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Article (Special Issue on the International Symposium on Environmental Catalysis (ISEC 2016))

Enhanced ethanol electro-oxidation on CeO₂-modified Pt/Ni catalysts in alkaline solution

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ARTICLE INFO

Article history:

Received 29 August 2016

Accepted 22 September 2016

Published 5 February 2017

Keywords:

Direct ethanol fuel cell

Ethanol oxidation

CeO₂ nanoparticle

Composite electrodeposition

Electrocatalyst

ABSTRACT

Pt/Ni catalysts modified with CeO₂ nanoparticles were prepared by simple composite electrodeposition of Ni and CeO₂, and spontaneous Ni partial replacement by Pt processes. The as-prepared CeO₂-modified Pt/Ni catalysts showed enhanced catalytic performance for ethanol electro-oxidation compared with pure Pt/Ni, and acetate species were proposed to be the main products of the oxidation when using these catalysts. The content of CeO₂ in the as-prepared catalysts influenced their catalytic activity, with Pt/NiCe₂ (obtained from an electrolyte containing 100 mg/L CeO₂ nanoparticles) exhibiting higher activity and relatively better stability in ethanol electro-oxidation. This was mainly due to the oxygen storage capacity of CeO₂, the interaction between Pt and CeO₂/Ni, and the relatively small contact and charge transfer resistances. The results of this work thus suggest that electrocatalysts with low price and high activity can be rationally designed and produced by a simple route for use in direct ethanol fuel cells.

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1. Introduction

The electrochemical oxidation of small organic molecules has attracted much attention over the last few decades owing to the development of direct liquid fuel cells. These cells offer many advantages over standard fuel cells, such as easy storage and transportation, high energy densities and high efficiencies [1–4]. Among the small organic molecules under investigation, ethanol has the most potential as a fuel owing to its non-toxicity, high energy density and high availability [5–7]. Pt has been investigated as an effective electrocatalyst in direct ethanol fuel cells (DEFCs) owing to its unique electrocatalytic activity. However, its high price and low poisoning tolerance

towards the CO-like intermediates formed in the ethanol oxidation process hinder its wide application in DEFCs [8]. Thus, numerous studies have sought efficient electrocatalysts for fuel cell applications with high activity and low cost.

Composite nanostructures often present distinct features because close contacts between hybrid materials on the nanoscale can synergistically induce electronic perturbations at the interface and improve the catalytic activity compared with those of the corresponding bulk counterparts. Recently, nanocomposites have been investigated in many fields, including for use as catalysts, adsorbents and electrode materials [9–13]. Pt-based nanocomposites, for example, those decorated with carbon materials, non-precious metals such as Sn or Ni, and/or

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This work was supported by the National Natural Science Foundation of China (21307038 and 21577046), Key Project of Chinese Ministry of Education (212115), and Physical Chemistry Experiment of Huanggang Normal University (2015CK12).

DOI: 10.1016/S1872-2067(16)62560-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 2, February 2017

oxides, have shown enhanced catalytic activities and anti-poisoning abilities in alcohol electro-oxidation relative to the sole Pt catalyst [14–20]. These enhanced properties are due to the modification of the Pt surface electronic structure, the high dispersion of Pt and the bifunctional mechanism involving Pt and the incorporated ingredient. For example, the overpotential for ethanol electro-oxidation was decreased by 200–300 mV by using Pt/Sn catalysts compared with that for pure Pt [21]. Among the previously reported Pt-based nanocomposites, Pt/Ni is a promising candidate because the Ni induces the lowering of the electronic binding energy of the noble metal [22–24]. Moreover, Ni compounds formed in the alcohol electro-oxidation reaction, such as NiOOH, could facilitate the oxidation of the adsorbed CO-like intermediates at lower potentials [25,26]. Chemical and electrochemical reduction methods have been reported for the preparation of Pt/Ni nanocomposites [22,27]. For example, Wu et al. [28] employed a chemical reduction method to synthesize graphene-supported hollow Pt/Ni nanocatalysts, in which K_2PtCl_6 and $NiCl_2 \cdot 6H_2O$ were used as the precursors and $NaBH_4$ as the reducing reagent. Ha et al. [29] prepared a Pt/Ni alloy at potential of -0.4 V (vs. a saturated calomel electrode (SCE)) in a Na_2SO_4 aqueous solution (0.1 mol/L) containing $H_2PtCl_6 \cdot 5H_2O$ and $NiCl_2$. However, the electrodeposited metal oxides and Ni composite supported Pt electrocatalysts have not yet been investigated in detail in DEFCs.

