Synthesis and characterization of non-precious metal binary catalyst for oxygen reduction reaction in proton exchange membrane fuel cells

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ABSTRACT

A promising non-precious metal FeCoTETA/C catalyst has been easily synthesized, by chelating Fe and Co with triethylenetetramine (TETA) in ethanol followed by pyrolyzing in an Ar atmosphere, as electrocatalyst for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). The catalyst has been characterized with various physicochemical techniques as well as electrochemical analysis and single cell performance measurement. The results showed that nano-intermetallic FeCo particles and several types of N and O species are present on carbon matrix. The catalyst delivers better electrocatalytic activity toward ORR compared with CoTETA/C catalyst, the %H_2O_2 is about 10% with an electron-transfer number of around 3.8. The PEMFC with this catalyst in cathode reaches a maximum power density of 256 mW cm^{-2} and has a current density of 514 mA cm^{-2} at 500 mV.

1. Introduction

Renewable energy sources attract growing attention to fulfill the energy requirements in the future while simultaneously reduce environment pollution. Cheap efficient catalysts with abundant raw materials for oxygen reduction reaction (ORR) are strongly needed in order for large scale commercialization of proton exchange membrane fuel cells (PEMFCs). Until now, Pt-based catalysts have been approved to be the best ones for the ORR in PEMFCs. However, Pt is an expensive metal of limited supply. Therefore, partial or complete replacement of Pt with non-precious metal in ORR catalysts is of worldwide interest and much progress has been made so far [1–3]. Some Pt-free catalysts, such as Fe/N/C [4], carbonized hemoglobin [5], CoTMPP/C [6], Co-PPy/C [7–9], and CoTETA/C [10], have been successfully developed in recent years and have shown promising catalytic performance toward ORR in PEMFCs.

The activity and selectivity of a monometallic catalyst can be greatly improved if a second metal is introduced to form a bimetallic catalyst. Typical examples are PtPd [11] and Pt$_3$Ni(1 1 1) [12] bimetallic catalysts. The introduction of Pd or Ni has significantly enhanced the catalytic activity compared with a Pt monometallic catalyst [11,12]. Metal alloys supported on carbon powder are commonly employed as heterogeneous catalysts. For example, Pt-based alloy/carbon nanocomposites, such as PtCo/C, PtNi/C and PtCr/C [13,14], are receiving great attention as cathode catalysts for low temperature fuel cells. Heat-treated binary-metal tetraphenyl-porphyrin (TMTPP, TM = V/Fe, Co/Fe, Ni/Fe, and Cu/Fe) have shown excellent activity toward ORR [15]. These catalysts were usually prepared from mixed-metal carbonyl cluster complexes or mixed metal macrocycle compounds, which caused high cost and difficult preparation.

A discovery of improved catalysts with low-cost, such as cheap and abundant raw materials, is the most favorite for wide use in PEMFCs. Recently, we have employed triethylenetetramine (TETA), a simple and cheap ligand, to prepare non-precious metal Co-based catalyst for the ORR [10–12]. Furthermore, we have found that the 3d transitional metals play an important role on the catalytic performance of metal-TETA/C catalysts [16]. In this paper, we study the catalytic activity of the binary catalyst when Co is partly replaced by Fe, in order to further improve the catalytic performance of CoTETA/C catalyst and reduce the cost. The structure and morphology of the obtained FeCoTETA/C catalyst have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) combined with energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS). Electrochemical performance of the catalyst toward ORR has been demonstrated by cyclic voltammogram (CV), rotating disk electrode (RDE), and rotating ring-disk electrode (RRDE) measurements in oxygen-saturated acidic solution, as well as in a single PEMFC test.

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2. Experimental

2.1. Catalysts preparation

A facile synthetic method was adopted as described elsewhere with some modification [10–12,16]. Briefly, 0.202 g cobalt chloride and 0.242 g iron chloride were dissolved in 50 ml ethanol. Next, 1 ml triethylenetetramine ($H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$, TETA) was added into the obtained solution followed by 1 g BP 2000. The resulted solution was stirred for 1 h and then dried by rotary evaporator under vacuum. The obtained powder was heat-treated at 800 °C for 90 min in an Ar atmosphere with the temperature raising rate of 5 °C min^{-1}. The total nominal loading of Co and Fe with respect to carbon was kept at 10 wt%. A CoTETA/C catalyst was also prepared with the same procedure for comparison, the amount of used cobalt chloride is 0.404 g to keep the same nominal loading of metal (10 wt%) with respect to carbon in both the FeCoTETA/C catalyst and the CoTETA/C catalyst.

2.2. Physical characterization

The XRD was performed on an automated Rigaku diffractometer equipped with a Cu Kα radiation at a tube current of 30 mA and a tube potential of 40 kV. Data acquisition was recorded in the 2θ range from 20° to 80° at a scan rate of 6° min^{-1}. The PDF (powder diffraction file database) from the ICDD (International Centre for Diffraction Data) was used as reference to interpret peak assignments in the XRD spectra.

TEM and EDX measurements were performed at a JEOL JEM-2010 operating at 200 keV. The catalyst was ultrasonically stirred in ethanol absolute for 5 min. A drop of the solution was deposited onto a carbon-coated copper grid and left in air to dry.

