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Low-Pt Content Carbon-Supported Pt–Ni–TiO_2 Nanotube Electrocatalyst for Direct Methanol Fuel Cells

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Abstract Low-Pt content (5%) carbon-supported Pt–Ni–TiO_2 nanotube electrocatalysts were prepared via a microwave-assisted polyol strategy. Physical and morphological properties of these electrocatalysts were characterized by X-ray diffraction (XRD), high resolution transmission electron microscope (HRTEM), and energy dispersive X-ray spectroscopy (EDX). Cyclic voltammetry and chronoamperometry studies clearly suggested that the Pt(5%)–Ni(10%)–TiO_2 nanotube (10%) supported by Vulcan XC-72 is better than the commercial 20% Pt/C electrocatalyst for methanol electro-oxidation in direct methanol fuel cells (DMFCs).

Keywords Platinum · Nickel · TiO_2 nanotube · Electrocatalyst · Methanol electro-oxidation

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1 Introduction

Direct methanol fuel cells (DMFCs) have potential applications as portable power source because of their numerous advantages, such as high energy density, low cost, and easiness in transportation and storage [1, 2]. Extensive efforts have focused on the development of better DMFCs, while their performance is still limited by poor anode kinetics [3] and catalytic instability [4]. In particular, the intermediates formed on the surfaces of Pt electrocatalysts can lower the catalytic activities by blocking the active catalytic sites [4]. One solution for this problem may come from the well-known alloy effects [4, 5]. It has been shown that the addition of Ru into these catalysts can greatly alleviate this effect [4]. However, the loadings of Pt in these catalysts are usually quite high and Ru is also a noble metal, which may result in an increase of the preparation costs. Hence, it is essential to find less expensive alternatives. Recently, Ni was added as alloy metal to the Pt-based catalysts, and the resulting catalysts were found to exhibit better catalytic stability and activity for methanol electro-oxidation than commercial Pt catalysts [6–10]. In this paper, we report an improvement of these Pt–Ni alloy catalysts by introduction of a new oxide component.

TiO_2 has been exhaustively investigated in the past because of its special photoelectric and electric properties [11]. One specific feature of TiO_2 relevant to this study is that TiO_2 can act as catalyst supports and change the electronic property of the supported metal nanoparticles [11]. The strong interaction between TiO_2 and Pt has been found to favor the catalytic activities for methanol electro-oxidation [12–14]. In addition, the forms of TiO_2 supports were shown to greatly affect this interaction: usually the TiO_2 support in nanotube form can yield better catalytic properties than those in nanoparticle form [15–17]. For instance, Pd catalyst supported on TiO$_2$ nanotube, developed by Wang et al. for methanol electro-oxidation, exhibited excellent catalytic properties compared with pure Pd and Pd supported by TiO$_2$ nanoparticles [17]. Our previous studies have also shown that TiO$_2$ nanotube can be a successful support for CoTMPP for oxygen reduction reaction [18], and for Pt for methanol electro-oxidation [13].

In this work, carbon-supported Pt–Ni–TiO$_2$ nanotube electrocatalysts (abbr. Pt-Ni-TiO$_2$NT/C, contained 5 wt.% Pt, 10 wt.% Ni, and 10 wt.% TiO$_2$ nanotube) were developed as anode materials for methanol electro-oxidation. Their catalytic performance was evaluated and compared to those of Pt–Ni (1:2) catalysts and commercial 20% Pt/C catalysts. A combination of analytical techniques including XRD, TEM, and EDX was employed to characterize these catalysts. A detailed description of our acquired results is shown below.

2 Experimental

2.1 Preparation of the Pt–Ni–TiO$_2$NT/C

Pt–Ni–TiO$_2$NT/C electrocatalysts were prepared via microwave-assisted polyol method. The weight rate of Pt, Ni, and TiO$_2$ nanotube was 1:2:2 and the content of Pt was 5%. Appropriate amounts of chloroplatinic acid, nickelous acetate, TiO$_2$ nanotube [19, 20], and carbon Vulcan XC-72 (Cabot Corp.) were added into the flask. Then, ethylene glycol was introduced into this mixture. The pH (>9) of solution was maintained with the use of 0.5 M NaOH. The mixed solution was then suspended in the microwave reactor over 60 s after being ultrasonically stirred about 30 min. The filtered products was aged for 12 h, washed by distilled water and dried at 60 °C in a vacuum oven overnight. The same procedures were followed during the synthesis of Pt–Ni (5%Pt, Pt:Ni is 1:2) catalyst.