In this work, Ni and CeO_2 nanocomposites supported Pt (Pt/Ni- CeO_2) were prepared for use in ethanol electro-oxidation. Compared with previously reported Pt/Ni catalysts, the addition of CeO_2 nanoparticles (NPs) is expected to enhance the catalytic activity of the Pt catalyst in ethanol electro-oxidation for the following two reasons: (1) co-deposition of CeO_2 with Ni will increase the roughness of the Ni coating, which will increase the number of Ni active sites and thus the number of Pt active sites; (2) the oxygen storage capacity of CeO_2 will generate more active oxygen species [30,31], which will facilitate the oxidation of the intermediates formed during the ethanol electro-oxidation reaction.

2. Experimental

2.1. Catalyst preparation

A Ni coating was electrodeposited on a commercial FTO conducting glass ($2\text{ cm} \times 1.5\text{ cm}$, Southern China Shenzhen Xiang Cheng Technology Co., Ltd) at a constant potential of -1.0 V for 1 h at room temperature under stirring. The electrolyte was $0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa}$. Pt foil with a large surface area was used as the

counter electrode and a saturated calomel electrode was used as the reference electrode. After electrodeposition, the obtained coating was carefully washed with distilled water and dried at 40°C . Then, $0.05\text{ mL H}_2\text{PtCl}_4$ solution ($1\text{ g}/100\text{ mL}$) was applied to the coated surface, and 0.05 mL of a mixed $NaBH_4$ (0.02 mol/L) and $NaOH$ (0.05 mol/L) solution was quickly added to the surface. After the electrocatalyst was dried at 40°C in a drying oven, it was carefully rinsed with distilled water, and the obtained sample was denoted Pt/Ni.

CeO_2 NPs were prepared using a microemulsion-assisted method. In a typical synthesis, a mixture containing 100 mL cyclohexane and 20.5 g polyethylene glycol (PEG 400) was magnetically stirred and heated to 70°C . Then, $20\text{ mL Ce(NO}_3)_4 \cdot 6H_2O$ (0.01 mol) was added and the mixture was stirred for 10 min. Next, 3.50 g NH_3 solution ($27\text{ wt\%}$) was added, and the mixture was aged for 2 h at 70°C . The mixture was separated by centrifugation, and the precipitate was carefully washed with distilled water and ethanol and dried at 80°C overnight.

The preparation process for the CeO_2 -modified Pt/Ni catalyst (Pt/Ni- CeO_2) was the same as that for the Pt/Ni catalyst, except that different amounts of CeO_2 (10 , 20 and 40 mg) were added to 200 mL of the mixed electrolyte ($0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa}$). The catalysts prepared from mixed electrolytes containing 50 , 100 and 200 mg/L CeO_2 NPs (Table 1), were denoted Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4, respectively.

2.2. Characterization

X-ray diffraction (XRD) measurements were carried out using a Philips X'Pert powder X-ray diffractometer (Philips, Netherlands) with $Cu K_\alpha$ radiation ($\lambda = 0.15419\text{ nm}$). The morphology and composition of the as-prepared samples were determined using a JSM-7500 field emission scanning electron microscope (FESEM, JEOL, Japan), linked with an X-Max 50 energy-dispersive X-ray spectrometer (Oxford Instruments, UK). Transmission electron microscopy (TEM) images of CeO_2 NPs were obtained with a JEM-2100F electron microscope (JEOL, Japan). Fourier transform infrared (FTIR) spectra were collected using a Shimadzu IR Affinity-1 FTIR spectrometer in the frequency range $4000\text{--}400\text{ cm}^{-1}$.

2.3. Electrochemical measurements

Multi-cyclic voltammetry and current-time curves were measured on a model LK-2000 microcomputer-based Electroanalysis System (LANLIKE, Tianjin, China). Electrochemical impedance spectroscopy (EIS) was performed on a CHI660E

Table 1

Experimental conditions used in the electrodeposition of active support on an FTO substrate.

