Electrochimica Acta 254 (2017) 72–78

Contents lists available at ScienceDirect

Electrochimica Acta

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

Research Paper

Vacancy-assisted oxygen reduction reaction on cobalt-based catalysts in direct borohydride fuel cell revealed by *in-situ* XAFS and XRD

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ARTICLE INFO

Article history:
Received 27 June 2017
Received in revised form 17 September 2017
Accepted 17 September 2017
Available online 20 September 2017

Keywords:
Direct borohydride fuel cell
Oxygen reduction reaction
Cathode
Oxygen vacancy
X-ray absorption fine structure

ABSTRACT

The oxygen reduction reaction mechanism is the key issue for designing novel non-Pt electrocatalysts of H_2-O_2 fuel cells. Although the $Me^{n+}/Me^{(n+1)+}$ redox model has been widely accepted, the valence state of the Me^{n+} was found to keep unchanged in this work. Polypyrrole-modified carbon-supported cobalt oxyhydroxide catalyst (CoOOH-PPy-BP) was prepared by impregnation-chemical method and used as cathode catalyst in direct borohydride fuel cells. The CoOOH-PPy-BP exhibited compatible electrochemical properties with $Co(OH)_2$-PPy-BP and a near 4e transfer oxygen reduction reaction. The variation of the local structure around Co ions during discharging was analyzed by *in-situ* X-ray absorption fine structure (XAFS) and X-ray diffraction (XRD) measurements. No new phase was detected by *in-situ* XRD while oxygen vacancies were detected by *in-situ* XAFS. Oxygen vacancies at the surface of CoOOH provided favorable sites for the O_2 absorption, accelerating the activation of the O_2. The electron holes generated due to the oxygen vacancies in the CoOOH can capture electrons from the anode to form excited cationic states [Co^{3+} + e]. Then the absorption oxygen molecule is reduced by capturing electrons from [Co^{3+} + e]. A new oxygen reduction reaction mechanism based on the oxygen vacancy instead of the previous $Co^{n+}/Co^{(n+1)+}$ model is proposed. This work provides lights for the design of novel catalysts with excellent performance by introducing defects of oxygen vacancies artificially.

1. Introduction

Direct borohydride fuel cell (DBFC) has attracted significant attention because of its possibility of using non-noble metals as electrode catalyst, which is one of the key factors for the commercial applications of fuel cells [1–6]. In order to improve the performance of DBFC and to reduce its cost, many efforts have been devoted to the study of non-Pt electrocatalysts including metal oxides [5,7], transition metal [8–11], metal-free catalysts [12,13]. Among them, carbon supported transition metal nitrogen compounds (Me/N/C, Me = Co, Fe, *etc.*) have been studied as one of the most promising candidates for cathode electrocatalysts for fuel cells. Those Me/N/C catalysts have exhibited competitive oxygen reduction reaction (ORR) activity and stability against to commercial Pt/C catalyst [13–25].

In order to reveal the reasons of the excellent catalytic properties of the classical Me/N/C, the chemical nature of the catalytic sites should be clearly identified. Some researchers believed that MeN_x is the active ORR site [1,26], while others confirmed that $Me^{n+}/Me^{(n+1)+}$ redox couple should be responsible for the mechanism of ORR [14,27–31]. Besides the classical Me/N/C catalysts, a new class of cobalt-polypyrrole composite catalyst was firstly designed by Bashyam and Zelenay [26]. Then $Co(OH)_2$-polypyrrole composite and CoOOH-polypyrrole composite were developed by Qin et al. [15,32] following the similar synthesis method. Those cobalt-based polypyrrole (PPy)-modified catalysts are composites containing particles of Co compounds and N-doped carbon, which is different with the classical Me/N/C compounds in which the Me is present as atoms coordinated by the N sites. Although the structure of the cobalt-based PPy-modified catalysts is not the same with the classical Me/N/C, those catalysts exhibited excellent electrochemical performance as electrodes in fuel cells [15,32]. It was thought that the circular change between Co^{2+} and Co^{3+} played a important role in the catalytic process of oxygen reduction on $Co(OH)_2$ cathode catalyst. The Co^{2+} in $Co(OH)_2$ was

