

Short communication

Promoting the current for methanol electro-oxidation by mixing Pt-based catalysts with CeO₂ nanoparticles

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Abstract

Pt particles were prepared through microwave radiation reduction of chloroplatinic acid in ethylene glycol and then adsorbed on carbon nanotubes (CNTs). The thus prepared catalyst was denoted as CNTs-Pt. CeO₂ nanoparticles were prepared through molten salt method. Transmission electron microscopy (TEM), X-ray diffraction (XRD) and scanning electronic microscopy (SEM) were used to characterize the morphology and structure of CNTs-Pt and CeO₂. Cyclic voltammetry (CV), CO stripping and chronoamperometry methods were used to characterize the electrochemical behaviors of the catalysts. The results showed that CeO₂ nanoparticles and CNTs-Pt catalysts can be mixed homogeneously and the current of methanol oxidation can be greatly increased by the mixed CeO₂ nanoparticles. The reason for the increased activity was analyzed and ascribed to the promotion of CO electro-oxidation reaction kinetics by CeO₂. The method of mixing co-catalyzing materials with Pt-based catalysts is effective and can find wide application in electro-catalysis.

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1. Introduction

Direct methanol fuel cell (DMFC), although viewed as potential power source with high energy conversion efficiency, still faces the problem of low kinetics of methanol electro-oxidation on Pt. The main reason for the low kinetics is generally ascribed to the CO species produced and strongly adsorbed on Pt surface during the electro-oxidation of methanol [1]. To promote the CO species release from Pt and spare more available surface for methanol electro-oxidation, oxygen-containing species adjacent to the poisoned Pt sites are required according to the bi-functional mechanism [2]. Due to the lower potential for producing oxygen-containing species on Ru, Ru element is intensively studied as a co-catalyzing component in PtRu catalysts [3,4].

Besides PtRu system, Pt-based catalysts containing other different components have also been studied, such as binary (PtSn,

PtNi) [5,6], ternary (PtRuNi, PtRuIr) [7,8], and quaternary (PtRuOsIr) [9] catalysts. Recently, several reports showed that CeO₂ can greatly improve methanol electro-oxidation on Pt in acid methanol solution [10–13]. From our preliminary work we found that CeO₂ can exhibit co-catalyzing effect together with Pt for methanol electro-oxidation. At the same time, CeO₂ is not good electron-conducting material. If Pt is directly deposited on carbon–CeO₂ composites, some Pt will inevitably be insulated by CeO₂, thus limiting its usage in electro-catalysis. Recently, we have designed the structure of CNTs–CeO₂/Pt and the Pt catalytic activity was improved by about 66% with no decrease of Pt utilization [14]. As for the co-catalyzing materials with bad electron conductivity, such as CeO₂, there is less paper dealing with the avoidance of bad electron conductivity. In this paper, we mixed the prepared CeO₂ nanoparticles directly with the as-prepared catalyst and the as-received commercial catalyst and gained a significant increase of methanol electro-oxidation current, with no decrease of Pt utilization. Since this method is simple, it may open a way for the utilization of low-electron-conductivity materials in electro-catalysis. At the same time, it may provide possibility for using transition metal oxides with various morphology and structures in catalyst layer.

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2. Experimental

Multi-walled carbon nanotubes (MWCNT) were obtained from Chemical Engineering Department, Tsinghua University. The as-received MWCNTs were boiled in HNO_3 for 3 h, rinsed and dried. Pt particles were prepared by microwave heating of ethylene glycol (EG) solutions of Pt precursor salts [15]. In a typical process, certain amount of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 50 mL NaOH EG solution in a 100 mL beaker, in which the concentration of NaOH is 0.05 M. The beaker was placed in the center of a household microwave oven (Glanz brand microwave, 750 W) and heated for 60 s.

