

Short communication

High performance rare earth oxides LnO_x ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}$ and Nd) modified Pt/C electrocatalysts for methanol electrooxidation

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Abstract

In this paper, the LnO_x ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}$ and Nd) modified Pt/C catalysts were prepared by wet precipitation and reduction method. The catalysts were characterized by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and X-ray diffraction (XRD). TEM showed that the Pt- PrO_x nanoparticles were uniformly dispersed on carbon with an average particle size of 5.0 nm in the $\text{Pt}_3\text{-(PrO}_x)_1/\text{C}$ catalyst. EDX showed that Pt and Pr were successfully loaded on the carbon support without obvious loss. XRD showed that all the Pt/C and LnO_x modified Pt/C electrocatalysts (except for the $\text{Pt}_3\text{-(ScO}_x)_1/\text{C}$ electrocatalyst) displayed the typical character of Pt face centered cubic (fcc) phase, whereas the $\text{Pt}_3\text{-(ScO}_x)_1/\text{C}$ electrocatalyst contained the diffraction pattern of Pt face centered cubic and Sc_2O_3 phase. LnO_x modified Pt/C electrocatalysts were compared with Pt/C in terms of the electrochemical activity and stability for methanol electrooxidation using cyclic voltammetry (CV) and chronoamperometry (CA) in 0.5 M $\text{H}_2\text{SO}_4 + 0.5 \text{ M CH}_3\text{OH}$ solutions. The results showed that all the LnO_x (except for NdO_x) modified the Pt/C electrocatalysts gave higher catalytic activity and stability than Pt/C. In particular, the $\text{Pt}_3\text{-(PrO}_x)_1/\text{C}$ electrocatalyst was found to be superior than others. Under this respect, several Pt- PrO_x/C catalysts with different atomic ratio of Pt/Pr were also identically prepared and characterized. It was found by CV and CA that the $\text{Pt}_3\text{-(PrO}_x)_1/\text{C}$ and $\text{Pt}_1\text{-(PrO}_x)_1/\text{C}$ catalysts showed better catalytic activity and stability than the $\text{Pt}_5\text{-(PrO}_x)_1/\text{C}$, $\text{Pt}_1\text{-(PrO}_x)_3/\text{C}$ and Pt/C catalysts. The $\text{Pt}_3\text{-(PrO}_x)_1/\text{C}$ and $\text{Pt}_1\text{-(PrO}_x)_1/\text{C}$ catalysts had high catalytic activity and good stability, which could be used as novel electrocatalysts for direct methanol fuel cell.

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1. Introduction

In the past decades, direct methanol fuel cells (DMFCs) have attracted extensive attention due to its advantages of low operating temperature ($<100^\circ\text{C}$), easy transportation and storage of fuel, high energy efficiency, low exhaustion and fast start-up of fuel [1–3]. However, two problems of the slow reaction of anode methanol oxidation at low temperature and the methanol crossover from anode to cathode are the main challenge for the commercialization of DMFCs [4]. Pt is the most active electrocatalyst for the oxidation of methanol, but intermediates species CO remain adsorbed on the surface and inhibit the oxidation reaction [5]. Therefore, Pt-based alloy or nanocomposite catalysts by alloying or mixing platinum with other elements need

to be designed and synthesized. The CO poisoned platinum can be regenerated via the reaction of surface CO with oxygen species associated with an oxophilic element such as ruthenium to yield CO_2 [6]. High activity, stability and CO-tolerance of Pt-based electrocatalysts under acid environment are suitable for electrooxidation of many small chemicals molecular such as methanol. So it is necessary to prepare some effective anode catalysts satisfying with the properties mentioned above. In order to improve the activity of methanol electrooxidation, many catalysts such as PtRu, PtSn, PtRe and PtOs [7–10], and many preparation methods such as impregnation, colloid and microemulsion [11–13] have been applied.

In recent years, it is found that certain metal oxides, such as RuO_2 [14], WO_3 [15], ZrO_2 [16], MgO [17] and CeO_2 [18], can enhance the catalytic activity for ethanol or methanol electrooxidation through synergetic interaction with Pt. Among those, rare earth oxides exhibit a number of characteristics that make them interesting for catalytic studies. For example, ceria is a

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fluorite oxide, whose cation can switch between +3 and +4 oxidation states and ceria-based catalysts have been investigated for water–gas shift reactions [19]. Recently, ceria-based electrocatalysts have also been reported by Xu and Shen [18] and Cabrera and co-workers [20]. However, though these electrocatalysts show an improved performance according to the report of Xu and Shen [18], the reaction environment is alkaline, not acid media. In addition, other rare earth oxides may have better performance than ceria, but have not been reported up to now. In this paper, we choose the wide-used rare earth oxides LnO_x ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}, \text{Ce}, \text{Pr}$ and Nd) as modifications to prepare the catalysts for methanol electrooxidation in acid electrolyte. The electrocatalytic activity and stability was evaluated using cyclic voltammetry (CV) and chronoamperometry (CA). The catalysts were characterized by means of XRD, TEM and EDX analysis.

2. Experimental details

2.1. Chemicals

All chemicals were analytically pure and used as received. The precursors of Y, La and Ce were their corresponding nitrates and the precursors of Sc and Pr were their corresponding oxides. The NdCl_3 and H_2PtCl_6 were used as precursors of Nd and Pt, respectively. All of the chemical reagents used in this article were purchased from Shanghai Chemical Reagents Corporation. Active carbon of Vulcan XC-72 with a BET area of about $240 \text{ m}^2 \text{ g}^{-1}$ (Cabot Corp.) was used as a carrier.