Sample	Electrolyte compositions
Pt/Ni	$0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa}$
Pt/NiCe1	$0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa} + 50\text{ mg/L CeO}_2$
Pt/NiCe2	$0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa} + 100\text{ mg/L CeO}_2$
Pt/NiCe4	$0.05\text{ mol/L Ni(NO}_3)_2 + 0.05\text{ mol/L NiSO}_4 + 0.005\text{ mol/L CH}_3\text{COONa} + 200\text{ mg/L CeO}_2$

electrochemical analyzer (Chenhua, Shanghai). The frequency used for EIS ranged from 1 Hz to 10 MHz and the alternating current (AC) signal amplitude was 5 mV. The EIS data were analyzed using Zview software. A classical three-electrode glass cell was used for the electrochemical tests. The prepared samples served as the working electrode, Pt foil with a large surface area as the counter electrode and a saturated calomel electrode as the reference electrode. All measurements were carried out at room temperature, and all reagents are analytical grade and purchased from Chinese Medicine Group Chemical Reagent Co., Ltd.

3. Results and discussion

Fig. 1 shows the XRD patterns of Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4. In the case of Pt/Ni, the diffraction peaks located at 40.1°, 46.7° and 68.6° could be indexed to the (111), (200) and (220) planes of alloyed Pt/Ni [30]. No other noticeable peaks from impurities were observed, which suggests that the bimetallic Pt/Ni catalyst had a relatively high purity. Compared with Pt/Ni, broad peaks with weak intensities were observed for all of the CeO₂-modified Pt/Ni catalysts; this indicates that the bimetallic Pt/Ni had poor crystallinity and/or very small crystallite sizes. This is presumably because co-electrodeposition of CeO₂ prevented the aggregation of Ni on the substrate electrode. A new peak at ca. 32° was observed in the XRD patterns of the CeO₂-modified Pt/Ni catalysts and indicated the

Fig. 1. XRD patterns of Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4.

presence of Ni(OH)₂ [32]. This result indicates that the presence of the CeO₂ NPs facilitates the alteration of the Ni electronic state. In addition, no diffraction peaks related to CeO₂ were observed for Pt/NiCe1 and Pt/NiCe2; this is mainly a consequence of the low CeO₂ content and/or the high dispersion of the CeO₂ NPs. In contrast, a new peak at ca. 28.3° related to the CeO₂ NPs [33] was observed for the Pt/NiCe4 catalyst, confirming the existence of CeO₂ in the as-prepared electrode.

The morphology of Pt/Ni and Pt/NiCe2 is shown in Fig. 2(a)

Fig. 2. SEM images of Pt/Ni (a) and Pt/NiCe2 (b) catalysts, and EDS spectra of Pt/Ni (c) and Pt/NiCe2 (d) electrodes. The inset in Fig. 2(b) shows the TEM image of CeO₂ NPs.

and (b), and the TEM image of the CeO₂ NPs is presented in the inset of Fig. 2(b). These figures show that the two samples presented irregular aggregated NPs. CeO₂ NPs prepared by the microemulsion method are ca. 4–5 nm in diameter. Compared with Pt/Ni, Pt/NiCe₂ consists of relatively small sized aggregated NPs and exhibits a more open nanostructure. This result indicates the effect of CeO₂ NPs (inset in Fig. 2(b)) on the nanostructure of Pt/Ni. Fig. 2(c) and (d) present typical energy-dispersive X-ray spectroscopy (EDS) spectra of the Pt/Ni and Pt/NiCe₂ catalysts. Peaks associated with O, Ni, Pt and Sn were found in both spectra. The O peak originates mainly from the rapid oxidation of the deposited coating and the Sn peak from the FTO substrate. The presence of Ni and Pt peaks confirms that Ni and Pt were successfully deposited on the substrate electrode. A small peak related to Ce is observed in Fig. 2(d), which indicates that CeO₂ was co-electrodeposited with the Ni coating. The EDS analysis shows that the Pt:Ni ratios of the Pt/Ni, Pt/NiCe₁, Pt/NiCe₂ and Pt/NiCe₄ catalysts were 8.2:1, 6.4:1, 3.7:1 and 2.4:1, respectively.