The above treated CNTs were dispersed in water under stirring and then the EG suspension of the prepared Pt particles was added drop-wise into the aqueous suspension. After 2 h adsorption of Pt particles on CNTs, the suspension was filtered, washed successively with deionized water and ethanol and dried under 80°C . In thus prepared catalyst the theoretical Pt content was 20 wt.%, and the catalyst was denoted as CNTs-Pt.

CeO_2 nanoparticles were prepared by molten salt method as described in other place [16]. For a typical synthesis process, $\text{K}_2\text{C}_2\text{O}_4$ solution was added drop-wise into the cerium nitrate solution under stirring to attain a pH of 10. The resulted precipitation was filtrated and washed with deionized water and ethanol repeatedly, dried at 80°C for 12 h, and then mixed with KNO_3 at a molar ratio of 1:3. The mixtures were calcined at 500°C for 3 h, and then cooled to ambient temperature. The products were immersed in deionized water, filtered and washed repeatedly. Finally, the products were dried at 120°C to obtain the CeO_2 nanoparticles.

The morphology of CNTs-Pt and CeO_2 nanoparticles was investigated using TEM (JEOL model JEM-1200EX). The XRD patterns were characterized on a Rigaku X-ray diffractometer using $\text{Cu K}\alpha$ as radiation source. Scanning electronic microscopy (SEM) image of samples was recorded on scanning microscope (JSM-6301F). The energy dispersive X-ray spectroscopy (EDX) analysis of samples was performed at 150 kV using an energy dispersive X-ray spectrometer (OXFORD INCA 300) attached to the microscope.

Electrochemical characterizations of the catalysts were conducted using a three-electrode cell at the Solartron electrochemical workstation. The working electrode was a gold plate covered with a thin layer of Nafion-impregnated catalyst. As a typical process, about 1 mg CNTs-Pt was ultrasonically mixed with Nafion EG solution to form homogeneous ink which was cast on the gold plate. In the case of mixing CNTs-Pt with CeO_2 nanoparticles, CeO_2 nanoparticles were first ultrasonicated in water and the suspension was then ultrasonically mixed with CNTs-Pt and Nafion ionomer in EG solution. The thus prepared ink was cast on the gold plate. Pt gauze and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. All potentials in this report are quoted against SCE. CV test was conducted at 50 mV s^{-1} in a solution of 1 M HClO_4 with and without 1.0 M CH_3OH . CO stripping was performed as follows: after purging the solution with N_2 gas for 10 min, gaseous CO was bubbled for 20 min to allow adsorption of CO onto the electro-catalysts while maintaining a

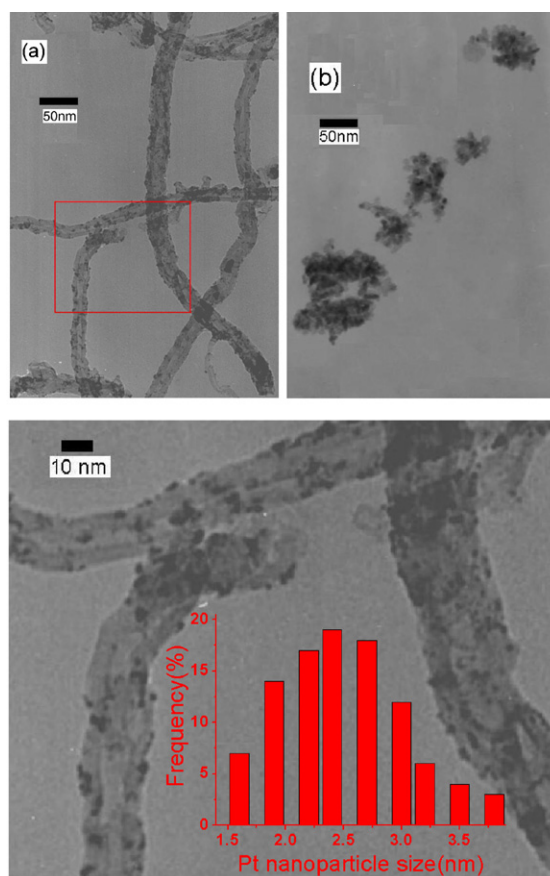


Fig. 1. TEM images of CNTs-Pt (a) and CeO_2 nanoparticles (b). (c) shows the Pt size distribution and magnification of rectangle part in (a); the inset in (c) is the Pt size distribution histogram.

