



Short communication

High efficiency Pt-CeO₂/carbon nanotubes hybrid composite as an anode electrocatalyst for direct methanol fuel cells

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ABSTRACT

Pt-CeO₂/carbon nanotubes (Pt-CeO₂/CNTs), based on glucose polymerization in the inner pores of anodic aluminum oxide templates under hydrothermal conditions followed by carbonization at high temperature, were synthesized using as precursors H₂PtCl₆ reduced by NaBH₄ and CeCl₃ deposited by NaOH. Pt nanoparticles and CeO₂ units were inserted onto the outer surfaces and inner surfaces of the as-prepared carbon nanotubes (CNTs). The resulting structures were characterized by scanning electron microscopy (SEM). The electrocatalytic performances of the Pt-CeO₂/CNTs modified glass carbon electrodes were investigated for methanol oxidation by cyclic voltammetric and chronoamperometric measurements. It was found that compared with Pt/CNTs, the hybrid Pt-CeO₂/CNTs electrodes showed superior catalytic performance when the molar ratio of Pt to CeO₂ in the catalyst was about 2:1. The increased catalytic efficiency of Pt is likely to result from its combination with CeO₂.

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1. Introduction

Pt-based electrocatalysts are usually employed as the anode material to electrocatalytically oxidize methanol. However, due to the fact that Pt anode catalysts are often poisoned by intermediates such as HCHO, HCOOH and CO_{ads} produced during methanol oxidation [1–5], the use of Pt anode catalysts in such applications is limited because of the slow kinetics of the anode methanol oxidation reaction. PtRuMO_x (M = W, Mo, V) catalysts obtained by adding non-noble metal oxides to PtRu [6–9] showed improved electrocatalytic performance as the mixed oxides are capable of reducing Pt poisoning and promoting methanol oxidation [10,11]. Other studies suggest that the Ru in the anode is dissolved during direct methanol fuel cell (DMFC) operation [12,13] and that the dissolved Ru is spanned across the membrane and reduced on the cathode electrode [14,15]. As this phenomenon leads to unexpected performance degradation of DMFCs, it is desirable to find a Ru-free catalyst to eliminate this degradation mechanism. In the meantime, catalysts should have higher catalyst activity, better stability, longer durability and lower cost, which are major focuses of research on DMFCs. Catalysts made up of the noble metal Pt and non-noble metal oxides may present the identity of anti-poison from CO.

Rare earth oxides have high activity, good stability and find application in the catalysis field. For example, CeO₂ catalysts exhibit high activity during the oxidation of CO at low temperatures. Since the favorable efficiency of CeO₂ to improve CO oxidation was

reported [16,17], many scholars believe that CeO₂ can effectively promote the oxidation of intermediates (CO) produced during methanol oxidation. Pt-CeO₂/C has been reported in some papers [18–23] to improve CO oxidation. CeO₂/C was prepared by doping a Pt/C catalyst (E-TEK) with CeO₂ sequentially [19] or by a one-step microwave polyol process with ethylene glycol as a carbon precursor [24].

As is known, well-ordered uniform porous carbon materials have extensive applications in electrode materials; the use of well-ordered porous carbons can improve much the catalytic activity of catalysts in methanol oxidation, as they allow a better dispersion of the catalysts [25–29]. In the same way, well-arranged CNTs with potentially improved electrical conductivity could also be useful for advanced technological applications [30]. In this research, we used anodic aluminum oxide (AAO) templates to synthesize CNTs with glucose as a carbon source. As AAO has a number of uniform straight nanochannels, a parallel aligned carbon nanotube structure can be obtained.

In this work, well aligned Pt-CeO₂/CNTs exhibiting a higher activity for methanol oxidation reaction than Pt/CNTs were synthesized. It is anticipated that the Pt-CeO₂/CNTs catalyst may be put to industrial practice for methanol oxidation because of its relatively simple preparation process and high efficiency.

2. Experimental

2.1. Preparation and characterization of Pt/CNTs and Pt-CeO₂/CNTs

The preparation of Pt/CNTs catalysts has been reported [30]. In brief, AAO membranes (Anodisc 25, Whatman International Ltd.)