The electrocatalytic properties of Pt/Ni, Pt/NiCe₁, Pt/NiCe₂ and Pt/NiCe₄ for ethanol oxidation were investigated in 1 mol/L NaOH + 1 mol/L C₂H₅OH by CV as shown in Fig. 3(a). For all electrodes, the two typical oxidation peaks of ethanol were observed in the forward and backward scans [34]. The peak in the forward scan was attributed to the oxidation of freshly chemisorbed species in the mixed solution, and the peak in the backward scan to the removal of carbonaceous species formed during the ethanol oxidation process. The most visible difference observed for Pt/Ni-CeO₂ was the higher peak current density compared with that of Pt/Ni, which indicates the higher activity of the CeO₂-modified Pt/Ni electrode. This could be attributed to the oxygen storage capability of CeO₂, which could produce active oxygen species and facilitate ethanol electro-oxidation [35,36]. Moreover, the peak current in the forward scan increased with increasing CeO₂ content and the peak potential shifted to a positive potential, illustrating the effect of CeO₂ content on the catalytic activity in ethanol electro-oxidation. A similar phenomenon was observed by Neto et al. [37], who reported that the catalytic performance increased

Table 2

Comparison of the electrochemical performances of ethanol oxidation on the as-prepared electrodes in a 1 mol/L ethanol + 1 mol/L NaOH solution.

Electro-catalyst	E_{on} (V)	E_p (V)	i_p (mA/mg _{Pt})	R_c (Ω /mg _{Pt})	R_t (Ω /mg _{Pt})	CeO ₂ ^a (wt%)
Pt/Ni	-0.641	0.15	9.43	150	15.3	—
Pt/NiCe ₁	-0.676	0.36	22.3	100	218.3	0.21
Pt/NiCe ₂	-0.720	0.45	59.6	75	48.9	0.37
Pt/NiCe ₄	-0.686	0.63	87.6	80	29.8	0.69

^a Determined by EDS.

with increasing CeO₂ content until a plateau was reached. The onset potential (E_{on}) for ethanol oxidation (Table 2) shown in the enlarged image during the positive scan (−0.9→+0.2 V, Fig. 3(b)) followed the sequence Pt/NiCe₂ < Pt/NiCe₄ < Pt/NiCe₁ < Pt/Ni. This suggests that the addition of CeO₂ facilitates ethanol electro-oxidation. However, the positive shift of the peak potential with increasing CeO₂ content mainly resulted from the higher amount of oxidized ethanol species adsorbed on the surface of the electrocatalyst. This required a more positive potential to oxidize the new freshly adsorbed ethanol species on the surface.

Fig. 4 presents the relationship between the forward peak current density (i_p) and the number of potential cycles for the Pt/Ni, Pt/NiCe₁, Pt/NiCe₂ and Pt/NiCe₄ electrodes. The peak current densities for ethanol electro-oxidation decreased with increasing numbers of CV cycles for all of the catalysts. This was mainly due to the reconstruction of the electrocatalysts during the potential cycling, as well as the poisoning of the catalysts. The decrease in peak current density for Pt/Ni, Pt/NiCe₁, Pt/NiCe₂ and Pt/NiCe₄ after 100 cycles was 42.0%, 34.3%, 13.1% and 39.1%, respectively. This indicates that Pt/NiCe₂ was relatively more stable towards ethanol electro-oxidation. In addition, the CeO₂-modified electrocatalysts showed considerably higher peak currents than did pure Pt/Ni, which further suggests that CeO₂ modification could improve the activity of the catalysts over extended testing periods.

Fig. 5 shows the FTIR spectra of the Pt/Ni, Pt/NiCe₁,

Fig. 3. (a) The first cyclic voltammogram of ethanol electro-oxidation and (b) enlarged image (−0.9→+0.2 V) during the positive scan with Pt/Ni, Pt/NiCe₁, Pt/NiCe₂ and Pt/NiCe₄ electrodes in 1 mol/L NaOH + 1 mol/L C₂H₅OH aqueous solution at a scan rate of 50 mV/s.

Fig. 4. Change in the peak current density (i_p) as a function of the number of potential cycles for the Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4 electrodes.

Pt/NiCe2 and Pt/NiCe4 electrodes before and after the ethanol electro-oxidation test in 1 mol/L C_2H_5OH + 1 mol/L NaOH. The broad band centered at ca. 3352 cm^{-1} and the small peak at ca. 1646 cm^{-1} in the spectra of the Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4 electrodes before ethanol electro-oxidation were respectively attributed to the stretching and bending vibrations of OH in adsorbed water. Moreover, the sharp peak at ca. 1113 cm^{-1} in these spectra was attributed to the sulfate ion residues, and the peak at ca. 614 cm^{-1} was associated with the Ni–O stretching vibrations [38]. The Pt/Ni catalyst presented a similar FTIR spectrum after ethanol electro-oxidation to that obtained before ethanol electro-oxidation. However, the CeO_2 -modified Pt/Ni catalysts showed three new FTIR peaks after ethanol electro-oxidation compared with their spectra before the test. Two of these new peaks appeared at ca. 1543 and 1374 cm^{-1} could be ascribed respectively to the asymmetric and symmetric stretching of COO [39]. This result indicates

