Electrochimica Acta 155 (2015) 335–340

Contents lists available at ScienceDirect

Electrochimica Acta

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

Promotional effect of phosphorus doping on the activity of the Fe-N/C catalyst for the oxygen reduction reaction

Yang Hu [a,c], Jianbin Zhu [a,c], Qing Lv [a,c], Changpeng Liu [a], Qingfeng Li [b,**], Wei Xing [a,*]

[a] State Key Laboratory of Electroanalytical Chemistry, Laboratory of Advanced Power Sources, Changchun Institute of Applied Chemistry, 5625 Renmin Street, Changchun 130022, PR China
[b] Department of Energy Conversion and Storage, Technical University of Denmark, Kemitorvet 207, Lyngby 2800, Denmark
[c] University of Chinese Academy of Sciences, Beijing, PR China

ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form 30 December 2014
Accepted 30 December 2014
Available online 3 January 2015

Keywords:
oxygen reduction reaction
catalyst
phosphorus
non-precious metal
heat-treatment

ABSTRACT

Cost-effective, active and stable electrocatalysts for the oxygen reduction reaction (ORR) are highly desirable for the wide-spread adoption of technologies such as fuel cells and metal-air batteries. Among the already reported non-precious metal catalysts, carbon-supported transition metal-nitrogen complexes, *i.e.*, M-N/C catalysts, are the most promising candidate. Herein, by comparing the ORR activities of standard Fe-N/C catalysts synthesized with or without the doped phosphorus species, the promotional effect of phosphorus doping is discerned. Such phosphorus doping is achieved by using an acidic phosphate ester as a dopant in the synthesis, which introduces no change in catalyst morphologies and structures. The linked structure of phosphate ester cations with the nitrogen precursor, *i.e.*, polyaniline chain, is favored for the evenly P doping of the catalyst, showing to a superior ORR activity to that for the undoped Fe-N/C catalyst. The activity and durability of the catalysts are demonstrated in direct methanol fuel cells.

1. Introduction

Energy production and use especially from renewable sources are one of the biggest challenges of the 21st century and have triggered global research interests in the last few decades [1,2]. In the further energy scenarios, electrochemical energy conversion and storage devices would play an important role [3]. In these devices such as fuel cells and metal-air batteries, oxygen conveniently from the abundant air is used in the cathode as the oxidant [4,5]. Nevertheless, the kinetically sluggish oxygen reduction reaction (ORR) poses significant performance limitations of these devices [6,7]. To date, platinum-based materials are the best ORR catalysts in acidic media. However, their prohibitive costs, limited resources, and insufficient durability preclude the widespread application of these technologies [8]. Therefore, enormous research efforts have been directed towards the search for alternative cost-effective non-Pt catalysts.

Of the already reported non-Pt ORR catalysts, the most promising candidate is the M-N/C catalyst, *i.e.*, pyrolyzed transition metal-nitrogen complexes supported on carbon materials, which have shown the highest ORR activity and best stability close to the DOE (Department of Energy, USA) targets [9,10]. Of several types of M-N/C catalysts under development, the one synthesized by Wu et al. [10,11] using a conductive polymer, *i.e.*, polyaniline, as the nitrogen precursor exhibited the best durability performance in fuel cells together with a relatively high ORR activity. As reported, less than 3% performance loss was observed during a 700-hour fuel cell test. This excellent stability was attributed to the strong interaction of PANI with the metal-ion centers and also to the ordered graphitic like structure formed in the catalyst. Accordingly, in the present work, such PANI nanofiber-derived catalysts were synthesized and used as the standard Fe-N/C ORR catalysts. Besides, the N doping in M-N_x/C catalysts is essential for the ORR active site formation and the electronic structure modification of the carbon substrate [12,13]. Concerning nitrogen-doped carbon materials, on one hand the more electronegative nitrogen atoms cause a favorably changed charge profile at the neighboring carbon atoms, improving its interaction with oxygen; on the other hand, nitrogen atoms bound in pyridinic sites at the edges of carbon sheets might also be the ORR active sites [14–18]. Instead of or together with N, several heteroatoms such as boron, phosphorus, sulfur and iodine have been investigated, showing optimized structure and enhanced electrocatalytic performance of

---

[*] Corresponding author. Tel.: +86 431 85262223.
[**] Corresponding author. Tel.: +45 45 252 318.
E-mail addresses: qfli@dtu.dk (Q. Li), xingwei@ciac.jl.cn (W. Xing).

http://dx.doi.org/10.1016/j.electacta.2014.12.163
0013-4686/

corresponding catalysts [19–22]. Though these results for heteroatoms doped carbon materials are encouraging, such doping of heteroatoms into M-N/C catalysts and the effect on the ORR activities is still seldom reported.

Herein, we reported the phosphorus doping into the standard Fe-N/C catalyst, *i.e.*, polyaline-derived Fe-N/C catalyst, and studied the effect on the eletrocatalytic activity for the ORR. The standard Fe-N/C catalyst was synthesized using PANI nanofibers as both the C and N precursors, and $FeCl_3$ as the iron precursor for the further 900 °C heat-treatment. As to the synthesis of phosphorus doped catalysts, an acidic phosphate ester was added as the phosphorus dopant in the precursor. Accordingly, the obtained doped and undoped catalysts exhibited mostly the same nanorod morphologies and structures. However, the phosphorus doping made the catalyst exhibit a much enhanced ORR performance compared with that for the standard Fe-N/C catalyst. Moreover, the activity and durability of thus prepared catalysts were tested in direct methanol fuel cells (DMFCs).