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were immersed in a 25 mL aqueous solution of 0.5 mol L⁻¹ glucose, then loaded into a 30 mL Teflon-lined stainless steel autoclave for 0.5 h, and subsequently heated at 180 °C for 10 h to afford carbon-impregnated AAO templates coated in a black slurry. The AAO templates were removed from the autoclave and the black slurry was delicately removed from the AAO templates. The carbon-impregnated AAO templates were pyrolyzed at 600 °C in flowing N₂ for 3 h. In order to fully impregnate PtCl₆²⁻ into the nanochannels of CNTs, the pyrolyzed carbon-impregnated AAO templates were immersed in a 0.01 mol L⁻¹ H₂PtCl₆ solution for 1 h; after centrifugation and drying, the AAO templates were dipped into a solution containing 0.04 mol L⁻¹ NaBH₄ and 0.02 mol L⁻¹ NaOH for 30 min, followed by drying at 60 °C. The above steps were repeated six times before removal of the AAO templates. The Pt/CNTs samples were obtained by dissolving the AAO templates in 2 mol L⁻¹ KOH solution for 4 h.

Pt-CeO₂/CNTs catalysts were prepared by the co-precipitation method. The procedures were similar to the preparation process of Pt/CNTs composites, but CeCl₃ solution was added to 0.01 mol L⁻¹ H₂PtCl₆ solution at different ratios instead of H₂PtCl₆ solution. When all the steps for preparing Pt/CNTs catalysts were complete, the pyrolyzed CNTs inside the AAO template containing Pt and Ce(OH)₃ were calcined in a N₂ atmosphere at 450 °C for 20 min to obtain CeO₂ [31,32]. Finally, after dissolving the AAO templates with 2 mol L⁻¹ KOH for 4 h, the resulting suspension was filtrated and the black product was washed with deionized water for four times. The black product was dried at 60 °C.

In this paper, three Pt-CeO₂/CNTs catalysts with the same Pt loading (about 20 wt%) but different molar ratios of Pt to CeO₂ were prepared. The molar ratios of Pt to CeO₂ were controlled by changing the concentrations of CeCl₃ and H₂PtCl₆ solution.

The morphology of the Pt-CeO₂/CNTs catalysts was observed by scanning electron microscopy (SEM; Hitachi, S-3400N, Tokyo, Japan) and the composition of the Pt-CeO₂/CNTs catalyst was analyzed by energy-dispersive spectroscopy (EDS; Horiba EMAX, Kyoto, Japan) attached to the scanning electron microscopy.

2.2. Electrochemical characterization and measurements

Cyclic voltammetric and chronoamperometric measurements were performed using a CHI 660 electrochemical workstation (CH Instruments, Austin, TX) in a conventional three-electrode electrochemical cell using a twisted platinum wire as the auxiliary electrode and a KCl-saturated Ag/AgCl electrode as the reference electrode.

The working electrode was prepared by the following method: 5 mg of Pt-CeO₂/CNTs catalyst was dispersed in 1 mL ethanol solution with 15 μm nafion. After sonicating for 10 min, 5.0 μL of the suspension was uniformly pipetted onto the glass carbon (GC) electrode surface. Then, the GC electrode was dried in air at room temperature.

Before taking the cyclic voltammetric (CV) and chronoamperometric measurements, the GC electrode was immersed in N₂-saturated electrolyte solution for 15 min to achieve a stable system. To obtain the hydrogen electro-adsorption curves, in 1 mol L⁻¹ H₂SO₄ solution the potential was cycled between -0.25 and 1.25 V at a scan rate of 50 mV s⁻¹. The electro-oxidation activity of the Pt-CeO₂/CNTs catalyst was measured by CV measurements in 1 mol L⁻¹ H₂SO₄ solution containing 1 mol L⁻¹ methanol with the potential cycled between 0 and 1 V and at a scan rate of 50 mV s⁻¹. Chronoamperometry data for the Pt-CeO₂/CNTs catalyst in a mixture solution of 1.0 mol L⁻¹ H₂SO₄ and 1.0 M methanol were collected for 1000 s at a fixed voltage of 0.7 V at room temperature.