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https://doi.org/10.1016/j.electacta.2017.09.102
0013-4686/

oxidized into Co^{3+} during oxygen reduction and the Co^{3+} was returned to Co^{2+} after the oxygen reduction reaction. Our previous *in-situ* X-ray diffraction (XRD) study [27] indeed found the presence of CoOOH during oxygen reduction, which confirmed the valence state change from Co^{2+} to Co^{3+}. Although the Me^{n+}/$Me^{(n+1)+}$ redox model has been widely accepted, is it possible that the valence state of the Me^{n+} keeps unchanged during ORR? In other word, is the change of valence state of the Me^{n+} the necessary and sufficient condition for the catalytic activity of ORR on cobalt-based PPy-modified catalysts?

In this work, CoOOH where Co was at +3 valence was directly used as cathode catalyst in DBFC. It was interesting to find that the DBFC using CoOOH also exhibited good electrochemical properties. Further *in-situ* X-ray absorption fine structure (XAFS) and *in-situ* XRD studies revealed a new ORR mechanism based on the oxygen vacancy on the surface of CoOOH instead of the previous Co^{n+}/$Co^{(n+1)+}$ model.

2. Experiments

2.1. Chemicals

Glacial acetic acid (≥98% purity), BP2000 (Carbot) and pyrrole (≥99% purity) were purchased from Alfa Aesar. $Co(NO_3)_2 \cdot 6H_2O$ (≥99% purity), H_2O_2 (30 wt.% purity), $NaBH_4$ (≥99% purity) and NaOH (≥99.9% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of polypyrrole-modified carbon-supported cobalt hydroxide ($Co(OH)_2$-PPy-BP)

Polypyrrole-modified carbon-supported cobalt hydroxide ($Co(OH)_2$-PPy-BP) was prepared by an impregnation-chemical method as described in previous work [26,27,33]. Polypyrrole-modified carbon-supported cobalt oxyhydroxide (CoOOH-PPy-BP) was prepared by further oxidation of $Co(OH)_2$-PPy-BP according to procedure published in reference [18]. In a typical synthesis of $Co(OH)_2$-PPy-BP, 2.5 g of BP2000 and 1.25 mL of glacial acetic acid were dispersed into 75 mL of de-ionized water, followed by 30 min stirring at room temperature. Then 1 mL of pyrrole and 5 mL of H_2O_2 (10 wt.%) were added and stirred for 3 h. The product was filtered, washed and then dried at 80 °C under vacuum for 3 h. Then 1.35 g of the product and 30 mL of de-ionized water were add into a three-necked bottle and stirred for 30 min at 80 °C. 0.74 g of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 7.5 mL of de-ionized water was added into the three-necked bottle and stirred at 80 °C for another 30 min. Then the solution containing $NaBH_4$ (1.57 g), NaOH (0.111 g) and de-ionized water (150 mL), was added and stirred for 30 min. At last the product was filtered, washed and then dried at 80 °C for 3 h to obtain $Co(OH)_2$-PPy-BP.

2.3. Synthesis of polypyrrole-modified carbon-supported cobalt oxyhydroxide (CoOOH-PPy-BP)

5 g of $Co(OH)_2$-PPy-BP was added into 200 mL of a 8 M NaOH solution. Then 19 mL of H_2O_2 (30 wt.%) was added and the stirred at 60 °C for 10 h. The product of CoOOH-PPy-BP was filtered, washed and dried at 90 °C. The CoOOH-PPy-BP was confirmed by the XRD and XAFS as shown in Fig. S1.