Electronic structures of C, N and O on the catalyst surface were evaluated by XPS, which was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Kα radiation ($h\nu$ = 1253.6 eV). The sample was directly pressed to a self-supported disk (10 mm × 10 mm) and mounted on a sample holder then transferred into the analyzer chamber. The whole spectra and the narrow spectra of several elements with high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the AugerScan 3.21 software. Binding energies were calibrated by using the containment carbon (C1s = 284.6 eV). The data analysis was carried out by using the RBD AugerScan 3.21 software provided by RBD Enterprises or XPSPeak4.1 provided by Raymund W.M. Kwok (The Chinese University of Hongkong, China).

2.3. Electrochemical characterization

Electrochemical characterizations were performed in a single-compartment, three-electrode cell filled with 0.5 M H_2SO_4 solution at room temperature. A rotating disk electrode with a glassy carbon disk (4.0 mm in diameter) was used as the working electrode. A Pt wire and a saturated calomel electrode were used as the counter and reference electrode, respectively. All potentials in this paper are referred to the normal hydrogen electrode (NHE). An ink-type electrode was prepared as follows: 5 mg finely ground catalyst powder, 0.5 ml doubly distilled water and 50 μl 5 wt% Nafion solution were blended in an ultrasonic bath, then 10 μl of this ink was deposited onto the surface of a glassy carbon disk and air-dried for use.

Before electrochemical measurements, the electrolyte solution was purged with pure oxygen for 15 min. Then, cyclic voltammograms (CVs) were repeated at a potential sweep rate of 50 mV s^{-1} in a range from 1.04 V to 0.04 V to remove any impurities and reach a steady performance. A CV curve was then recorded at the potential scan rate of 5 mV s^{-1}. For rotating disk electrode (RDE) study, the current–potential polarization curves were obtained at various electrode rotation speeds from 100 rpm to 900 rpm. For rotating ring-disk electrode (RRDE) study, a Pt disk-Pt ring electrode (5 mm in diameter for the Pt-disk) was employed, and 10 μl of the catalyst ink prepared with the same procedure was dropped onto the disk only, and the ring potential was kept at 1.2 V.

All electrochemical measurements were operated using a 750A bipotentiostat (CHI instrument, USA) along with a 636 RRDE system (Pine instrument, USA) at room temperature.

2.4. Single cell test

Single cell performance based on FeCoTETA/C as well as Pt/C as cathode catalyst, respectively, was examined under actual H_2–O_2 PEMFC condition. The surface area used for the fuel cell test was 2.5 cm × 2.5 cm. The preparation of MEA follows the procedure described in literature [17]. A non-precious metal cathode electrode was formed by ultrasonically blending 20 mg FeCoTETA/C catalyst powder with 0.2 g 5 wt% Nafion® solution in ethanol for 1 h and depositing the ink on the gas diffusion layer. A Pt/C cathode electrode was prepared by ultrasonically blending 20 mg 20 wt% Pt/C catalyst powder (Johnson Matthey) with 0.2 g 5 wt% Nafion® solution in ethanol for 1 h and depositing the ink on the gas diffusion layer. The anode with Pt loading of 1 mg cm^{-2} was formed using a catalyst paste prepared by dispersing 10 mg 20 wt% Pt/C into a solution containing ethanol absolute and 0.1 g 5 wt% Nafion® solution. Both hydrogen and oxygen were non-humidified and passed into the apparatus at 200 ml min^{-1}. The current–potential relationships were recorded at 50 °C when the fuel cell performance was steady.

3. Results and discussion

3.1. XRD analysis

Fig. 1 displays the XRD patterns of (a) the FeCoTETA/C catalyst and (b) the CoTETA/C catalyst. The standard diffraction peaks of FeCo (PDF 65-4131) and α-Co (PDF 89-4307) are also shown for comparison. Several characteristics could be found in Fig. 1: (1) for each catalyst, there is a large broad diffraction peak around 24.5° which can be ascribed to the characteristic peak of the C(0 0 2); (2) for the FeCoTETA/C catalyst, there are two diffraction peaks at 45° and 65°, which can be ascribed to the characteristic peaks of FeCo(1 1 0) and FeCo(2 0 0), respectively. This indicates that face-centered cubic (*fcc*) crystalline FeCo particles appear on carbon matrix in the FeCoTETA/C catalyst; and (3) the CoTETA/C catalyst
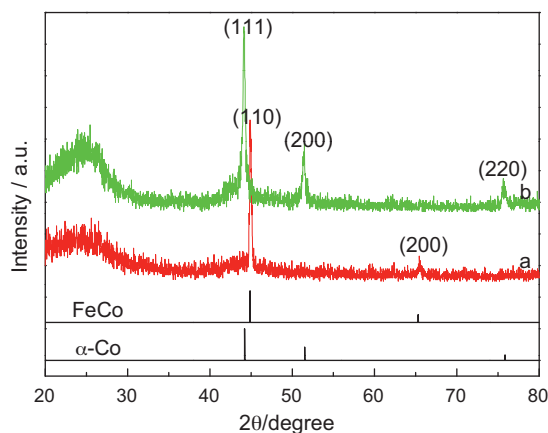

Fig. 1. XRD patterns of (a) the FeCoTETA/C catalyst and (b) the CoTETA/C catalyst. Standard characteristic diffraction peaks of FeCo (PDF 65-4131) and α-Co (PDF 89-4307) are also shown for comparison. Each spectrum is arbitrarily shifted for easier comparison.