Pt decorated PdFe/C: Extremely High Electrocatalytic Activity for Methanol Oxidation

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A carbon supported Pt-decorated PdFe alloy nano-core catalysts (Pt-PdFe/C) for methanol oxidation is prepared via metathetical reaction between PdFe alloy nanoparticles (deposited on carbon) and $PtCl_4^{2-}$ in aqueous solution. Morphology and composition of the synthesized catalyst are characterized by Transmission Electron Microscope and X-ray diffraction. Experimental results show the electrochemical active surface area of the Pt-PdFe/C catalyst is much larger than those of the PdFe/C and Pt/C catalysts. Furthermore, the mass specific peak current is 1.01 A mg⁻¹ for methanol oxidation on the Pt-PdFe/C electrode, an increase by a factor of 3.5 times and 12.6 times as compared to PtRu/C and Pt/C, respectively. The facile fabrication and high electrochemical performance of Pt-PdFe/C highlight its potential application as anode for DMFCs.

Keywords: Electrocatalyst; Methanol-oxidation; Pt-decorated; Direct methanol fuel cell

1. INTRODUCTION

Platinum based electrocatalysts are exclusively used for catalyzing oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) in Direct Methanol Fuel Cells (DMFCs) [1-4]. There are, however, several limitations such as high cost, low availability of platinum and irreversible inactivation of the catalysts by CO-like poisoning species, hindering the widespread commercialization of DMFCs [5,6] It is therefore desired to develop low cost catalysts with comparable activity towards methanol oxidation reaction and better CO-tolerance for DMFCs. It has been well documented that

improving electrochemical activity of Pt, introducing non Pt metals into the catalyst and reducing the Pt loading are effective ways to alleviate the limitations of platinum based catalysts for DMFCs [7,10].

Currently, PtRu alloy catalyst is still considered as the best binary catalyst for methanol oxidation reaction in DMFCs. Alloying with Ru can significantly enhance the CO-tolerance of Pt due to the bi-functional mechanism [11]. Although PtRu alloy catalysts exhibit high MOR activity, the high cost of Pt and Ru, restrains their widespread application in anode catalysts for DMFCs [12]. Compared to Pt, it has been reported that Pd is a low cost metal with high catalytic activity towards methanol oxidation[13]. Although Pd is a promising candidate to replace Pt, its electrochemical activity for MOR needs to be improved. As a means of improving electrochemical activity of Pd, alloys of various compositions based on Pd have been developed as an alternative to Pt based electrocatalysts for MOR. In order to lower the cost and enhance the electrochemical activity, development of tri-metallic catalysts adding a third low cost metal such as Ni, Fe, Co, has also attracted a lot of attention since it results in higher methanol electrooxidation activity and better CO-tolerance[14,15]. In addition, core-shell structure is another efficient measure to improve the utilization of noble metal and further lower the cost of catalyst without sacrificing the electrochemical activity[16,17]. However, these modifications still require a relatively high Pt loading. Further reducing the Pt loading and introducing low cost metal are still required.

It was found that Fe was an effective additive to improve the performance of electrocatalyst for MOR [18,19]. In this work, a carbon supported Pt-decorated PdFe alloy nano-core catalyst (Pt-PdFe/C) for methanol oxidation was synthesized via a two-step procedure. A low cost PdFe alloy was used as the core because Pd and Fe belong to the same column of the VIII group in the periodic table and both metals could form a homogeneous solid solution with face centered cubic structure at all compositions and within a large range of temperatures, as observed from the Pd-Fe binary alloy phase diagram [20,21]. The results show that the Pt-PdFe/C catalyst exhibits superior MOR activity as compared to commercial Pt/C and PtRu/C, presenting a great potential for use as a low cost and highly active anode catalyst for DMFCs.