2.4. Physiochemical characterizations and electrochemical tests

The crystal structure of the synthesized CoOOH-PPy-C was identified by X-ray diffractometer, and the microstructure was observed by scanning electron microscopy (SEM). The electrochemical properties of CoOOH-PPy-BP were tested at ambient temperature by using cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements in a CHI-1140A station. A saturated calomel electrode (SCE) as the reference electrode was connected to the fuel tank with a salt bridge. The CV curve was recorded between −1.0 and 0.2 V (*vs.* Hg/Hg_2Cl_2) at a scan rate of 10 $mV \cdot s^{-1}$ in Ar and O_2-saturated 0.1 M KOH solution. The RDE measurement was performed by scanning the electrode potential from −0.9 to 0.2 V (*vs.* Hg/Hg_2Cl_2) at a scan rate of 10 $mV \cdot s^{-1}$ and with rotation rates of 400, 600, 800, 1250 and 1800 rpm in an oxygen-saturated 0.1 M KOH solution. A pristine glassy carbon electrode was used as the counter electrode, while a catalyst-covered glassy carbon electrode (3 mm diameter, 0.07 cm^2 geometrical area) was used as the working electrode. The working electrode was prepared as follows: 4 mg catalyst and 0.2 mL Nafion suspension (5 wt.%) were ultrasonically mixed in 3 mL ethanol to form a homogenous ink. Then 5 μL of the ink was deposited onto the glassy carbon electrode and dried at room temperature. All current densities were normalized to the geometric surface area of the disk electrode. All the potentials were converted to the values *vs.* revisable hydrogen electrode (RHE).

2.5. In-situ synchrotron radiation tests

The cathodes were prepared by coating CoOOH-PPy-BP or $Co(OH)_2$-PPy-BP slurry onto carbon papers with the catalyst load of 2.5 mg cm^{-2}. The anode was coated by Pt/C catalyst with a load of 2.5 mg cm^{-2}. Then air–breathing DBFCs with area of 3.06 cm^2 were assembled, using Nafion membrane N117 as electrolyte and $NaBH_4$ solution (5 wt.% $NaBH_4$ and 10 wt.% NaOH) as fuel. The *in-situ* tests were carried out at 25 °C. The cell performance of the DBFCs was tested during the *in-situ* experiment. *In-situ* XRD and XAFS measurements were performed on BL15U1 and BL14W1, respectively. The details of the setup of the *in-situ* experiments was described in our previous work [27]. XRD experiments including the *ex-situ* XRD experiments were performed at the energy of 20 keV in transmission mode by MarCCD165 with a duration period of 10 s. XAFS measurements were performed under fluorescent mode with a duration period of 3 s for each energy point. Computer program IFEFFIT was used to analyse the XAFS data.

3. Results and Discussions

3.1. Physiochemical characterizations and electrochemical results

The XRD pattern of the CoOOH-PPy-BP composite is shown in Fig. 1a. The main peaks at ~20, 38, 50 and 68° are consistent with the standard PDF card of 07-1069 well, which confirms the successful synthesis of CoOOH. The dispersive peak at ~26° corresponds to the main peak of graphite. The co-existence of the CoOOH and carbon support is also confirmed by the SEM observation (Fig. 1b). Fig. 2a shows the CV curves of CoOOH-PPy-BP in Ar- or O_2-saturated 0.1 M KOH solution. When O_2 is introduced into the solution, a remarkable oxygen reduction peak appears at 0.79 V *vs.* RHE, suggesting that CoOOH-PPy-BP catalyst indeed has ORR activity. Fig. 2b and c show the RDE voltammograms for CoOOH-PPy-BP catalyst and the corresponding Koutecky-Levich plots at 0.15, 0.20 and 0.25 V *vs.* RHE. According to the Koutecky-Levich equation and RDE LSVs at different rotation rates, the electron transfer number of ORR on CoOOH-PPy-BP electrode are calculated to be 3.65, 3.81 and 3.85 at 0.15, 0.2, and 0.25 V *vs.* RHE, respectively. The average number of electrons exchanged in the O_2 reduction reaction on the CoOOH-PPy-BP catalyst is 3.77. This indicates that ORR may occur via the 4- electron transfer pathways on the CoOOH-PPy-BP catalyst. It is should be pointed out, the 2 + 2 electron transfer pathways are difficult to be ruled