2. Experimental

2.1. Preparation of acidic phosphate ester doped PANI (PE-PANI) nanofiber

The acidic phosphate ester and PANI nanofibers were prepared separately using the procedures described previously [23–25]. Briefly, to synthesize the phosphate ester, 25.6 g of phosphorus pentoxide was added to 22.8 g of ethylene glycol monomethyl ethers ($M_n = 76$, Aldrich) in 50 mL of tetrachloride carbon and then the mixture was heated to 65 °C and stirred for 24 h. Afterwards, 12 mL of deionized (DI) water was added into the mixture, which was kept stirring for 2 h. After decoloring by activated carbon, the acidic phosphate ester was collected as a pale yellow transparent liquid. As to the synthesis of PANI nanofibers, 1.91 g of freshly distilled aniline was dissolved in 100 ml of 1 M hydrochloric acid solution while 5.72 g of ammonium peroxydisulfate (APS) was dissolved separately in 100 ml of 1 M hydrochloric acid solution. Then, the APS solution was added quickly to the aniline solution, which gives aniline to APS molar ratio of 1:1.25. After that, a 2 ml of aqueous sodium hypochlorite (5 wt.%) solution was added under agitation. The reaction vessel was left without stirring for 25 min. The precipitated PANI polymer was filtered, washed sequentially with DI water and acetone. Thus obtained PANI nanofiber, (referred to as **blank-PANI**) was dedoped by treatment with excess 1.0 M NH_4OH solution for 24 h followed by drying at 80 °C overnight. Afterwards, the phosphate ester doped PANI (**PE-PANI**) was prepared by adding 0.8 g of dedoped PANI and 3.1 g of acidic phosphate ester into 100 mL of DI water at 60 °C with stirring for 24 h. To remove the excess acidic phosphate ester, the obtained mixture was washed with excess DI water followed by drying at 80 °C overnight. For comparison purposes, the doped PANI nanofiber without removing the excess acidic phosphate was also collected, which was referred to as **PE*-PANI**.

2.2. Catalyst preparation

First, 34.7 mg $FeCl_3$ and 400 mg PE-PANI were added into 200 ml of DI water to give a Fe mass content, *i.e.*, Fe/(Fe + PE-PANI), of 3.0 wt.%. The resulting suspension was stirred and ultrasonically blended for 12 h, followed by drying at 80 °C for 24 h. Afterwards, the precursor powder was grounded and transferred to a quartz boat and heat-treated at 900 °C for 1 h in N_2 atmosphere. After cooling, the product was leached in 0.5 M H_2SO_4 at 80 °C for 8 h to remove dissolvable phases. The obtained catalyst was referred to as **FeNP-C**. For comparison purposes, two other samples were also prepared. One is prepared using the blank-PANI (without phosphate ester doping) as the precursor, which is referred to as **FeN-C**. The other is prepared with the PE*-PANI (excess phosphate ester doped PANI) as the precursor, which is referred to as **FeNP*-C**.

2.3. Physical characterizations

Powder X-ray diffraction (XRD) measurements were performed with a PW1700 diffractometer (Philips Co.) using a Cu Kα (λ = 1.5405 Å) radiation source. Scanning electron microscope (SEM) images and Energy-dispersive X-ray spectroscopy (EDS) were taken on a LEO 1525 FE-SEM scanning electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250 (Thermo Electron) with a monochromatic Al K α (1486.6 eV) source. Survey scans were obtained using a pass energy of 100 eV while high resolution scans of specific elements were obtained using a 20 eV pass energy. Data quantification was performed on the Avantage program.

2.4. RDE and RRDE measurements

Electrochemical measurements were conducted using the Versa STAT3 (Princeton Applied Research) and 760 C Bipotentiostat (CH Instruments). Catalyst inks were prepared by ultrasonically dispersing 10 mg catalyst in a suspension containing 80 μL Nafion (5 wt.%) solution and 514 μL ethanol. The catalyst loading on rotating ring-disk electrode (RRDE) was 0.6 mg cm^{-2}. A conventional three-electrode cell was employed incorporating a saturated calomel electrode (SCE) as the reference electrode, a Pt wire as the counter electrode and the catalyst film coated RRDE as the working electrode. The electrolyte was a 0.1 M $HClO_4$ solution. In all figures, the potentials were converted to values versus the reversible hydrogen electrode (RHE). RRDE measurements were conducted by liner sweep voltammetry (LSV) from 1.1 V to 0.2 V at a scan rate of 10 mV s^{-1} at 1500 rpm, while the ring electrode was held at 1.2 V vs. RHE. All the ORR currents presented in the figures are Faradaic currents, *i.e.*, after correction for the capacitive current. The ORR onset potential was defined as a potential required for generating an ORR current density of 0.01 mA cm^{-2}. The following equations were used to calculate $\%H_2O_2$ (the percentage of H_2O_2 released during ORR) and n (the apparent number of electrons transferred during ORR),

$$\%H_2O_2 = \frac{200 I_R/N}{I_D + (I_R/N)} \tag{1}$$

$$n = \frac{4 I_D}{I_D + (I_R/N)} \tag{2}$$

where I_D is the Faradaic current at the disk, I_R the Faradaic current at the ring and N is the H_2O_2 collection coefficient at the ring (37%). The apparent number of electrons transferred for ORR was also determined by the Koutechy–Levich equation given blow:

$$\frac{1}{J} = \frac{1}{J_L} - \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} \tag{3}$$

$$B = 0.62 n F C_0 (D_0)^{2/3} \nu - \frac{1}{6} \tag{4}$$

where J is the measured current density, J_K is the kinetic current density, J_L is the diffusion-limited current density, ω is the electrode rotation rate, F is the Faraday constant (96485 C mol^{-1}), C_0 is the bulk concentration of O_2 (1.3×10^{-3} mol L^{-1}), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2 s^{-1}) and v is the kinetic viscosity of the electrolyte (1.0×10^{-2} cm^2 s^{-1}) [26]. For reference,