Electrochemistry Communications 88 (2018) 19–23

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

A CeO_2 modified phenylenediamine-based Fe/N/C with enhanced durability/stability as non-precious metal catalyst for oxygen reduction reaction

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ARTICLE INFO

Keywords:
CeO_2
H_2O_2
Fe/N/C catalyst
Durability/stability
Oxygen reduction reaction

ABSTRACT

The poor durability/stability of non-precious metal catalysts (NPMCs) hampers their substitution for Pt-based catalysts. Here, phenylenediamine-based Fe/N/C catalysts modified with CeO_2 were synthesized by a hydrothermal method to eliminate hydrogen peroxide (H_2O_2), thereby improving the durability/stability of the catalyst. Oxygen reduction reaction (ORR) and catalytic durability/stability were evaluated by linear sweep voltammetry and accelerated durability tests (ADTs). The results show that the yield of H_2O_2 evaluated by rotating ring disk electrode (RRDE) measurement decreased obviously when the CeO_2 mass ratio in catalyst is optimal. The loss of current density at 0.8 V of catalyst with 6 wt% CeO_2 and catalyst without CeO_2 were 51.1% and 91.5%, respectively. The addition of CeO_2 can improve the durability/stability of Fe/N/C catalysts obviously due to the elimination of H_2O_2 during ORR.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is promising in transportation applications [1,2]. Pt-based catalysts have been accepted as oxygen reduction reaction (ORR) materials in PEMFCs due to their high activity and stability. However, the high price and rare reserves still restrict the large-scale application of Pt-based catalysts [3,4]. In recent years, non-precious metal catalysts (NPMCs) have been paid more and more attention due to their significant performance improvement. Fe/N/C catalysts are the most promising one among NPMCs [5–8] and considered as a viable substitute for Pt-based catalysts [9–12]. However, Fe/N/C catalysts' durability/stability must be further improved for commercial applications [9,13]. It is hypothesized that hydrogen peroxide (H_2O_2) generation, de-metalation, and protonation/anion binding are the most widely accepted factors that result in the degradation of Fe/N/C catalysts. The active sites oxidation caused by H_2O_2 which is a by-product of ORR is a widely agreed-on mechanism for the performance loss of Fe/N/C catalysts [14–17]. Previous articles mentioned that CeO_2 in Pt-based catalysts can eliminate H_2O_2 (Eqs. (1), (2) and (3)) [18]. As far as we know, it is firstly reported by this article that the elimination of H_2O_2 by the cocatalyst of CeO_2 in Fe/N/C catalysts can improve their durability/stability [19].

$$O_2 + 2H^+ + 2e \rightarrow H_2O_2, \tag{1}$$

$$2CeO_2 + 2H^+ + 2e \rightarrow Ce_2O_3 + H_2O, \tag{2}$$

$$Ce_2O_3 + H_2O_2 \rightarrow 2CeO_2 + H_2O. \tag{3}$$

In this work, we report a phenylenediamine-based Fe/N/C catalyst embedded with CeO_2 nanoclusters (PpPD-Fe-ZnO-CeO_2) prepared via a hydrothermal method [20,21]. ORR tests and accelerated durability tests (ADTs) show the stability/durability of the catalyst with optimized CeO_2 has been improved obviously.

2. Experimental

2.1. Reagents and materials

Sulfuric acid (H_2SO_4, AR), ammonia solution ($NH_3{\cdot}H_2O$, AR), iron sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, AR), hydrogen peroxide solution (H_2O_2, AR), ethanol (CH_3COOH, AR) were purchased from Sinopharm

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https://doi.org/10.1016/j.elecom.2018.01.011
Received 12 January 2018; Accepted 18 January 2018