3. Results and discussion

Fig. 1 shows a series of scanning electron microscopy (SEM) images. Fig. 1a shows as-synthesized carbonaceous polymer nanotubes after the removal of the AAO template with 2 M KOH. Fig. 1a clearly reveals that the Pt/CNTs catalysts comprise filamentous bundles of aligned arrays. Fig. 1b shows an SEM image of the Pt/CNTs catalysts amplified 10,000-fold. In this image the morphology of the samples clearly shows that the Pt/CNTs catalysts comprise carbon nanotubes (CNTs) with many Pt nanoparticles decorated on the surface of the as-prepared CNTs. This demonstrates that the Pt/CNTs hybrid composites have been obtained successfully. Fig. 1c and d displays single CNTs, where the nanoparticles encased in the CNTs can be clearly observed. The morphology of the Pt/CNTs sample in Fig. 1c and d is consistent with what is shown in reference [31]. Fig. 1e, f and g shows images of Pt-CeO₂/CNTs catalysts with the molar ratios of Pt to CeO₂ of 1:1, 2:1 and 3:1, respectively. Fig. 1h shows a magnified SEM image of Pt-CeO₂ on a single nanotube. It can be observed that CNTs embedded with uniformly distributed Pt-CeO₂ particles were achieved by the incipient wetness impregnation method.

An EDS spectrum of the Pt-CeO₂/CNTs (Pt:CeO₂ = 2:1) catalyst corresponding to Fig. 1f is shown as in Fig. 2. The EDS analysis reveals that the atomic composition of Pt:CeO₂ is 3.55:1.58%, which is close to 2:1 (molar ratio) and the mass fraction of Pt is 23%. All those values are consistent with our initial design. Other sets of data for the atomic composition were also obtained with the same method.

It is known that the electrochemical active surface of Pt particles in the catalysts is an important factor to evaluate the catalytic activity of electrocatalysts for methanol electro-oxidation. The electrochemical active surface (EAS) of platinum for the catalysts could be estimated from the integrated charge in the hydrogen adsorption region (Q_H) of the cyclic voltammograms. Fig. 3 shows the cyclic voltammogram of Pt-CeO₂/CNTs catalyst (Pt:CeO₂ = 2:1) modified electrodes in 1 M H₂SO₄ solution. The ESA areas, in terms of m² g⁻¹, were calculated from the following formula [20,33]:

$$EAS = \frac{Q_H}{(0.21 \times 10^{-3} \times M_{Pt})}$$

where Q_H is the amount of charge exchanged during the hydrogen atom electro-adsorption, M_{Pt} represents the platinum loading (mg cm⁻²) in the electrode. The EAS values calculated for Pt/CNTs or Pt-CeO₂/CNTs are shown in Table 1. The data reveals that the addition of CeO₂ is beneficial to improve the EAS values, it may be similar to the rapid hydrogen spillover effect in the Pt-WO₃ system [34,35]. Namely, there is a synergistic effect between CeO₂ and platinum, where the addition of CeO₂ promotes the hydrogen spillover rate of Pt-H, so it increases the reaction rate, releases the activity sites of platinum and increases the dissociation of hydrogen adsorption [36]. The value for sample C is the biggest in the four samples, indicating that the methanol electrochemical oxidation is more active on the glass carbon electrode modified with sample C for the same surface area of the electrode.