2.2 Characterization of the Pt–Ni–TiO$_2$NT/C

Pt–Ni–TiO$_2$NT/C electrocatalyst was characterized by XRD on a Rigaku diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å). The morphology and the distributions of the Pt nanoparticle and TiO$_2$ nanotube were examined by HRTEM on a JEOL JEM-2100F (Instrumental Center of Shanghai Jiao Tong University) at an accelerating voltage of 200 kV. The surface composition of the Pt–Ni–TiO$_2$NT/C catalyst was measured by EDX.

2.3 Electrochemical Measurement

Electrochemical measurements were carried out on a CHI 750 electrochemical workstation (CH Instrument). The performance of the Pt–Ni–TiO$_2$NT/C catalyst and commercial 20% Pt/C catalyst (Johnson Matthey) were measured in a conventional three-electrode cell with 3 mm diameter glassy carbon (GC) as working electrode. A Pt wire and a saturated calomel electrode (SCE) were employed as a counter electrode and a reference electrode, respectively. All electrode potentials were measured against the SCE and later converted to against a reversible hydrogen electrode (RHE). The catalyst inks used in these measurements contained 4 mg catalyst, 1 mL double distilled water, and 50 µL Nafion solution, and were pretreated with 30 min of sonication. Ten µL of these catalyst inks were then pipetted on the surface of the GC and dried. Before the electrochemical measurements, the electrolyte of 0.5 M H$_2$SO$_4$ and 0.5 M H$_2$SO$_4$ containing 0.5 M CH$_3$OH were de-aerated by bubbling pure nitrogen gas for 30 min. All of these voltammograms data were obtained under steady state.

3 Results and Discussion

3.1 Electrochemical Performances

Figure 1 shows the CVs of the commercial 20% Pt/C, 5% Pt–Ni/C, and 5% Pt–Ni–TiO$_2$NT/C catalysts in 0.5 M H$_2$SO$_4$ solution at room temperature. The scan rate was 50 mV S^{-1}. All curves have obvious hydrogen adsorption-desorption region (0–0.3 V). Figure 2 shows the typical CVs of the above catalysts in N$_2$ saturated 0.5 M H$_2$SO$_4$ containing 0.5 M CH$_3$OH solutions. The results clearly suggest that the TiO$_2$ nanotube catalyst with only 0.032 mg cm^{-2} content of Pt exhibits significantly better performance than that of the Pt–Ni catalyst with same

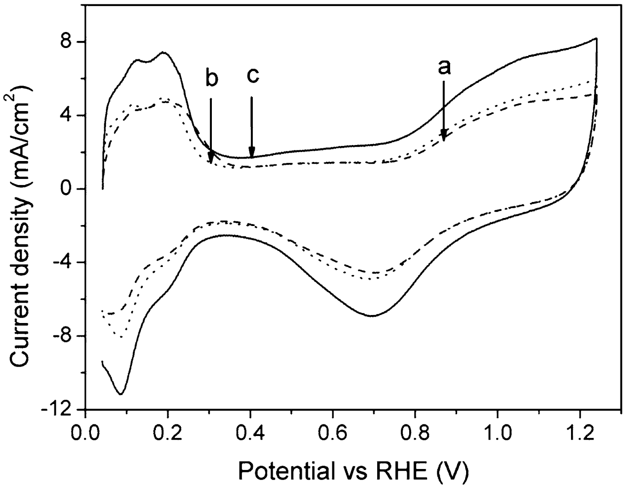

Fig. 1 CVs of commercial 20% Pt/C (a), 5% Pt-10% Ni/C (b), and 5% Pt-10% Ni-10% TiO$_2$NT/C (c) in 0.5 M H$_2$SO$_4$ solution at room temperature, with a scan rate of 50 mV/s