2. EXPERIMENTAL

The detail procedure is as follows: Firstly, Palladium chloride (PdCl₂) (66.6 mg) was dissolved in hydrochloric acid in a flask and 25 mL ethylene glycol (EG) was added as solvent. Then, iron (III) chloride hexahydrate (193.6 mg) and sodium citrate (662.4 mg) were introduced to the above solution and stirred for 0.5 h. The pH value of the mixture was adjusted to 8 by a 5 wt% KOH/EG solution under vigorous stirring. Sodium formate (321.8 mg) and pretreated carbon black Vulcan XC-72R (Cabot Corp., BET: 237 m² g⁻¹, denoted as C) (120 mg) were introduced to the flask under stirring and further ultrasonicated for 0.5 h. The mixture was then transferred into a teflon-lined autoclave and heated at 180 °C for 6 h, filtered, rinsed thoroughly with deionized water and dried in air at 70 °C to obtain thePdFe/C catalyst (metals loading: 40 wt % and weight ratio Pd:Fe = 1:1). Secondly, H₂PtCl₆ (8 mg) was dissolved in 20 ml deionized water. The pH of the system was adjusted to 10 by the addition of 5 wt% KOH solution. PdFe/C (50 mg) was introduced to the flask and stirred for 0.5 h, and then the mixture was heated at 80 °C for 4 h. Subsequently, the solid product was recovered by centrifugation, rinsed with deionized water, and dried in air at 70 °C. The PtRu/C sample was prepared using the same procedure. Before electrochemical measurements, the Pt-PdFe/C was thermally treated in a tubular oven under H_2/N_2 atmosphere at 300 °C for 2 h.

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD–3A (Japan) diffractometer, using Cu Ka radiation operated at 35 kV and 30 mA. 2θ diffraction angles ranged from 20 ° to 90 °. All X-ray diffraction patterns were analyzed using Jade 7.5 of Material Data Inc. (MDI): peak profiles of individual reflections were obtained by a nonlinear least-square fit of the Cu Ka corrected data. Morphological and particle size distribution studies were carried out with Tecnai G220S-TWIN (FEI Company) TEM operated at 200 kV. The average chemical composition for Pt-PdFe/C catalyst was determined using the EDX technique coupled to TEM.

A conventional electrochemical cell with a three-electrode setup was used for electrochemical measurements. A platinum wire and an Ag/AgCl electrode were used as counter and reference electrode, respectively. A glassy carbon disk (5 mm in diameter), coated with the catalyst, was employed as the working electrode. The electrochemical measurements were performed using an electrochemical work station (CHI604). The working electrode was prepared as follows: the catalyst powder suspension was prepared by adding 5 mg catalyst and 1 mL Nafion/ethanol (0.25 % Nafion). The suspension was dispersed in an ultrasonic bath for 15 min and 8 μ L suspension was then quantitatively transferred to the surface of polished glassy carbon electrode, followed by solvent evaporation at room temperature.

3. RESULTS AND DISCUSSION



Scheme 1. Illustration of the approach to synthesize Pt-PdFe nanoparticle.

Scheme 1 illustrates the synthesis route of carbon supported Pt-PdFe nanoparticles. The standard reduction potential of $PtCl_6^{2-}/Pt$ redox couples (0.735 V vs. the standard hydrogen electrode (SHE)) is much higher than that of the Fe²⁺/Fe redox couple (-0.440 V vs. SHE)), while Fe³⁺/Fe²⁺ and Pd²⁺/Pd redox couples are +0.771 V and +0.987 V, respectively (vs. SHE). Therefore, Fe atoms on the surface of PdFe alloy can be easily oxidized to Fe²⁺ when H₂PtCl₆ solution is added. The Fe atoms on

the surface of PdFe nano-cores should react completely with H_2PtCl_6 on the basis of the stoichiometric relationship in Equation (1) [22].

$$2Fe + PtCl_6^{2-} = Pt + 2Fe^{2+} + 6Cl^{-}$$
(1)

As this metathetical reaction occurs, the Pt atoms is reduced and deposited on the surface of PdFe nano-cores, instead of independent Pt particles being deposited on the carbon support as in the case of conventional Pt/C catalysts. Due to the intimate interaction between Pt and core metal, the Pt particles immobilized on metal cores are much stable than the Pt particles deposited on carbon[23]. After Pt atoms was deposited on the PdFe nano-cores via metathetical reaction, the surface will be rich with Pt- entities.



Figure 1. The XRD patterns of the commercial Pt/C, PdFe/C and Pt-PdFe/C catalysts. The insert shows the detailed XRD peak profile analysis catalyst in the 36-43 $^{\circ}$ of 2 θ degree.