The cyclic voltammograms of methanol electro-oxidation over Pt-CeO₂/CNTs and Pt/CNTs catalysts in 1 mol L⁻¹ N₂-saturated H₂SO₄ aqueous solution containing 1 mol L⁻¹ CH₃OH are shown in Fig. 4, measured at a scan rate of 50 mV s⁻¹. The catalytic activity of the Pt-CeO₂/CNTs and Pt/CNTs catalysts was evaluated as the specific current of mass. It can be seen from the data listed in Table 1 that the onset potentials for the electro-oxidation of methanol on the prepared catalyst samples A, B and C, began at about 0.30–0.40 V. The onset potential of methanol oxidation with the electrode modified with sample C is lower than the electrode

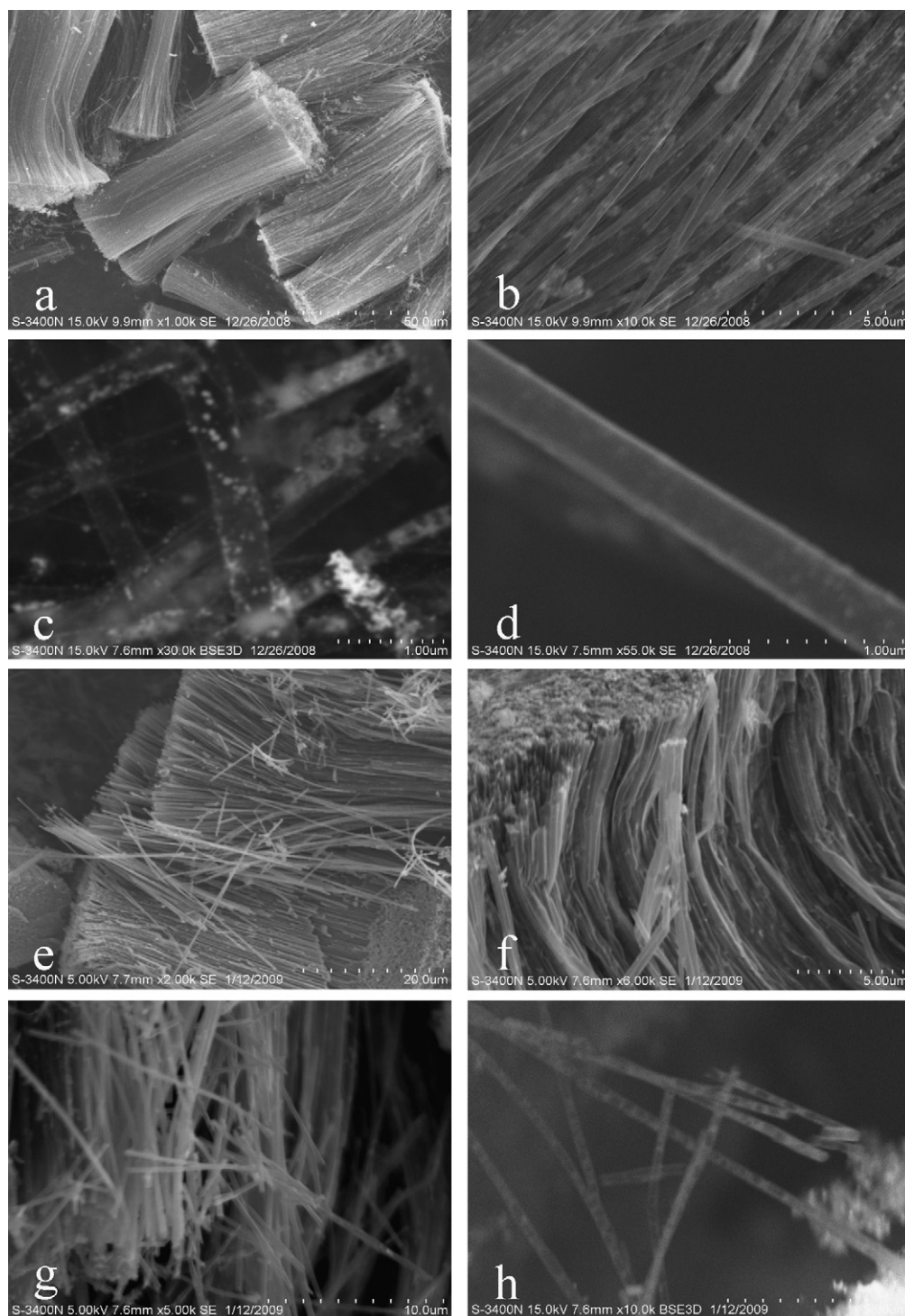


Fig. 1. SEM images of (a–d) Pt/CNTs structures; (e) Pt-CeO₂/CNTs with Pt/CeO₂ at an atomic ratio of 1:1; (f) Pt-CeO₂/CNTs with Pt/CeO₂ at an atomic ratio of 2:1; (g) Pt-CeO₂/CNTs with Pt/CeO₂ at an atomic ratio of 3:1; (h) Pt-CeO₂/CNTs with Pt/CeO₂ at an atomic ratio of 2:1 (a magnified SEM image of a single CNTs with Pt/CeO₂).