constant voltage of 0.1 V versus SCE. Excess CO dissolved in solution was purged out with N_2 for 10 min and CO stripping voltammetry was recorded in 1 M HClO_4 solution at a scan rate of 20 mV s^{-1} . Chronoamperometric curves of CO ad-layer oxidation were recorded in 1 M HClO_4 at 0.5 V. The CO was adsorbed at 0.1 V for 20 min followed by N_2 bubbling for 10 min at 0.1 V.

In the case of mixing CNTs-Pt with CeO_2 nanoparticles, the composites were denoted as CNTs-Pt + CeO_2 . PtRu/C (a commercial catalyst from E-Tek Company) was also mixed with CeO_2 , which was denoted as PtRu/C + CeO_2 .

In the following experiments, the weight ratio of CeO_2 to catalysts was 30:100. All the electrochemical measurements were conducted under 25°C .

3. Results and discussion

To see the morphology of the prepared CNTs-Pt and CeO_2 nanoparticles, we recorded their TEM images as shown in Fig. 1(a) and (b), respectively. To get clear view of the Pt dispersion on CNTs, we selected part of TEM image in Fig. 1(a) (see the red rectangle) and the magnified image was shown in Fig. 1(c), in which the Pt size distribution histogram was also inset. From Fig. 1(a) it can be seen that Pt nanoparticles are homogeneously dispersed on the CNTs with no agglomeration. Fig. 1(c) showed that the average Pt particle size is about 2.5 nm.

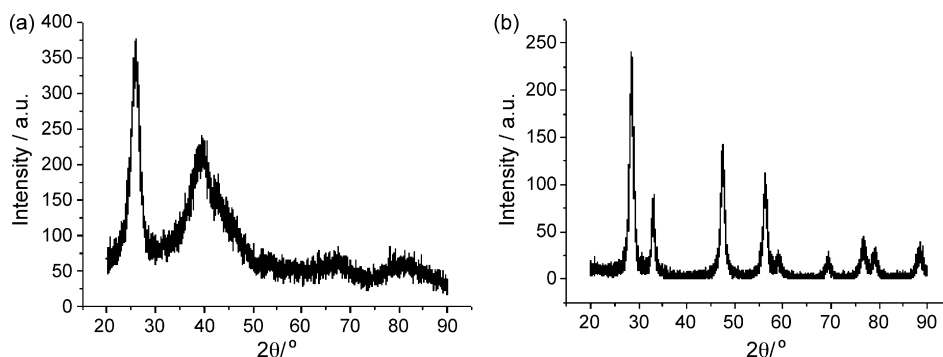


Fig. 2. XRD patterns of (a) CNTs-Pt and (b) CeO₂ nanoparticles.

In Fig. 1(b) we cannot see mono-dispersed CeO₂ nanoparticles. In fact the CeO₂ nanoparticles are agglomerated and the average size of the agglomerations is between 50 and 100 nm. Since the CNTs are rigid and can form large amounts of voids, as can be seen from Fig. 1(a), it is possible for the CeO₂ nanoparticles to enter into the voids and have contacts with the Pt nanoparticles on CNTs.

The XRD patterns of CNTs-Pt and CeO₂ were shown in Fig. 2(a) and (b), respectively. From the XRD patterns of CNTs-Pt (see Fig. 2(a)), we can see the three peaks characteristic of Pt, that is, (1 1 1) at $2\theta = 39.8$, (2 2 0) at $2\theta = 67.5$, and (3 1 1) at $2\theta = 81.3$. In the XRD pattern for CeO₂, typical diffraction peaks of CeO₂ were observed, such as (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (4 2 0) corresponding to $2\theta = 28.5, 33, 47.5, 56.3, \text{ and } 79$.