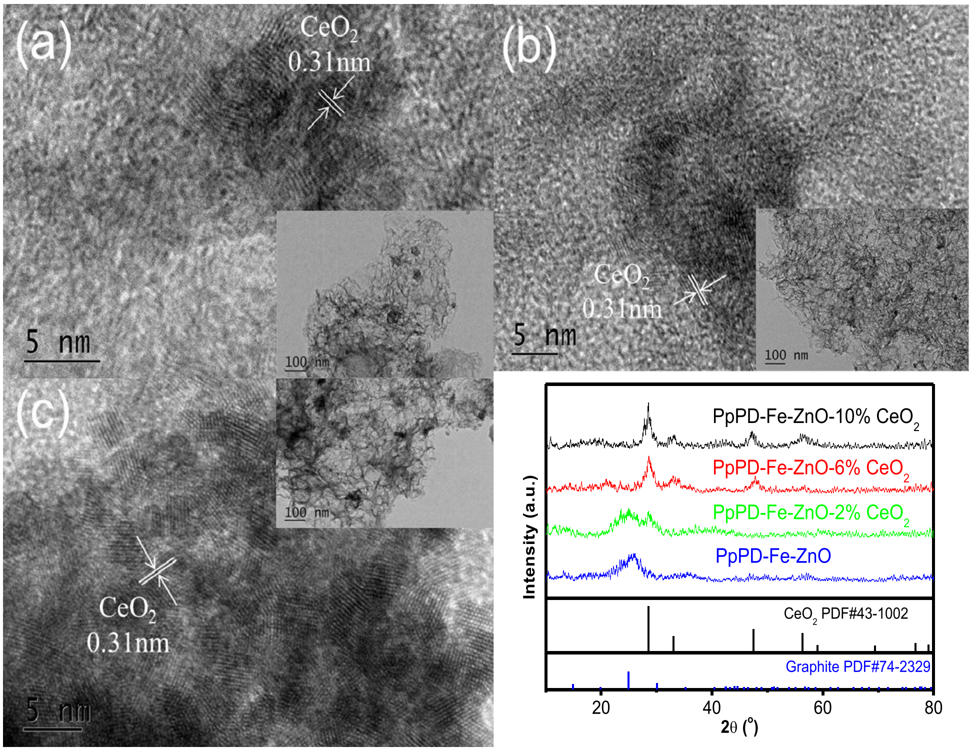

Fig. 1. TEM images of (a) PpPD-Fe-ZnO-2% CeO$_2$, (b) PpPD-Fe-ZnO-6% CeO$_2$ and (c) PpPD-Fe-ZnO-10% CeO$_2$ (the insets show the low-magnification TEM images of corresponding catalysts). (d) XRD patterns of the catalysts.

Group Chemical Reagent Co. (China). Cerium (III) acetate sesquihydrate ((CH$_3$COO)$_3$Ce·xH$_2$O, 99.9%) was purchased from Alfa-Aesar. Nafion solution (5 wt%) was purchased from Sigma-Aldrich. Pt/C (60 wt%) catalyst was purchased from Johnson Matthey. All chemicals were used as received.

2.2. Preparation of PpPD-Fe-ZnO-CeO$_2$ catalysts

In the present work, PpPD-Fe-ZnO was employed as a support for CeO$_2$ to prepare PpPD-Fe-ZnO-CeO$_2$ catalysts. PpPD-Fe-ZnO catalyst was prepared as described in the previous paper [10].

In a typical synthesis of PpPD-Fe-ZnO-CeO$_2$ catalysts, (CH$_3$COO)$_3$Ce·xH$_2$O (4.8 mg) and ammonia solution were added into deionized water (10 mL) with constantly stirring until the pH was ca. 9. Then, PpPD-Fe-ZnO catalyst (40 mg) was added into the solution. The obtained suspension was transferred into a hydrothermal synthesis reactor (50 mL) and maintained at 150 °C for 12 h. Afterwards, the obtained catalyst was thoroughly washed, and then dried at 60 °C. Finally, catalyst with 6 wt% CeO$_2$, named as PpPD-Fe-ZnO-6% CeO$_2$, was synthesized. PpPD-Fe-ZnO-2% CeO$_2$ and PpPD-Fe-ZnO-10% CeO$_2$ were synthesized with the same method, by changing CeO$_2$ mass ratios, respectively.

2.3. Physical and electrochemical characterizations

The morphologies and structures of the catalyst were observed by transmission electron microscopy (TEM; JEM-200CX; 200 kV). The crystal structures of the catalysts were characterized by an X-ray diffractometer (XRD; D/Max 2500 V, Rigaku, Japan).

The rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements were performed by a CHI Electrochemical Station in a standard three-electrode cell. Catalyst (5 mg), Nafion solution (50 μL) and ethanol (175 μL) were ultrasonically mixed for 40 min to make a homogeneous suspension. Then the ink (4.5 μL) was deposited onto the glassy carbon electrode with the catalyst loading of 0.8 mg cm^{-2}. ORR was conducted in O$_2$-saturated 0.1 M HClO$_4$ aqueous solution at 900 rpm at a sweep rate of 10 mV s^{-1}. The ADTs were performed in the potential range from 0.6 to 1.0 V at a scan rate of 100 mV s^{-1} for up to 10,000 cycles in O$_2$-saturated electrolyte. RRDE measurements were arranged in the same way as RDEs. During the RRDE test, a potential of 1.20 V vs. RHE was applied to the Pt ring electrode. The H$_2$O$_2$ yield during ORR can be calculated by Eq. (4):

$$H_2O_2(\%) = 200 \times \frac{I_R/N}{(I_R/N) + I_D} \tag{4}$$

where I_D and I_R are the disk current and ring current, respectively, and $N = 0.37$ is the RRDE collection efficiency.

2.4. Single-cell tests

Catalyst inks were prepared by uniformly mixing catalyst (15 mg), Nafion solution (225 μL), ethanol (300 μL) and ultrapure water (300 μL). The suspension was then electrosprayed onto the gas diffusion layer until the cathode catalyst loading reached 3.5 mg cm^{-2}. The loading of Pt in the anode was 0.8 mg cm^{-2}. Then, the membrane electrode assembly (MEA) was prepared by hot-pressing the electrodes and Nafion 211 membrane.

The fuel cell polarization curves and Open Circuit Voltage (OCV) tests were performed at 80 °C on a fuel cell test system (Model 850e, Scribner Associates Inc.). H$_2$ and O$_2$ flow rates were 300 sccm at 100% RH without back pressure applied, and each cycle of OCV was held for 5 h.

3. Results and discussion

TEM images of increased CeO$_2$ mass ratios on PpPD-Fe-ZnO are shown in Fig. 1a–c. CeO$_2$ nanoclusters with single nanoparticle size of 1–5 nm were embedded in the catalyst surface. Further, TEM images are shown in Fig. 1a–c, where lattice fringes with a d-spacing of 0.31 nm are observed, corresponding to the (111) plane of CeO$_2$. X-ray diffraction patterns of the catalysts are shown in Fig. 1d. The broad graphite diffraction peak of PpPD-Fe-ZnO was observed at 24.9°. With the increase of CeO$_2$ mass ratio, the graphite peaks became weaker, as well as