modified with sample A or sample B, which reveals that methanol is easier to oxidize on sample C at the lower potential.

The oxidation peak which appeared at about 700 mV in the positive direction sweep is attributed to methanol electro-oxidation, the oxidation peak appeared at about 500 mV in the negative direction sweep is due to the electro-oxidation of intermediates. As shown in curves B, C, D, peak currents of Pt-CeO₂/CNTs catalysts with different ratios of Pt to CeO₂ at 1:1, 2:1 and 3:1 were 5.0, 10.3 and 2.6 mA, respectively. All those values were higher than the 1.6 mA obtained for the Pt/CNTs catalyst (curve A). These

results indicated that the addition of CeO₂ to Pt/CNTs significantly improved the electrocatalytic activity.

As shown in Fig. 5, the electrocatalytic activity of the Pt-CeO₂/CNTs catalysts on methanol oxidation increases at first and then decreases with increasing of the amounts of CeO₂ in the catalysts. The highest current value of the Pt-CeO₂/CNTs catalysts was obtained at the molar ratio of Pt to CeO₂ at 2:1. All the phenomena indicate that the methanol electrochemical oxidation is more active on the Pt-CeO₂/CNTs electrode than on the Pt/CNTs electrode.

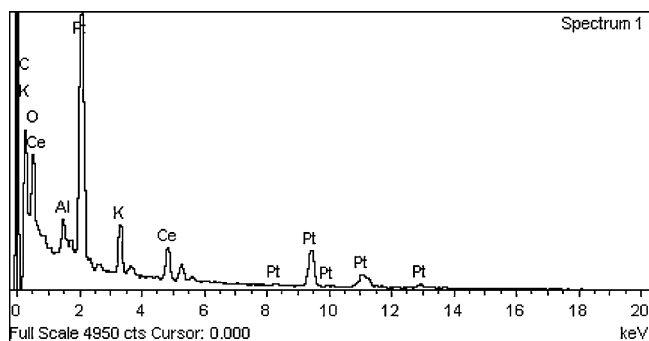


Fig. 2. A typical EDS spectrum of Pt-CeO₂/CNTs (Pt:CeO₂ = 2:1) catalyst.

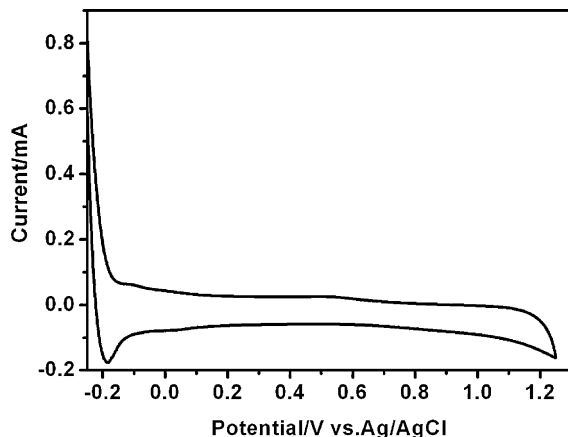


Fig. 3. Cyclic voltammogram of Pt-CeO₂/CNTs (Pt:CeO₂ = 2:1) catalyst modified glass carbon electrode in 1 M H₂SO₄ aqueous solution at a scan rate of 50 mV s⁻¹.

Table 1

The ESA and onset potential for the Pt/CNTs and Pt-CeO₂/CNTs catalysts.