Fig. 3(a) and (b) shows the SEM images of CNTs-Pt and CNTs-Pt + CeO₂, respectively. It can be seen that the CNTs in Fig. 3(a) were inter-connected and large amount of voids were formed. In Fig. 3(a) the voids are mainly sized between 100 and 200 nm (as indicated by the red lines in Fig. 3(a)), therefore the CeO₂ nanoparticles have possibility to enter the voids formed by CNTs. After mixing CNTs-Pt with CeO₂ nanoparticles, certain amounts of the voids were filled by CeO₂ nanoparticles and the number and length of CNTs seems decreased, as seen in Fig. 3(b). It can also be seen that some part of CNTs was covered by CeO₂ agglomerates, as illustrated by the red circle in Fig. 3(b). From Fig. 3(b) we know that the CNTs-Pt and CeO₂ nanoparticles can have direct contacts. As CeO₂ is not good electron conductor, question arises whether the CeO₂ would influence the electron conductivity of the catalyst layer. In our viewpoint, the electron conductivity in the catalyst layer can still be maintained by CNTs because CNTs were inter-connected and can acts as the electron-conducting path. Fig. 3(c)–(e) shows the SEM image of CNTs-Pt + CeO₂ and the corresponding EDX analysis of Ce, Pt and S elements, respectively. The EDX results indicate that CeO₂, CNTs-Pt and Nafion were homogeneously mixed. From the result in Fig. 3(b) we can assume that certain amounts of interface between CNTs-Pt and CeO₂ would inevitably be formed, which is necessary for promoting the methanol electro-oxidation.

To analyze the effect of CeO₂ on CNTs-Pt, we first compared the electrochemical active surface (EAS) areas and methanol electro-oxidation activity corresponding to CNTs-Pt and CNTs-Pt + CeO₂. EAS is calculated from the H region area by assuming

that Pt surface is covered by monolayer adsorbed H and taking 0.21 mC cm^{-2} as the reference [17]. The CV curves are shown in Fig. 4.

From Fig. 4 we can see that the methanol electro-oxidizing current is significantly increased and the onset potential of methanol electro-oxidation shifted to a lower value after mixing CNTs-Pt with CeO₂. On the other hand, the H region area has no large difference, as can be seen from the inset in Fig. 4. Such a result indicates that the CeO₂ can promote the electro-oxidation of methanol on Pt with no influence on EAS of Pt. To gain quantitative insight into the CeO₂ effects, we compared the EAS, onset potential (E_{onset}) and peak current (I_m) of methanol electro-oxidation corresponding to CNTs-Pt and CNTs-Pt + CeO₂, as listed in Table 1.

From Table 1 we can see that the methanol electro-oxidizing current (I_m) is increased by 75% from 280 to 490 mA mg^{-1} after mixing CeO₂ with CNTs-Pt. On the other hand, the onset potential (E_{onset}) of CNTs-Pt + CeO₂ is lower than that of CNTs-Pt, from 0.51 to 0.46 V. This fact indicates that methanol is more easily electro-oxidized on CNTs-Pt + CeO₂ than on CNTs-Pt.

To compare the potentiostatic behavior CNTs-Pt + CeO₂ and CNTs-Pt, we recorded their chronoamperometry curves in 1 M HClO₄ + 1 M CH₃OH at 0.6 V for 3600 s, as shown in Fig. 5. From Fig. 5 we see that the current for CNTs-Pt + CeO₂ keeps higher than that for CNTs-Pt, indicating that the former is more active than the latter for methanol electro-oxidation, as is consistent with the CV results in Fig. 4.