Fig. 5. FTIR spectra of Pt/Ni (1), Pt/NiCe1 (3), Pt/NiCe2 (5) and Pt/NiCe4 (7) before ethanol electro-oxidation, and Pt/Ni (2), Pt/NiCe1 (4), Pt/NiCe2 (6) and Pt/NiCe4 (8) after ethanol electro-oxidation.

the possible formation of acetate species during the ethanol electro-oxidation process, which agrees with previous reports [40,41]. The peak at ca. 929 cm^{-1} was attributed to the vibration of the C=C fragment, which further confirmed that ethanol oxidation occurred on the CeO_2 -modified Pt/Ni catalysts. However, an in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) investigation is needed to fully explore the mechanism of ethanol oxidation on the as-prepared electrocatalysts.

Fig. 6 shows the current–time curves for ethanol electro-oxidation on Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4 electrodes in 1 mol/L NaOH + 1 mol/L C_2H_5OH solution at a potential of 0.15 V. The current densities for all of the electrocatalysts decreased quickly in the first 600 s, and then decreased gradually with increasing test time. The fast decline in the current density at the initial stage mainly resulted from the charging current of the pseudo-capacitance on the electrodes; the following slow decay was related to the poisoning of the catalysts by chemisorbed carbonaceous species formed in the ethanol electro-oxidation process [42]. However, the CeO_2 -modified catalysts showed a higher current density than that of Pt/Ni. This indicates their superior activity and poisoning tolerance compared with the Pt/Ni catalyst. This enhancement in the activity of the Pt catalyst caused by CeO_2 was attributed to the bifunctional mechanism, in which CeO_2 facilitates the formation of chemisorbed oxygen species and the oxidation of adsorbed species such as carbon monoxide on the Pt surface [43–46]. Pt/NiCe2 exhibited the highest current density among all of the studied catalysts, which is consistent with the CV results.

EIS measurements were carried out to compare the reaction kinetics of ethanol oxidation at the prepared electrodes. Fig. 7 shows the typical Nyquist plots of the prepared electrodes in 1 mol/L NaOH + 1 mol/L C_2H_5OH solution. The Nyquist plots consist of two depressed capacitive semicircles at high and low frequencies. The depressed semicircle in the high frequency region corresponds to the contact capacitance (CPE1) in parallel with the contact resistance (R_c) of the NPs, and the low frequency semicircle is attributed to the charge transfer resistance (R_t) in parallel with the double layer capacitance (CPE2) [47].

Fig. 6. Current–time curves of Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4 electrocatalysts in 1 mol/L NaOH + 1 mol/L C_2H_5OH solution at a potential of 0.15 V.

Fig. 7. Nyquist plots for Pt/Ni, Pt/NiCe1, Pt/NiCe2 and Pt/NiCe4 in 1 mol/L NaOH + 1 mol/L C₂H₅OH solution at a potential of 0.10 V.

The experimental data were analyzed using non-linear least-squares (NLLS) and the electrical equivalent circuit is displayed in the inset of Fig. 7. In the equivalent circuit, R_s is the total ohmic resistance of the electrode system and CPE is a constant phase element associated with the double layer capacity of the electrodes. The fitting values of R_c and R_t are listed in Table 2. Among the studied electrodes, Pt/NiCe2 showed relatively smaller R_c and R_t values, which is one of the reasons why this electrode exhibited relatively higher catalytic performance for ethanol electro-oxidation.

4. Conclusions

Pt/Ni catalysts modified with CeO₂ NPs were successfully obtained by composite electrodeposition of Ni and CeO₂ and substitution reaction processes. Incorporation of CeO₂ enhanced the catalytic performance of Pt/Ni towards ethanol electro-oxidation. Based on FTIR analysis, acetate species were

proposed to be the main product of the ethanol electro-oxidation process on the CeO₂-modified Pt/Ni catalysts. In addition, the amount of deposited CeO₂ influenced the catalytic performance of the prepared catalysts. Among the investigated electrocatalysts, Pt/NiCe2 showed relatively higher activity and better stability. This was mainly attributed to the oxygen storage capacity of CeO₂ and the relatively smaller contact and charge transfer resistances.