Catalyst	Pt loading (mg cm ⁻²)	EAS (m ² g ⁻¹)	Onset potential of methanol oxidation (V)
Pt/CNTs (A)	0.09	3.56	0.43
Pt-CeO ₂ /CNTs (B)	0.107	9.76	0.4
Pt-CeO ₂ /CNTs (C)	0.11	11.13	0.35
Pt-CeO ₂ /CNTs (D)	0.10	5.78	–

Pt/CNTs (A) is the catalyst without CeO₂; Pt-CeO₂/CNTs (B) is the catalyst with a Pt/CeO₂ atomic ratio of 1:1; Pt-CeO₂/CNTs (C) is the catalyst with a Pt/CeO₂ atomic ratio of 2:1; Pt-CeO₂/CNTs (D) is the catalyst with a Pt/CeO₂ atomic ratio of 3:1.

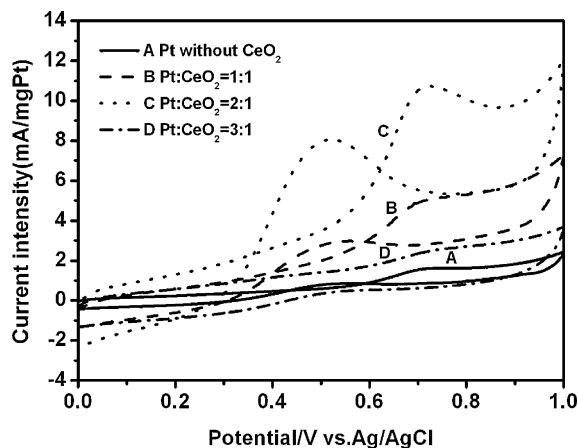


Fig. 4. Cyclic voltammograms of glass carbon electrodes modified with catalysts in 1 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ CH₃OH solution at a scan rate of 50 mV s⁻¹: (a) Pt/CNTs; (b) Pt/CeO₂ with an atomic ratio of 1:1; (c) Pt/CeO₂ with an atomic ratio of 2:1; (d) Pt/CeO₂ with an atomic ratio of 3:1.

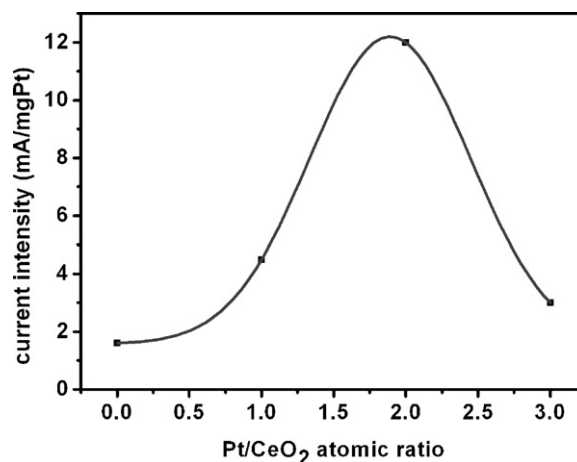


Fig. 5. Variation of current intensity for electro-oxidation of methanol with a Pt-CeO₂/CNTs catalyst having a Pt to CeO₂ atomic ratio of without CeO₂, 1:1, 2:1 and 3:1.

The chronoamperometric technique is an effective method to evaluate the electrocatalytic activity and stability of an electrode material. Fig. 6 shows typical current density–time responses for methanol oxidation measured at a fixed potential of 0.7 V of all catalyst systems supported on CNT electrodes in 1 mol L⁻¹ N₂-saturated H₂SO₄ aqueous solution containing 1.0 mol L⁻¹ CH₃OH. For different Pt-CeO₂/CNTs catalysts, the methanol electro-oxidation current decreases moderately with time. The current measured for the Pt-CeO₂/CNTs (Pt:CeO₂ = 2:1) catalysts is higher for all corresponding potentials than those of other samples. This result proved that sample C with Pt: CeO₂ ratio at 2:1 has better activity, which is consistent with the results obtained from the cyclic voltammograms of methanol electro-oxidation.