From above we can see that by mixing CeO₂ nanoparticles with CNTs-Pt in catalyst layer, the methanol electro-oxidation current can be greatly enhanced. But what is the reason for such a result? According to our experimental experiences, the methanol electro-oxidation current can be enhanced by two approaches. One is to improve the electro-oxidizing kinetics of CO species on Pt through bi-functional mechanism and another is to increase the mass transfer rates of reactants (such as methanol) and prod-

Table 1
Data collected from Fig. 4

	EAS _m ^a ($\text{cm}^2 \text{ mg}^{-1} \text{ Pt}$)	E_{onset} (V)	I_m ^a ($\text{mA mg}^{-1} \text{ Pt}$)
CNTs-Pt	436	0.51	280
CNTs-Pt + CeO ₂	413	0.46	490

^a The subscript m denotes that the EAS and current are mass normalized.

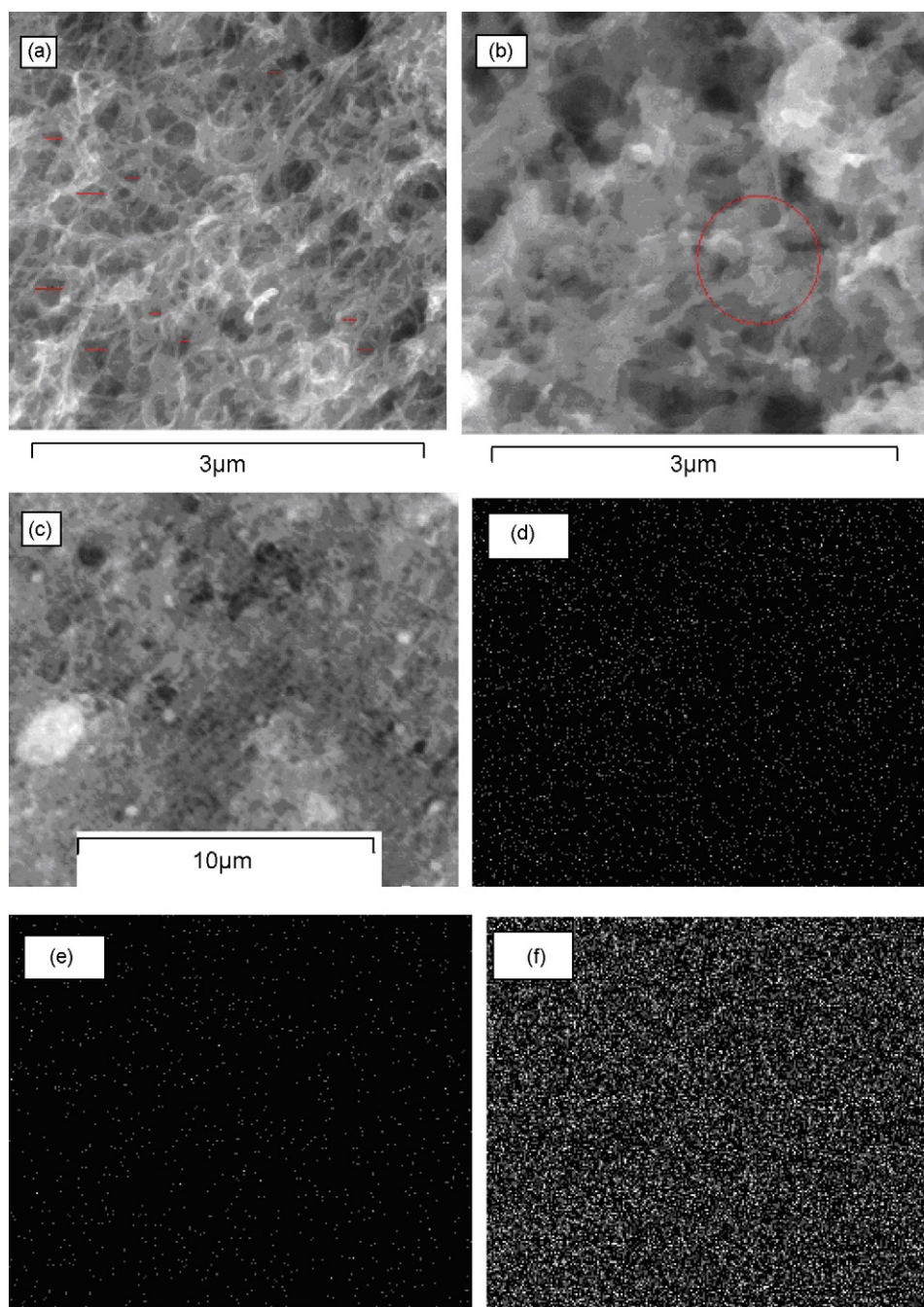


Fig. 3. (a) SEM image of CNTs-Pt; (b) SEM image of CNTs-Pt + CeO₂; (c) SEM image of the CNTs-Pt + CeO₂ recorded under lower magnification; (d)–(f) show the distribution of Ce, Pt and S element in (c), respectively.

ucts (such as CO₂) by stirring or by increasing large pores in catalyst layer. At present, since certain amounts of voids were filled by CeO₂ nanoparticles, the amounts of large pores would not be increased and correspondingly, the