The crystal structures of Pt/C, Pt-PdFe/C and PdFe/C catalysts were examined by XRD as shown in Fig. 1. The first peak located at about 24.8° in all three catalysts is associated to the carbon. The other four peaks are characteristic of face-centered cubic (fcc) crystalline Pt (PdFe alloy), corresponding to the planes (1 1 1), (2 0 0), (2 2 0) and (3 1 1), at 2θ values of ca. 40°, 46.5°, 67.8° and 82°, respectively. The inserted figure shows the detailed XRD peak profile of 2θ ranging from 36° to 43°. The (1 1 1) crystal face of the catalyst has been fitted to a Gaussian curve. Compared to PdFe/C, the (111) diffraction of Pt-PdFe/C shifts slightly to low 2θ region which imply that some Fe atoms on

the surface of PdFe nano-cores have been replaced by larger Pt atoms leading to an expansion of lattice.



Figure 2. TEM images and the corresponding particle size distribution histograms of (A) PdFe/C and (B) Pt-PdFe/C catalysts.

Fig. 2 shows the TEM images and the corresponding particle size distribution histograms of Pt-PdFe/C and PdFe/C catalysts. The TEM images show that the alloy nanoparticles are well dispersed on the carbon support. The as-synthesized Pt-PdFe/C catalyst shows a broader size distribution centered at about 4.7 nm compared to that of PdFe/C at about 5.0 nm. There is not any distinctive difference in TEM images of the particles of Pt-PdFe/C and PdFe/C, both of which possess similar atom size and crystal structure.

Fig. 3 presents the cyclic voltammetric (CV) curves of PtRu/C, commercial Pt/C and Pt-PdFe/C catalysts between -0.2 and 1.2 V (versus Ag/AgCl) with a scanning rate of 50 mV s⁻¹. The CV curves exhibit two distinctive potential regions associated with H_{upd} adsorption/desorption processes ($H^+ + e_- = H_{upd}$) between -0.2 V< E < 0 V (vs. Ag/AgCl) and the formation of an OH_{ad} layer (2H₂O = OH_{ad} + H₃O⁺ + e_-) beyond ~ 0.5 V (vs. Ag/AgCl), where H_{upd} and OH_{ad} refer to the under potentially deposited hydrogen and adsorbed hydroxyl species, respectively. The feature of the curve is in good

agreement with the literature [24]. The electrochemically surface area (ECSA) can be calculated according to Equation (3).

$$A_{EL}(m^2 g^{-1}Pt) = Q_H / (2.1 \times m)$$
 (3)

where A_{EL} is the active surface obtained electrochemically, $Q_H(cm^{-2})$ is the average integrated charge of hydrogen desorption/desorption peak area; m (g m⁻²) is the total metal loading on the electrode.



Figure 3. Cyclic voltammograms of PtRu/C, commercial Pt/C and Pt-PdFe/C catalysts measured in N_2 -saturated 0.5 M H_2SO_4 solution at room temperature and sweep rate of 50 mV s⁻¹. Scan rotation speed: 300 rpm.

The ECSA per unit weight of metal are 42.80 m² g⁻¹ for Pt-PdFe/C, 37.19 m² g⁻¹ for PtRu/C and 49.86 m² g⁻¹ for commercial Pt/C, respectively. Based on the Pt mass, the ECSA per unit weight of Pt are 285.33 m² g⁻¹ for Pt-PdFe/C and 56.46 m² g⁻¹ for PtRu/C. The ECSA and ECSA per unit weight of Pt of Pt-PdFe/C are more than 5 times and 5.7 times than that of the PtRu/C and commercial Pt/C catalyst, respectively. Compared to commercial Pt/C catalyst, the specific ECSA of Pt-PdFe/C is much higher because Pt atomsare deposited only on the surface of alloy core leading to high utilization of Pt.



Figure 4. Cyclic voltammograms measurement of Pt-PdFe/C, PtRu/C and commercial Pt/C electrode in N₂-saturated 0.5 M CH₃OH + 0.5 M H₂SO₄ solution. The sweep rate was 50 mV s⁻¹. Rotation speed: 300 rpm.