So far, the most commonly adopted mechanism to account for the electro-oxidation of methanol on the Pt-Ru catalyst surfaces is the promotional or bifunctional mechanism. Referring to the depiction of methanol oxidation on Pt-Ru alloy [37], a tentative reaction mechanism for the methanol electro-oxidation on Pt-CeO₂/C catalysts was proposed as follows. The surface oxygen of ceria may oxidize the CO on the surface of Pt. This is a kind of bifunctional mechanism [18,38].

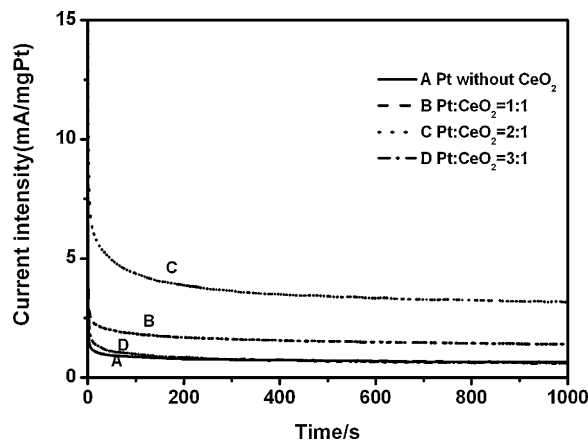
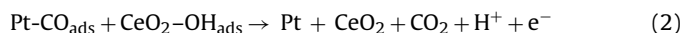
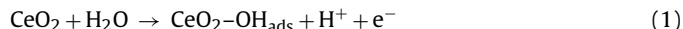


Fig. 6. Chronoamperometry curves for glass carbon electrodes modified with catalysts in 1 mol L⁻¹ H₂SO₄ and 1 mol L⁻¹ CH₃OH solution at 0.7 V for 1000 s: (a) Pt/CNTs; (b) Pt/CeO₂ with an atomic ratio of 1:1; (c) Pt/CeO₂ with an atomic ratio of 2:1; (d) Pt/CeO₂ with an atomic ratio of 3:1.

and/or



CeO₂ acts in the same manner as Ru does in Pt-Ru/C catalysts. The formation of OH_{ads} species at the lower potential can transform the CO-like poisoning species (CO_{ads}) on Pt to CO₂, thereby releasing the active sites on Pt for further electrochemical reaction [38]. On the other hand, a large concentration of oxygen vacancies in the CeO₂ is formed by the interaction of Pt and CeO₂ [39], which provides active sites for CO adsorption. This feature can transform CO-like poisoning species on Pt to CO₂, releasing the active sites on Pt for further electrochemical reaction.

Cyclic voltammetric studies and chronoamperometric determination reveal that compared to Pt/CNTs, the addition of CeO₂ to Pt/CNTs catalysts results in greater activity in methanol electro-oxidation, which is important evidence for the above proposed mechanism. There may be two reasons for the decrease in current with increasing content of CeO₂: on one hand, the decrease may be due to the diminution of Pt active sites with higher contents of CeO₂; on the other hand, the decrease in current is perhaps due to the decreasing electrode conductivity on account of CeO₂ being a semiconductor.

4. Conclusion

In the present investigation, an interesting, simple and convenient method to prepare well-arranged carbon nanotubes (CNTs) was developed. Well-arranged CNTs exhibited better electrical conductivity and allowed a higher degree of dispersion of catalysts. Pt and CeO₂ were deposited on the walls of the CNTs by co-precipitation. Pt-CeO₂/CNTs hybrid composites with appropriate Pt:CeO₂ ratio at 2:1 exhibited high electrocatalytic activities for methanol electro-oxidation, as proved by cyclic voltammetric and chronopotentiometric characterization. The high electrocatalytic activities for methanol oxidation can be attributed to simultaneous catalyst in methanol oxidation by CeO₂ with Pt in CNTs which extensively improve the electrocatalytic activity of Pt/CNTs catalysts. A Pt-CeO₂/CNTs hybrid composite prepared with this method is a promising practical catalyst for direct methanol fuel cells (DMFCs) because the preparation process is simple and CeO₂ is a relatively inexpensive additive.

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