mass transfer in catalyst layer would less possibly be improved after mixing CeO₂. Therefore the most possible reason maybe that the methanol electro-oxidation kinetics is improved by CeO₂. Since CO is the main poisoning species that control the rates of methanol electro-oxidation, to confirm the CeO₂ co-catalyzing effect, we analyzed the CO electro-oxidizing behavior on CNTs-Pt and CNTs-Pt + CeO₂, as shown in Figs. 6 and 7, respectively.

From Fig. 6 we can see that the CO stripping on CNTs-Pt + CeO₂ starts at a lower potential than on CNTs-Pt and the peak potential for CO stripping on CNTs-Pt + CeO₂ lies at 0.53 V, lower than 0.58 V on CNTs-Pt by 50 mV. In Fig. 7 we compared the CO electro-oxidizing rates on CNTs-Pt + CeO₂ and CNTs-Pt. From Fig. 7 we can see that the CO electro-oxidation peak appears at about 1.85 s for CNTs-Pt + CeO₂ while 4.35 s for CNTs-Pt.

Since time (t) for CO electro-oxidation is inversely proportional to the reaction velocity (v), we calculated the percentage of v increase from t , using $(v_2 - v_1)/v_1 = (1/t_2 - 1/t_1)/(1/t_1)$,

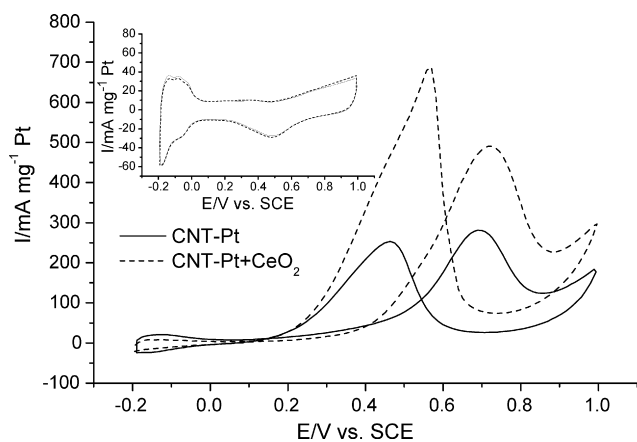


Fig. 4. CV curves for CNTs-Pt and CNTs-Pt+CeO₂ in 1 M HClO₄+1 M CH₃OH. Inset is the corresponding CV curves recorded in 1 M HClO₄.