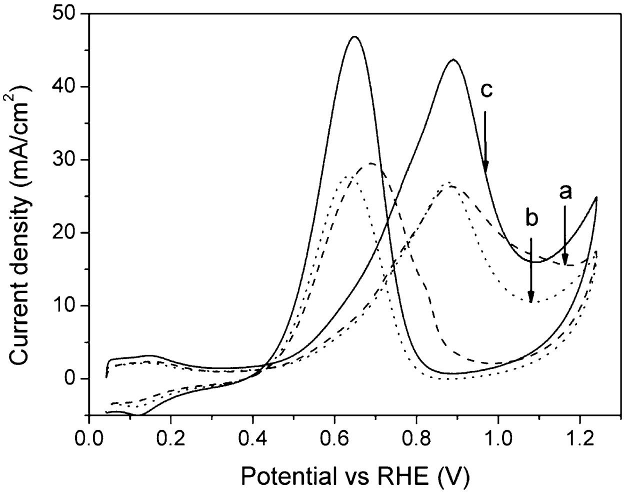

Fig. 2 CVs of commercial 20% Pt/C (a), 5% Pt-10% Ni/C (b), and 5% Pt-10% Ni-10% TiO_2NT/C (c) in 0.5 M H_2SO_4 + 0.5 M CH_3OH solution at room temperature, with a scan rate of 50 mV/s

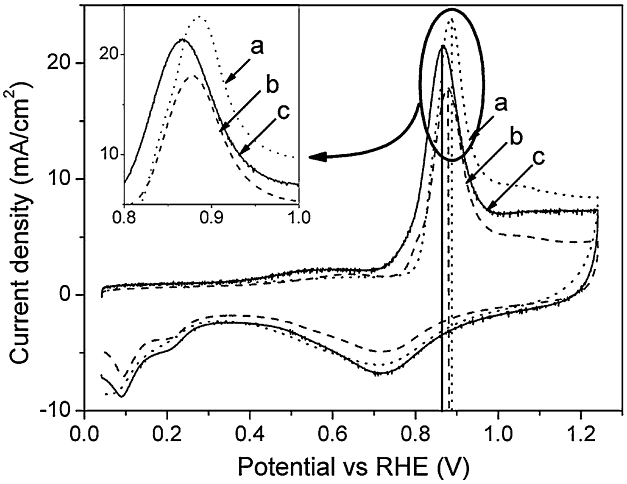

Fig. 3 CO-stripping voltammograms of commercial 20% Pt/C (a), 5%Pt-10% Ni/C (b), and 5% Pt-10% Ni-10% TiO_2NT/C (c) in 0.5 M H_2SO_4 at room temperature, with a scan rate of 50 mV/s

amount (5%) of Pt loading and of the commercial catalyst with 20% Pt loading (0.16 mg cm^{-2}). The onset potential corresponding to a current rise for methanol electro-oxidation is earlier in the case of Pt–Ni–TiO_2NT/C catalyst than the cases of the other two catalysts. The addition of TiO_2 nanotube might activate the water to form OH radical which oxidizes the intermediate [21], so the onset potential of the electrocatalyst has some shift. Ongoing work will continue to explore it. The peak potentials of the three catalysts are similar, between 0.88 and 0.89 V, but the peak current density of the Pt–Ni–TiO_2NT/C catalyst is the highest one, which is about 43.74 mA cm^{-2} (vs. 25.5 mA cm^{-2} of commercial Pt/C catalyst).

