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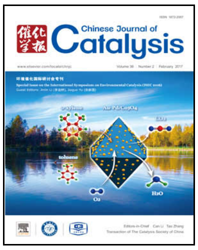

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Enhanced ethanol electro-oxidation on CeO_2-modified Pt/Ni catalysts in alkaline solution

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ABSTRACT

Pt/Ni catalysts modified with CeO_2 nanoparticles were prepared by simple composite electrodeposition of Ni and CeO_2, and spontaneous Ni partial replacement by Pt processes. The as-prepared CeO_2-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 CeO_2 in the as-prepared catalysts influenced their catalytic activity, with Pt/NiCe2 (obtained from an electrolyte containing 100 mg/L CeO_2 nanoparticles) exhibiting higher activity and relatively better stability in ethanol electro-oxidation. This was mainly due to the oxygen storage capacity of CeO_2, the interaction between Pt and CeO_2/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.

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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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 $NiCl_2·6H_2O$ 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 $H_2PtCl_6·5H_2O$ 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 cm × 1.5 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 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa. 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 mL H_2PtCl_4 solution (1 g/100 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 mL $Ce(NO_3)_4·6H_2O$ (0.01 mol) was added and the mixture was stirred for 10 min. Next, 3.50 g NH_3 solution (27 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 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa). 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_α radiation (λ = 0.15419 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 4000–400 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 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa
Pt/NiCe1	0.05 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa + 50 mg/L CeO_2
Pt/NiCe2	0.05 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa + 100 mg/L CeO_2
Pt/NiCe4	0.05 mol/L $Ni(NO_3)_2$ + 0.05 mol/L $NiSO_4$ + 0.005 mol/L CH_3COONa + 200 mg/L CeO_2