The electrocatalytic activities of Pt-PdFe/C, PtRu/C and commercial Pt/C for methanol oxidation reaction were investigated. Fig. 4 shows CV curves of Pt-PdFe/C, PtRu/C and commercial Pt/C electrode in N₂-saturated 0.5 M CH₃OH + 0.5 M H₂SO₄ solution at 50 mV s⁻¹.



Figure 5. The chronoamperometric curves of 0.5 M $CH_3OH + 0.5$ M H_2SO_4 solution at Pt-PdFe/C, PtRu/C and commercial Pt/C catalyst electrodes for 1000 s; fixed potential: 0.6 V. Rotation speed: 300 rpm. The insert shows the current of three catalysts after 1000 s.

The onset potential of methanol oxidation reaction occurs at 0.2 V for the Pt-PdFe/C, which is relatively lower than those of PtRu/C (0.27 V) and Pt/C (0.26V). The mass activity of Pt electrocatalysts for methanol oxidation is a critical parameter regarding the practical application of Pt electrocatalysts. The peak currents of the Pt-PdFe/C, PtRu/C and commercial Pt/C catalysts are 1.01 A mg⁻¹Pt, 0.29 A mg⁻¹Pt and 0.08 A mg⁻¹Pt, respectively. It is clear that the catalytic activity of Pt-PdFe/C is 3.5 times and 12.6 times higher than that of PtRu/C and commercial Pt/C, respectively. This clearly indicates that the utilization of the precious metal by the Pt-PdFe/C is much higher than that of the PtRu/C and commercial Pt/C catalyst. Besides the high utilization of Pt resulting in high electrocatalytic activity for Pt-PdFe/C, the presence of Fe in the core can also promote electrocatalytic activity via the electronic interaction between Pt and underlying Fe [25].

Fig.5 shows the chronoamperometric studies of the samples which reveals the stability of the Pt-PdFe/C, PtRu/C and commercial Pt/C catalyst towards the methanol electrooxidation. In the initial stage, all potentiostatic currents are found to decrease rapidly, corresponding to the formation of intermediate species such as CO_{ads}, CH₃OH_{ads}, and CHO_{ads} during methanol oxidation reaction [26]. As is known, the accumulation of intermediate species on the catalyst surface, which leads to "catalyst poisoning", is the major deficiency of all Pt-based catalysts used for methanol oxidation [27]. As expected, the methanol oxidation current after 1000 s for Pt-PdFe/C is higher than others. It was observed that the current of the Pt-PdFe/C, PtRu/C and commercial Pt/C catalyst at 1000 s are 0.0417 A mg⁻¹, 0.0346 A mg⁻¹ and 0.0271 A mg⁻¹, respectively. These results indicate that the stability of Pt-PdFe/C catalyst is higher than those of PtRu/C and commercial Pt/C. The enhancement of methanol tolerance of Pt-PdFe/C may be caused by the high methanol tolerance of Pd and dilution effect. Firstly, Pd and its alloys are known for their good methanol tolerance as oxygen reduction reaction catalyst for DMFCs [28-30]. Therefore, the presence of Pd in Pt-PdFe/C catalyst can enhance the methanol tolerance. Secondly, Pt atoms are not completely cover the whole surface of the catalyst, and some Pd atoms locate on the surface of alloy particles. Since the density of Pt atom on the surface of catalyst is much lower than that of PtRu/C and Pt/C, dissociative chemisorption of methanol and the chemidesorption of intermediate material on Pt active sites would easily occur due to the dilution effect [31-32].

4. CONCLUSION

A carbon supported Pt-decorated PdFe alloy nano-core catalysts was synthesized via metathetical reaction. In terms of the Pt mass, the specific ECSA of Pt-PdFe/C is much higher than that of the PtRu/C and commercial Pt/C catalysts. The CV experiments show that the peak current of the Pt-PdFe/C catalysts is much greater than that of PtRu/C and commercial Pt/C catalysts. Compared to PtRu/C and commercial Pt/C, Pt-PdFe/C catalyst exhibits better stability toward the electrooxidation of methanol after 1000 s. The work shows that metathetical reaction is an efficient way to synthesize Pt decorated alloy nanoparticle catalysts with high catalytic activitytowards methanol oxidation reaction for DMFC applications.

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