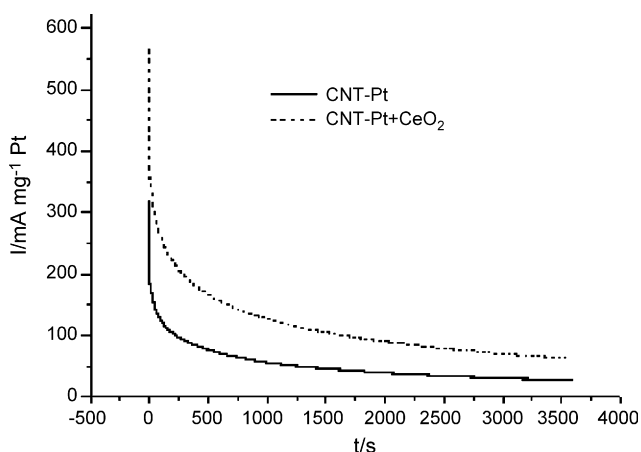


Fig. 5. Chronoamperometry curves for CNTs-Pt and CNTs-Pt+CeO₂ in 1 M HClO₄+1 M CH₃OH at 0.6 V.

in which 2 and 1 denote the case corresponding to CNTs-Pt+CeO₂ and CNTs-Pt, respectively, and obtained a value of 135%. Such a value indicates that the CO electro-oxidation velocity can be greatly increased by mixing CeO₂ with CNTs-Pt. From the above result we have reason to ascribe the increased

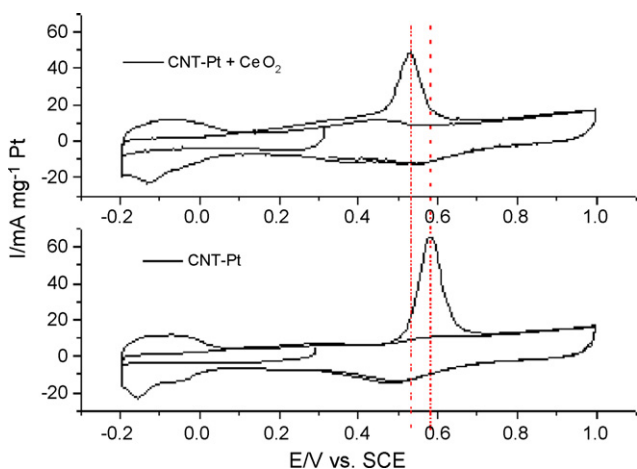


Fig. 6. CO stripping curves for CNTs-Pt and CNTs-Pt+CeO₂ in 1 M HClO₄.

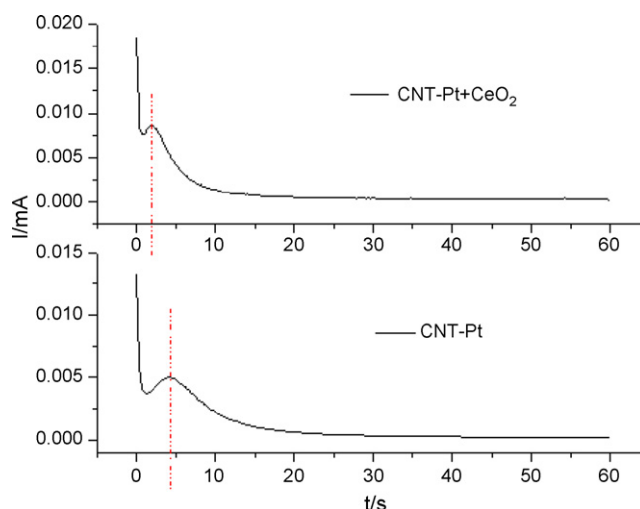


Fig. 7. CO ad-layer electro-oxidation curves for CNTs-Pt and CNTs-Pt+CeO₂, recorded under 0.5 V in 1 M HClO₄.

methanol electro-oxidation current in Fig. 4 to the co-catalyzing effect of CeO₂. However, in the case of methanol electro-oxidation, the I_m is increased by 75% (see Table 1), lower than 135%. Such a difference is understandable because the methanol electro-oxidation is a more complex process and the CO electro-oxidation is only one step in this process.

From the result on CNTs-Pt+CeO₂, we know that CeO₂ can accelerate the CO electro-oxidation kinetics on Pt. Since CO poisoning is a phenomenon occurred on all Pt-based catalyst, we also tested the effect of mixing CeO₂ on PtRu/C, a widely used commercial catalyst from E-Tek Company. The CV curves and chronoamperometry curves are recorded in Figs. 8 and 9, respectively.