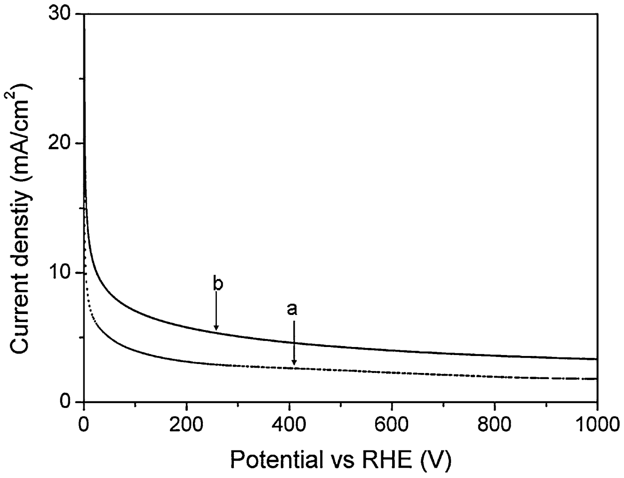

Fig. 4 Chronoamperometric curves of commercial 20% Pt/C (a) and 5%Pt-10% Ni-10% TiO_2NT/C (b) for methanol electro-oxidation in 0.5 M H_2SO_4 + 0.5 M CH_3OH at room temperature

Figure 3 compares the first positive scans of the commercial Pt/C, Pt–Ni/C, and Pt–Ni–TiO_2NT/C catalysts for CO electro-oxidation. The peak potential of the Pt–Ni–TiO_2NT/C is lower than these of the commercial Pt/C and Pt–Ni/C catalysts, which is in well accordance with the trend seen for the methanol electro-oxidation (Fig. 2). In fact similar results have also been acquired by Hogarth et al., in which they found that the catalytic activity of Pt electrodes supported by TiO_{2-x} is comparable to that of the best commercial alloy catalyst for methanol oxidation [22]. The origin for the strongest oxidation capacity seen in the Pt–Ni–TiO_2NT/C catalyst will be discussed below.

A short durability test (Fig. 4) of the Pt–Ni–TiO_2NT/C and commercial Pt/C catalysts was carried out at $E = 0.58$ V in 0.5 M H_2SO_4 with 0.5 M CH_3OH at room temperature. The initial high currents mainly originate from a double-layer charging. In both cases, the currents were found to decay within ~200 s, thus the stabilities of the two catalysts for methanol electro-oxidation are fairly similar.

3.2 Characterization of Pt–Ni–TiO_2NT/C

The XRD data acquired for Pt–Ni/C and Pt–Ni–TiO_2NT/C catalysts were shown in Fig. 5. It is obvious that in both spectra there are two diffraction peaks at 39° and 20–25°, corresponding to the Pt (111) planes and to the (002) reflection of the hexagonal structure of Vulcan XC-72 carbon, respectively. While one small but reproducible peak can be seen at around 36° only in the XRD patterns acquired for the catalysts with TiO_2 nanotube; this should correspond to the (004) diffraction peak of anatase TiO_2 (Fig. 5, inset panel). Because the content of TiO_2 nanotube is lower, there are no other obvious peaks of anatase TiO_2 nanotube.

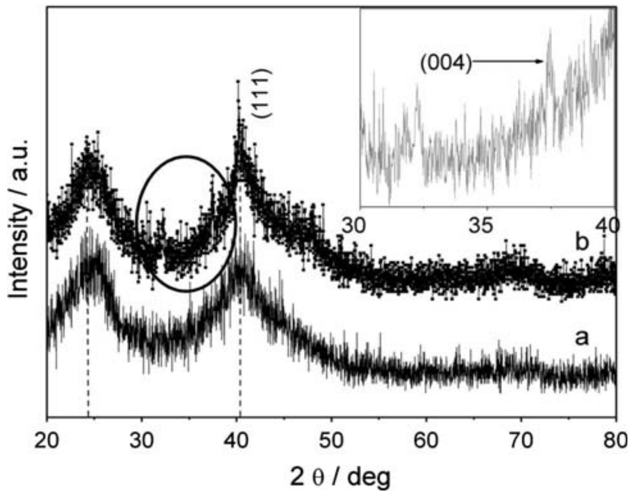

Fig. 5 XRD data acquired for electrocatalysts of 5%Pt-10%Ni (a), and 5%Pt-10%Ni-10%TiO_2NT/C (b)

