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Development of high-performance cathode catalyst of polypyrrole modified carbon supported CoOOH for direct borohydride fuel cell

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HIGHLIGHTS

- CoOOH-PPy-C where Co was +3 valence was produced by impregnation-chemical way.
- CoOOH-PPy-C exhibited good electrocatalytic activity towards ORR.
- There was only 4% decrease of the cell voltage after operating for 80 h.
- The bonding of Co ion with N atoms should be a key issue regardless the valence of Co ion.

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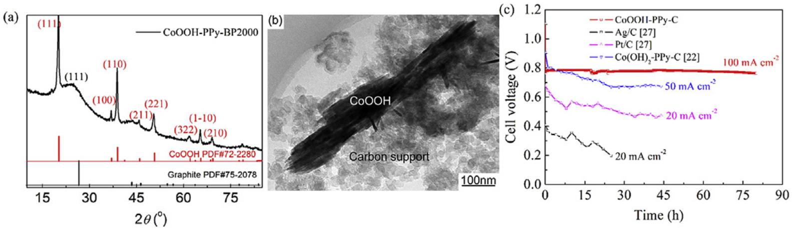
GRAPHICAL ABSTRACT



ABSTRACT

Polypyrrole modified carbon supported CoOOH electrocatalyst (CoOOH-PPy-C) is prepared by impregnation-chemical method, and the catalytic properties for the oxygen reduction reaction (ORR) in alkaline media are investigated. The X-ray diffraction and transmission electron microscopy results confirm the presence of the expected CoOOH. The electrochemical tests show that the CoOOH-PPy-C catalyst exhibits good electrocatalytic activity towards ORR. The direct borohydride fuel cell using CoOOH-PPy-C as the cathode catalyst demonstrates a good stability performance. There is only 4% decrease of the cell voltage after 80-h operation. The ORR occurs an average 4-electron transfer pathway on the CoOOH-PPy-C catalyst. The good catalytic activity towards ORR benefits from the Co–N bond, which is identified by X-ray photoelectron spectroscopy test. X-ray absorption fine structure experiments further show that two nearest O atoms are substituted by two N atoms bonding to Co ion at a distance of 1.64 Å. The CoOOH-PPy-C exhibits better electrochemical properties than the $Co(OH)_2$ counterpart even though the valence state of Co ion is +3 in CoOOH-PPy-C. Those results indicate that the bonding of Co ion with N atoms should be a key issue regardless the valence of Co ion.

1. Introduction

The consumption of fossil fuel and ever-increasing energy demands have stimulated intense research on alternative and sustainable energy conversion and storage source like solar, hydrogen, etc [1–3]. Due to its merit of high power density, low operating temperature and environmental-friendly emissions, direct borohydride fuel cell (DBFC) has attracted extensive attentions as a potential power source for transportable and stationary applications in recent years [4–6]. For DBFCs, the cathode catalyst

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involving the oxygen reduction reaction (ORR) is the key factor determining the cell's performance. Till now, Pt and/or its alloys are well known as active and efficient catalysts for ORR, but their high cost and limited resource prevent them from commercialization [7,8]. Therefore, the development of low cost and stable non-precious metal catalysts with high ORR activity and high durability is an active area in present research.

In recent years, a large number of promising candidates of non Pt based catalysts have emerged, including transition metal, metal nitrides and metal oxides, as well as metal-free catalysts like conducting polymers, carbon materials, graphitic carbon nitride and so on [9–11]. Among them, the N-containing transition metal catalysts adsorbed on carbon support (Me—N—C, Me=Co, Fe, *etc.*) have been paid much attention due to their competitive ability against Pt in terms of ORR activity [12–14]. Different N-containing macrocycles, such as porphyrins, phthalocyanines, phenanthrolines, polypyrrole (PPy) and tripyridyl triazine, have been employed for the preparation of those Me—N—C catalysts. PPy is a promising and cost-effective N-rich precursor [15–17]. Yuasa et al. [18,19] synthesized a carbon-supported cobalt-PPy catalyst (Co-PPy-C) and investigated the effect of heat-treatment on the ORR activity. It's found that Co-PPy-C catalyst exhibited promising electrocatalytic activity towards ORR. The heat-treatment changed the ORR from a 2-electron to a 4-electron transfer process. Extensive research on applications of Co-PPy-C catalysts in alkaline media started along with their first usage in the direct hydrazine fuel cell by Asazawa et al. [20]. Subsequently, we prepared the Co-PPy-C similarly and used it in a DBFC as a cathode catalyst [21]. The results revealed that the DBFC using a Co-PPy-C cathode demonstrated similar cell performance with that using a Pt/C cathode. The maximum power density of the DBFC using Co-PPy-C and $Co(OH)_2$-PPy-C cathodes have achieved 65 and 83 mW cm^{-2} at ambient conditions, respectively [22].

Besides the promising electrocatalytic performance, the underlying mechanism of the ORR on the Me—N—C catalysts received enormous attentions recently. Our previous work proposed a model of the Co^{2+}/Co^{3+} redox couple for $Co(OH)_2$-PPy-C based on the *in-situ* experiments [13]. $Co(OH)_2$ was found to be oxidized into CoOOH during ORR and the generated CoOOH was reverted to $Co(OH)_2$ with the help of water and external electrons. This model was further confirmed by the recent results of Fe^{2+}/Fe^{3+} redox couple in Zelenay and Mukerjee's work [23]. They documented that the catalytically active sites were $Fe^{2+}—N_x$ rather than $Fe^{3+}—N_x$ sites in FeTPP-C and PANI-Fe-C. The active sites in Co—N—C may be $Co^{2+}—N_x$ rather than $Co^{3+}—N_x$ sites similarly. The preservation of further oxidization capacity for the transition-metal compound in ORR may be a key issue. It is interesting to investigate the phenomenon when the Co is used as cathode catalyst at the +3 valence.