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Graphical Abstract

Chin. J. Catal., 2017, 38: 305–312 doi: 10.1016/S1872-2067(16)62560-3

Enhanced ethanol electro-oxidation on CeO₂-modified Pt/Ni catalysts in alkaline solution

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CeO₂-modified Pt/Ni catalysts containing aggregated nanoparticles and relatively open nanostructures showed enhanced catalytic activity towards ethanol electro-oxidation in alkaline solution compared with unmodified Pt/Ni catalysts.

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CeO₂修饰的Pt/Ni催化剂在碱性溶液中对乙醇电催化氧化性能的增强

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摘要: 有机小分子直接燃料电池具有高能量密度和转换效率、易贮存及运输方便等优点。在过去几十年, 有机小分子化合物尤其是乙醇的电催化氧化引起了研究者的关注, 高活性和稳定性及低价格的电催化剂的设计和制备一直是乙醇燃料电池的研究热点。本文采用复合电沉积方法制备了Ni和CeO₂复合镀层, 然后利用Ni置换铂前驱体中Pt的方法制备了纳米CeO₂修饰的Pt/Ni电催化剂(Pt/Ni-CeO₂)。采用X射线衍射(XRD)、扫描电子显微镜(SEM)及能谱仪(EDS)等手段表征了所制样品的组成和相结构、表面形貌及组成成份。

XRD结果表明, 所制Pt/Ni催化剂主要是PtNi合金相结构。与Pt/Ni相比, Pt/Ni-CeO₂催化剂的XRD峰强明显变弱, 表明纳米CeO₂修饰的Pt/Ni电催化剂的结晶性较差或者其晶体颗粒较小。这可能是由于CeO₂的共沉积阻止了Ni纳米颗粒的进一步生长或团聚。当电镀液中CeO₂含量为50和100 mg/L时, 所制Pt/Ni-CeO₂催化剂样品Pt/NiCe1和Pt/NiCe2的XRD谱上未观察到CeO₂相关的衍射峰, 这主要可归因于催化剂中沉积的CeO₂量少或其高度分散。随着电镀液中CeO₂浓度进一步增大到200 mg/L时, 在Pt/Ni-CeO₂催化剂(Pt/NiCe4)的XRD谱上出现了CeO₂相关的衍射峰。这表明采用复合电沉积-化学还原法可以成功制备CeO₂修饰的Pt/Ni电催化剂。SEM结果显示, 所制催化剂都是由团聚状态的纳米颗粒组成, 并且Pt/NiCe₂表现出比Pt/Ni更开放的微结构, 从而有利于反应物扩散至催化剂内部。该结果进一步表明共沉积的CeO₂对所制Pt/Ni催化剂微结构的影响。此外, EDS结果也证实成功制备了CeO₂修饰的Pt/Ni电催化剂。

采用多次循环伏安、电流时间曲线和电化学阻抗谱(EIS)等手段研究了所制电催化剂的电化学性能。与Pt/Ni相比, Pt/Ni-CeO₂催化剂表现出更好的电催化氧化乙醇活性和稳定性, 这可能与CeO₂的贮氧特性及其共沉积增大了电极的粗糙度有关。红外光谱测试结果表明, 在CeO₂修饰的Pt/Ni电催化剂催化氧化乙醇过程中, CH₃COO⁻可能是乙醇氧化的主要产物。在所制催化剂中, CeO₂含量影响其电催化氧化乙醇性能。循环伏安和电流时间曲线测试结果表明, 随着催化剂中CeO₂

含量增大, 催化剂活性先增加后减弱. 电化学阻抗谱结果表明, 随着 CeO_2 含量增大, CeO_2 修饰的Pt/Ni电催化剂的接触电阻先增大后变小再变大; 而电荷转移电阻不断变小. 在电解液中含有100 mg/L CeO_2 时所制电催化剂(Pt/NiCe₂)具有最佳的电催化氧化乙醇活性和稳定性. 这主要与 CeO_2 的贮氧功能、Pt与 CeO_2 /Ni间的相互作用和其较小的接触电阻和电荷转移电阻有关. 该结果可为设计和制备低价格、高活性乙醇燃料电池中的催化剂提供思路.

关键词: 直接乙醇燃料电池; 乙醇氧化; 纳米二氧化铈; 复合电沉积; 电催化剂

收稿日期: 2016-08-29. 接受日期: 2016-09-22. 出版日期: 2017-02-05.

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基金来源: 国家自然科学基金(21307038, 21577046); 教育部重点项目(212115); 黄冈师范学院物理化学实验改革项目(2015CK12).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).