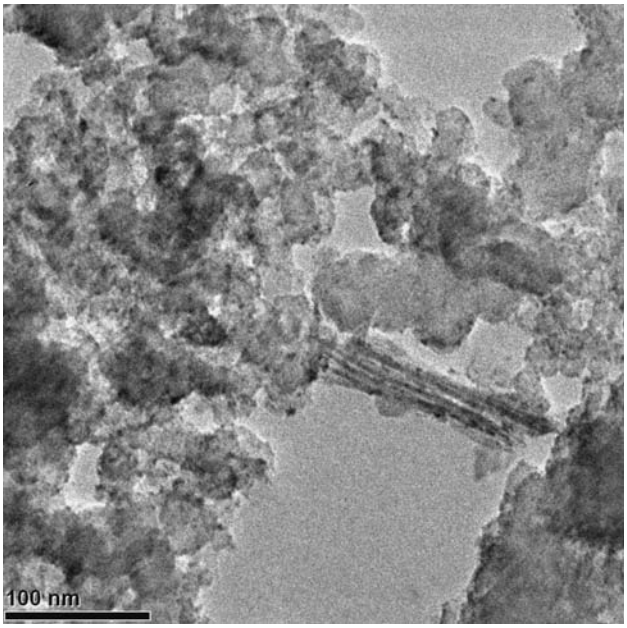

Fig. 6 HRTEM images of 5%Pt-10%Ni-10%TiO_2NT/C electrocatalyst

Figure 6 shows the HRTEM image of the Pt–Ni–TiO_2/C catalyst. The results suggest that both Pt and TiO_2 nanotube can be highly dispersed on the support, and that the catalyst prepared by us is remarkably uniform. Note that some of the Pt nanoparticles can indeed be found on the surface of TiO_2 nanotube. The interaction among Pt, TiO_2 nanotube and Vulcan XC-72 carbon might explain the good electrocatalytic activity for methanol oxidation on the low-Pt content carbon-supported Pt–Ni–TiO_2/C electrocatalysts.

Finally, the composition of this Pt–Ni–TiO_2NT/C catalyst was also measured by EDX (Fig. 7). The content of Pt was 4.22%, but the contents of Ni and Ti had some deviation from the nominal values. It might be indicative of the inhomogeneous distribution of the Ni and TiO_2 species on the surface of the carbon support.

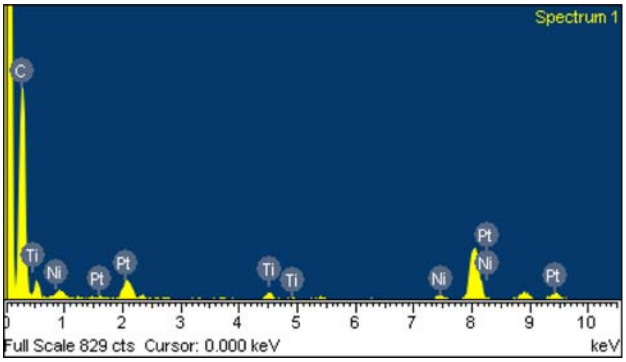

Fig. 7 EDX spectrum of 5%Pt-10%Ni-10%TiO_2NT/C electrocatalyst

3.3 Discussion

From the results shown above, it can be concluded that the Pt–Ni–TiO_2NT/C catalyst prepared by us possess better catalytic activity for methanol electro-oxidation than Pt–Ni/C and commercial Pt/C catalysts. It is not surprising that Pt/C catalyst is the least active among the three catalysts examined in our study [6–8]. It has been proposed that the introduction of Ni into Pt-based catalysts may increase the 5d-band vacancy of platinum, thus enhancing the methanol tolerance of those catalysts [6]. While the origin of the catalytic improvement seen after the introduction of TiO_2 nanotube is quite difficult to assess. TiO_2 as a catalytic support has been widely investigated for many metal catalysts [11], in particular for the gold [23–25]. The much more improved catalytic activity for methanol electro-oxidation seen here can be attributed to either highly dispersed Pt phases, or to a strong metal–support interaction (SMSI), in analogy to what has been frequently seen for CO hydrogenation on oxide-supported Pt catalysts [26, 27]. The presence of the interface between Pt phase and TiO_2 phase can indeed be evidenced by our HRTEM image (Fig. 6). But it also cannot be excluded that the formation of carbon deposit during the methanol oxidation can be inhibited by the presence of contacting TiO_2 phase, thus delaying the poisoning of Pt active site [14]. Overall speaking, our interpretation on this observed improvement is still quite preliminary, and further mechanistic investigation is still under way in our research group.