To test aforementioned phenomenon, in this work, CoOOH-PPy-C where Co was at the +3 valence, was used as the cathode catalyst in DBFC.

2. Experimental

$Co(OH)_2$-PPy-C was firstly prepared by impregnation-chemical method using black pearl carbon (BP2000) as carbon support. First, carbon dispersion was produced by dispersing 1.4 g of BP2000 and 2.5 mL of glacial acetic acid into 150 mL of de-ionized water and then stirring at room temperature for 30 min. Then 2 mL of pyrrole was added into the carbon dispersion stirring for 5 min, which progress was occluded light using tin foil in order to constrain decomposition of pyrrole. After that 10 mL of H_2O_2 (10 wt %) was added and then constantly stirred at room temperature for 3 h to obtain polypyrrole modified carbon dispersion (PPy-C). The PPy-C dispersion was filtered, washed and then dried at 80 °C for 3 h. To synthesize $Co(OH)_2$-PPy-C, 1.35 g of PPy-C was stirred with 30 mL of de-ionized water for 30 min at 80 °C in a three-necked bottle. Then 0.74 g of $Co(NO_3)_2 \cdot 6H_2O$, which was dissolved in 7.5 mL of de-ionized water, was added into the three-necked bottle with condensing reflux under stirring at 80 °C for 30 min. A solution, which consisted of $NaBH_4$ (1.57 g), NaOH (0.111 g) and de-ionized water (150 mL), was added into the three-necked bottle slowly and stirred at a high stirring speed for 30 min. In the end, the obtained $Co(OH)_2$-PPy-C dispersion was filtered, washed and then dried at 80 °C for 3 h. The CoOOH-PPy-C was synthesized according to published methods [24] by using the $Co(OH)_2$-PPy-C as the precursor. The $Co(OH)_2$-PPy-C was moved to 200 mL of an 8 M NaOH solution and was oxidized at 60 °C for 10 h after adding 19 mL of H_2O_2 (30 wt%). Finally, the obtained precipitate was washed with distilled water to neutral, filtered, and dried at 90 °C to gain the final product of CoOOH-PPy-C with a nominal CoOOH loading of 15%.

DBFCs with an active area of 6 cm^2 were assembled to test the cell performance. Details of testing can be found elsewhere [24], which the cathode was prepared by coating catalyst slurry on to a piece of hydrophobic carbon cloth with a catalyst loading of 5 mg cm^{-2}. The anode was prepared by coating the $Co(OH)_2$-PPy-C catalyst slurry on to a piece of Ni foam with a catalyst loading of 10 mg cm^{-2}. The Nafion membrane N117 was used as the electrolyte membrane. An alkaline $NaBH_4$ solution (5 wt% of $NaBH_4$, 10 wt % of NaOH) was used as the fuel. Cell performance was measured at ambient temperature with a fuel flow rate of 50 mL min^{-1} and a humidified O_2 flow rate of 150 mL min^{-1} (0.3 MPa). Linear scan voltammetry (LSV), rotating disk electrode (RDE), and rotating ring-disk electrode (RRDE) techniques were used to evaluate the electrochemical performances of the catalyst by employing an electrochemical station (CHI 733e) with a RDE instrument (Gamry 710) in a conventional three-electrode electrochemical cell. A saturated calomel electrode (SCE) as the reference electrode was connected to the fuel tank with a salt bridge. A Pt-wire electrode was used as the counter electrode. All the potentials reported in the following contents were converted to the values against the reversible hydrogen electrode (RHE) scale. The data of Pt/C and $Co(OH)_2$-PPy-C catalysts were recorded under the same condition for comparison. The catalysts were ultrasonically dispersed in an alcoholic solution containing suspended Nafion® ionomer for 30 min to form a catalyst "ink" before painting onto the glassy-carbon disk surface. The LSV curves were recorded in oxygen-saturated 0.1 M KOH solution between 0.2 and 1.2 V (*vs.* RHE) at a scan rate of 10 mV s^{-1}. The RDE measurements were performed by scanning from 0.2 to 1.2 V (*vs.* RHE) at a scan rate of 10 mV s^{-1} and with rotation rates of 100, 400, 900, 1600 and 2500 rpm in an oxygen-saturated 0.1 M KOH solution. The RDE voltammogram curves were analyzed using the following Koutecky–Levich (K-L) equation [25]:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{0.62nFAC_0D_0^{2/3}\nu^{-1/6}\omega^{1/2}} \tag{1}$$

where I and I_k represent the limiting disk current and the kinetically limited current, respectively; n is the ORR electrons; F is the Faraday constant; A is the electrode area; C_0 represents the concentration of O_2; D_0 represents the diffusion coefficient of O_2 in 0.1 M KOH solution; ν is the kinematic viscosity of 0.1 M KOH solution; and ω is the angular frequency of rotation. In this experiment, C_0, D_0 and ν were set to 1.15×10^{-3} M, 1.95×10^{-5} cm^2 s^{-1}, and 0.008977 cm^2 s^{-1}, respectively [25].

RRDE tests were carried out to detect hydrogen peroxide during the catalyzed ORR experiments. The ring electrode collection