 3b), which represents a significant increase as compared to Pt/C and suggests that NiPcTs promotes CO_{ads} electro-oxidation. Therefore, it appears that NiPcTs enhances methanol electro-oxidation on Pt/C because it can promote CO_{ads} electro-oxidation on Pt/C.

It was reported that metal phthalocyanines of Fe, Co, Ni, and Sn have no catalytic activity in methanol oxidation [11]. CO stripping voltammetry of NiTsPc in 1 M H_2SO_4 solution with purged CO was studied and the results are shown in Fig. 4. These results show the absence of any significant changes in the CV curve after the CO stripping voltammetry measurements. The CO desorption peaks did not appear on NiPcTs either before or after CO adsorption suggesting that NiPcTs displays no catalytic activity in CO_{ads} oxidation.

NiPcTs-Pt/C exhibited superior performance in methanol oxidation, while NiPcTs displayed no activity in methanol and CO electro-oxidation. XPS was further used to characterize NiPcTs-Pt/C in order to provide insights into the possible mechanism of methanol oxidation on Pt/C promoted by NiPcTs. Figure 5 shows the Pt *4f* XPS spectrum of the NiPcTs-Pt/C catalyst. In the XPS spectrum of NiTsPc-Pt/C, Pt^0 is characterized by two Pt *4f* peaks at 72.3 and 75.6 eV, while Pt^{2+} has two peaks at 74.0 and 77.3 eV. The binding energy of Pt^0 *4f* electrons in NiTsPc-Pt/C exhibits a ca. 1.4 eV shift to higher energies as compared to the Pt^0 in Pt, which displays two Pt^0 *4f* peaks at 70.9 and 74.25 eV [22]. The electrons back-donated by Pt transfer to an anti-bonding orbital of C to form a hard d-π anti-bond

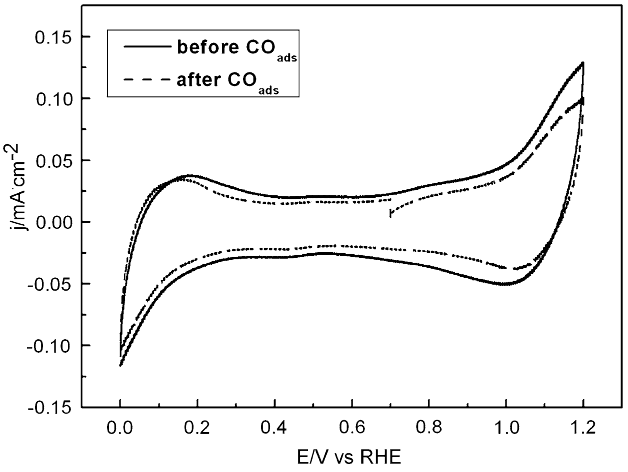

Fig. 4 Cyclic voltammetry of NiTsPc/C in 0.5 M CH_3OH + 1 M H_2SO_4, 25 °C, 50 mV s^{-1}. Gaseous CO was passed through the cell for 45 min to allow complete adsorption of CO onto the electrocatalysts while maintaining a constant voltage of 300 mV vs. RHE

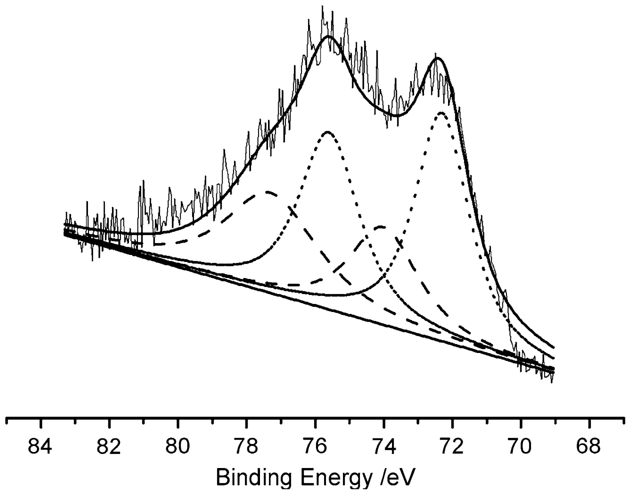

Fig. 5 XPS of Pt 4f of NiPcTs-Pt/C (———Pt4f; ……Pt^{0}4f; – – – Pt^{2+} 4f)

which results in strong CO chemisorption on Pt, which is the primary reason for poisoning in Pt-based catalysts [23, 24]. The shift of Pt^0 *4f* peaks to higher binding energies indicates the decrease of electron density on Pt, which reduces the extent of back-donation of electrons from Pt to the anti-bonding orbital of C and results in weakened Pt–CO bonding [25]. Therefore, CO electro-oxidation on NiPcTs-Pt/C occurs more readily than on Pt/C. However, the exact mechanism how NiPcTs reduces electron density on Pt remains unclear. Other methods and future work are necessary to explore it further.

4 Conclusions

NiPcTs alone displays a lack of activity in methanol electro-oxidation, but the presence of the NiPcTs co-catalyst enhances the catalytic activity of Pt/C in methanol electro-oxidation. The promotion of electro-oxidation of chemisorbed CO (CO$_{ads}$) is proposed to be responsible for the rate enhancement in methanol oxidation. NiPcTs promotes CO$_{ads}$ electro-oxidation on Pt/C by decreasing the electron density on Pt^0, which reduces the extent of electron back-donation from Pt^0 to anti-bonding orbital of C, resulting in weaker Pt–CO bonding and easier CO$_{ads}$ electro-oxidation.

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