4 Conclusions

In summary, the addition of TiO_2 nanotube into Pt-based catalyst can significantly improve the performance of the electrocatalysts for methanol electro-oxidation. The low-Pt content of Pt–Ni–TiO_2NT/C catalyst (5% Pt, 10% Ni, and 10% TiO_2 nanotube) has a better activity than that of commercial 20% Pt/C catalyst, as evidenced by the lower onset potential corresponding to a current rise and by the higher peak current density seen for methanol electro-oxidation, and the current density is enhanced about 72% vs. that of commercial Pt/C catalyst. The presence of TiO_2 nanotube might be important for the preventing catalyst deactivation owing to a SMSI effect or by inhibiting the formation of carbon residues on Pt surface sites.

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References

1. Dillon R, Srinivasan S, Arico AS, Antonucci V (2004) J Power Source 127:112
2. Wasmus S, Kuver A (1999) J Electroanal Chem 461:14
3. Reddington E, Sapienza A, Gurau B, Viswanathan R, Sarangapani S, Smotkin ES, Mallouk TE (1998) Science 280:1735
4. Liu HS, Song CJ, Zhang L, Zhang JJ, Wang HJ, Wilkinson DP (2006) J Power Source 155:95
5. Christoffersen E, Liu P, Ruban A, Skriver HL, Norskov JK (2001) J Catal 199:123
6. Antolini E, Salgado JR, Gonzalez ER (2005) J Electroanal Chem 580:145
7. Antolini E, Salgado JR, Dos Santos AM, Gonzalez ER (2005) Electrochem Solid-State Lett 8:A226
8. Antolini E, Salgado JRC, Gonzalez ER (2006) J Power Source 155:161
9. Park KW, Choi JH, Kwon BK, Sung YE, Yong H, Hong SA, Kim HS, Wieckowski A (2002) J Phys Chem B 106:1869
10. Deivaraj TC, Chen WX, Lee JY (2003) J Mater Chem 13:2555
11. Diebold U (2003) Surf Sci Rep 48:53
12. Hayden BE, Malevich DV (2001) Electrochem Commun 3:395
13. Wu X, Jiang QZ, Ma ZF, Hu LQ (2007) Chin J Power Source 9:713
14. Xiong L, Manthiram A (2004) Electrochim Acta 49:4163
15. Maiyalagan T, Viswanathan B, Varadaraju UV (2006) J Nanosci Nanotechnol 6:2067
16. Macak JM, Schmidt-Stein F, Schmuki P (2007) Electrochem Commun 9:1783
17. Wang M, Guo DJ, Li HL (2005) J Solid State Chem 178:1996
18. Xie XY, Ma ZF, Wu X, Ren QZ, Yuan XX, Jiang QZ, Hu LQ (2007) Electrochim Acta 52:2091
19. Wu X, Jiang QZ, Ma ZF, Fu M, Shangguan WF (2005) Solid State Commun 136:513
20. Wu X, Jiang QZ, Ma ZF, Shangguan WF (2006) Chin J Inorg Chem 22:341
21. Luo J, Njoki PN, Lin Y, Mott D, Wang L, Zhong C (2006) Langmuir 22:2892
22. Hogarth MP, Hards GA (1996) Plat Met Rev 40:150
23. Huruta M (1997) Catal Today 36:153
24. Chen MS, Goodman DW (2006) Catal Today 111:22
25. Ma Z, Brown S, Overbury SH, Dai S (2007) Appl Catal A 327:226
26. Vannice MA, Twu CC, Moon SH (1983) J Catal 79:70
27. Benvenutti EV, Franken L, Moro CC, Davanzo CU (1999) Langmuir 15:8140