2.2. Catalyst preparation

Rare earth oxides modified Pt/C electrocatalysts, such as Pt- ScO_x/C , Pt- YO_x/C , Pt- LaO_x/C , Pt- CeO_x/C , Pt- PrO_x/C and Pt- NdO_x/C were prepared according to the report [16] with some modifications. First, Sc_2O_3 and Pr_2O_3 were dissolved in 1.0 mL of concentrated HNO_3 . Then the rare earth precursors were dissolved in 20 mL of mixture of distilled water and ethanol ($v:v = 1:1$) and mixed with 129.6 mg of carbon black (Vulcan XC-72). After ultrasonically mixed for 10 min, 2 mL of 0.02 M Na_2CO_3 aqueous solutions were then added into the mixture to form precipitates. The precipitates were washed with distilled water and dried in oven at 373 K for 10 h. The materials were finally calcinated at 600 °C for 2 h in Ar atmosphere to obtain LnO_x/C . Pt- LnO_x/C catalysts were prepared by reducing of H_2PtCl_6 with excessive NaBH_4 on LnO_x/C powders. The amount of H_2PtCl_6 was varied to control the molar ratio of Pt to LnO_x in the final catalysts. The nominal loading of Pt + LnO_x in the catalysts was 10%. All catalysts were marked as $\text{Pt}_m(\text{LnO}_x)_n/\text{C}$, where the subscript denoted the atomic ratio of Pt with LnO_x .

2.3. Physical characterization

The samples after reaction were transferred under a N_2 atmosphere to the diffractometer, and powder X-ray diffraction (XRD) patterns of the samples were recorded on a Rigakel B/Max-RB diffractometer with a nickel filtrated $\text{Cu K}\alpha$ radi-

ation. 2θ angles from 10° to 90° were recorded at a scanning speed of 2° min^{-1} .

Specimens were prepared for TEM analysis by ultrasonically suspending the catalyst powder in ethanol. A drop of suspension was then applied onto clean copper grids and dried in air. Samples were examined using the JEOL JEM-2010 electron microscope operated at 100 kV. The bulk composition of the as-prepared catalysts was evaluated by energy dispersive X-ray analysis (EDX) in a transmission electron microscopy.

2.4. Preparation of electrodes and electrochemical measurements

Electrochemical activities of catalysts were measured by cyclic voltammetry and chronoamperometry method using a standard three-electrode cell at the computer-controlled CHI660A electrochemical workstation. Five milligram of catalysts were suspended in 1.0 mL ethanol and 20 μL 10.0% Nafion was added as adhesive and proton conductor. The mixtures were ultrasonically scattered for 10 min to form homogeneous ink. Then, 20 μL ink was dropped on the glassy carbon (GC) electrode to act as the working electrode. A Pt wire and saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. Methanol oxidation experiment was measured in a solution of 0.5 M H_2SO_4 + 0.5 M CH_3OH at room temperature. For all experiments the sweep rate was 50 mV s^{-1} . The chronoamperometry curves were investigated in a solution of 0.5 M H_2SO_4 + 0.5 M CH_3OH at 0.65 V at room temperature. The unit of mA mg^{-1} used in the article was the theory loadings of Pt without accounts the actual loadings.

3. Results and discussion

The different diffractograms of various LnO_x modified Pt/C catalysts and Pt- PrO_x/C catalysts with different ratios are shown in Figs. 1 and 2. By examining the XRD patterns reported in Figs. 1 and 2, there are no obvious differences among those

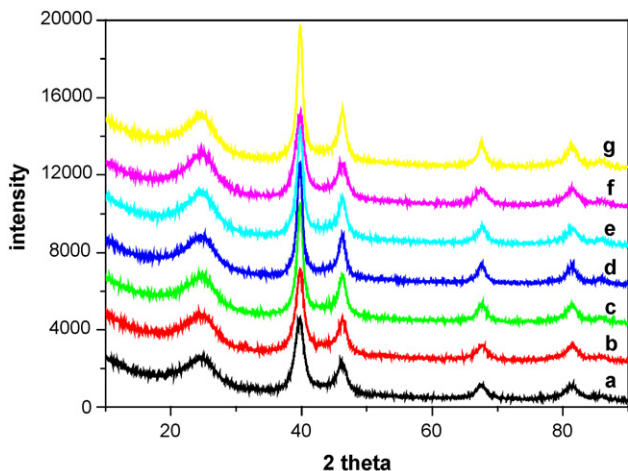


Fig. 1. X-ray diffraction patterns of the Pt/C and LnO_x modified Pt/C electrocatalysts. (a) Pt/C; (b) $\text{Pt}_3\text{-(ScO}_x)_1/\text{C}$; (c) $\text{Pt}_3\text{-(YO}_x)_1/\text{C}$; (d) $\text{Pt}_3\text{-(LaO}_x)_1/\text{C}$; (e) $\text{Pt}_3\text{-(CeO}_x)_1/\text{C}$; (f) $\text{Pt}_3\text{-(PrO}_x)_1/\text{C}$; (g) $\text{Pt}_3\text{-(NdO}_x)_1/\text{C}$.

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