From Fig. 8 we can see that after mixing PtRu/C with CeO₂ nanoparticles the methanol electro-oxidizing current was increased by about 60% from 700 to 1140 mA mg⁻¹ and the onset potential also shifted to a lower value. Besides, the chronoamperometry curves in Fig. 9 also supported that CeO₂ can promote the PtRu/C catalysis for methanol electro-oxidation. From Fig. 9 we see that the current for PtRu/C+CeO₂

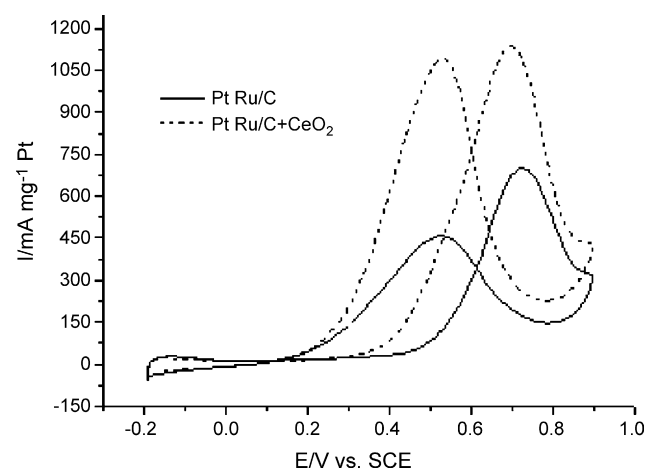


Fig. 8. CV curves for PtRu/C and PtRu/C+CeO₂ in 1 M HClO₄+1 M CH₃OH.

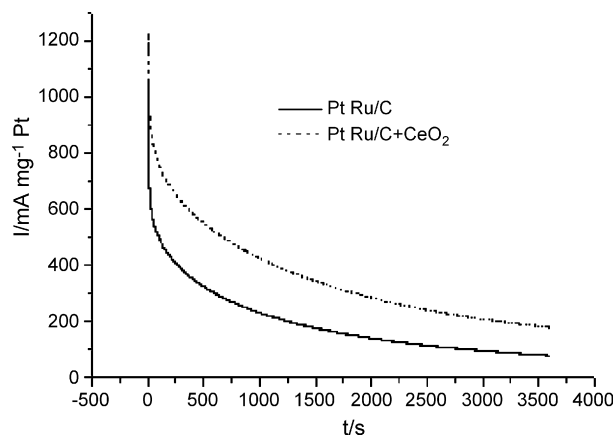


Fig. 9. Chronoamperometry curves for PtRu/C and PtRu/C+CeO₂ in 1 M HClO₄ + 1 M CH₃OH at 0.6 V.

keeps higher than that for PtRu/C during the whole test range. Such a result indicates that the mixed CeO₂ nanoparticles can also promote PtRu/C catalysis greatly during methanol electro-oxidation.

From above we know that the method of mixing CeO₂ nanoparticles with Pt-based catalysts is simple and effective. Therefore, if we can prepare well controlled CeO₂ nanoparticles and other co-catalyzing materials through simple and cheap process, we believe that this method can find wide application in electro-catalysis.

4. Conclusion

Pt particles were prepared through microwave radiation reduction of chloroplatinic acid in ethylene glycol and then adsorbed on carbon nanotubes (CNTs). CeO₂ nanoparticles were prepared through molten salt method. By mixing the CeO₂ nanoparticles with the as-prepared CNTs-Pt and the as-received PtRu/C catalyst, the methanol electro-oxidation current can be promoted greatly. The reason for the increased activity was analyzed and ascribed to the promotion of CO electro-oxidation reaction kinetics by CeO₂. The method of mixing co-catalyzing

materials with Pt-based catalysts is effective and can find wide application in electro-catalysis.

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