Electrochimica Acta 85 (2012) 399–410

Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

# Carbon catalyst codoped with boron and nitrogen for oxygen reduction reaction in acid media

Mitsuharu Chisaka*, Tomohiro Iijima, Yuki Ishihara, Yuta Suzuki, Ryoji Inada, Yoji Sakurai

*Department of Electrical and Electronic Information Engineering, Toyohashi University of Technology, 1-1 Hibarigaoka, Tempaku, Toyohashi, Aichi 441-8580, Japan*

ARTICLE INFO

*Article history:*
Received 16 April 2012
Received in revised form 6 July 2012
Accepted 8 July 2012
Available online 30 August 2012

*Keywords:*
BCN
Micropore
Edge site
Cathode catalyst
PEMFC

ABSTRACT

A carbon matrix codoped with boron and nitrogen atoms was synthesized for use as an oxygen reduction reaction (ORR) catalyst in acid media. The sol–gel route developed to produce $CO_2$ adsorbents was modified for the synthesis of the present catalysts using boric acid, urea, activated carbon, and iron acetate precursors. The effects of doped boron and nitrogen atoms as well as iron species on ORR activity and selectivity were investigated by analyzing X-ray photoelectron spectra, field emission-transmission electron microscope images, X-ray diffraction patterns, Brunauer–Emmett–Teller surface areas, cyclic voltammograms, rotating disk electrode voltammograms, and rotating ring-disk electrode voltammograms. Both boron and nitrogen atoms were simultaneously doped into a carbon matrix by two heat-treatment steps, the first under $N_2$ gas at 1173 K and the second under $NH_3$ gas at 1223 K with the remaining boric acid-derived oxygen species that limited ORR activity. The remaining oxygen atoms were primarily bonded to the boron atoms and removed by adding iron acetate in the precursor dispersion, resulting in increased ORR activity. The iron species also played a role in increasing edge sites in the carbon matrix, whereas boron doping increased the amount of pyridinic nitrogen. The ORR activity was maximized by the simultaneous doping of boron and nitrogen atoms into the carbon matrix in the presence of iron species. The optimum mass fraction of iron for both ORR activity and selectivity was 0.014, and the activity and selectivity levels were retained after the acid leaching step and reheat treatment under Ar gas. Based on the experimental results, the edge sites in the carbon matrix containing pyridinic-nitrogen atoms near the boron atoms and/or the boron atoms were suggested to be responsible for the ORR activity.

## 1. Introduction

Fuel cells with an acid electrolyte have suffered from sluggish oxygen reduction reaction (ORR) kinetics at the cathodes compared with those with an alkaline electrolyte. Even carbon-supported platinum (Pt-C), which has been regarded as the best ORR catalyst in polymer electrolyte membrane fuel cells (PEMFCs) from the viewpoint of activity, exhibits a large cathode overpotential, e.g., ~400 mV at a current density of 1.5 A $cm^{-2}$ in a single cell [1]. Further, platinum resources are limited; world reserves of all platinum-group metals including platinum, palladium, rhodium, ruthenium, iridium, and osmium are estimated to be only 66,000 tons [2]. Because typical PEMFCs require a platinum mass of 0.85–1.1 g to obtain an electrical power of 1 kW, reduction of platinum usage without increasing the overpotential or the development of a non-platinum-group metal catalyst is necessary, especially for automotive applications [1].

Several types of the non-platinum-group metal catalyst for ORRs, including (1) organic polymer matrices containing trapped metals such as cobalt, iron, nickel, and copper [3–8], (2) compounds synthesized from precursors containing iron or cobalt, carbon, and nitrogen [5,9–35], (3) compounds of carbon and nitrogen (and boron or sulfur in some cases) free from metal precursors [36–43], (4) metal oxide compounds [44–55], and (5) metal nitrides [56–59] have been extensively developed. Among these catalyst types, recent worldwide efforts have been particularly focused on the type (2) catalyst because of its high ORR activity.

Origin of the type (2) catalyst can be attributed to Jasinski's discovery of cobalt phthalocyanine [3], which belongs to the type (1) catalyst. After his report on ORR activity in alkaline media in 1964, other types of metal-containing organic macrocycles were reported to be active in alkaline and acid media [4,5]. Among several metals used for these macrocycles, iron and cobalt showed the highest activity toward ORRs, and these metals surrounded by four nitrogen atoms (metal-$N_4$) have been considered as active sites [4]. In the late 1970s, it was reported that heat treatment of

---

* Corresponding author. Present address: Department of Electronics and Information Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561 Japan. Tel.: +81 172 39 3559; fax: +81 172 39 3559.
*E-mail address:* chisaka@eit.hirosaki-u.ac.jp (M. Chisaka).

0013-4686/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.electacta.2012.07.131

these macrocycles with carbon at temperatures up to 1073–1173 K improved their activity as well as their stability in acid media [5,9]. Bagotzky et al. [9] attributed the improved stability of their heat-treated cobalt tetra(p-metoxyphenyl)porphin catalyst to the increased reduction rate of hydrogen peroxide produced during the ORR process, which is often hypothesized to attack the active sites. However, the heat treatment above 1073 K in inert atmosphere could decompose these macrocycles, thus destroying some metal-$N_4$ structures [10,14]. Gupta et al. proposed a model of active sites for these heat-treated macrocycles that suggested the residual nitrogen derived from the heat treatment interacts with the metal ions adsorbed on the carbon surfaces [13]. In 1989, they reported a new method for the synthesis of the type (2) catalyst without using macrocycles or their components for the first time; in this method, a mixture of polyacrylonitrile, cobalt or iron salt, and carbon black were heat-treated at 1073 K under Ar [13]. Ten years later, Dodelet et al. synthesized the type (2) catalyst with two heat-treatment steps using polymer-free precursors: an iron salt, $NH_3$ gas, and carbon black [15]. After making continuously significant progress [19,21,22], they came to the conclusion that the active sites are $Fe^{2+}$ surrounded by four nitrogen atoms hosted in the walls of micropores (pores whose diameters are below 2 nm) which have been created during heat treatment under $NH_3$ gas [28]. Their recent catalyst, synthesized using iron acetate, phenanthroline, and a zeolitic-imidazolate-framework, exhibited a quite high initial performance in a single cell cathode, comparable to that of Pt-C [35]. Some other groups also demonstrated high performances of the type (2) catalyst used in cathodes of a single cell [23,25,29,31,34]. Numerous researchers synthesized the type (2) catalyst with a certain level of ORR activity using different precursors; however, some of them claimed different active sites composed of carbon and nitrogen [11,18,20,24–27,30–32]. This idea first proposed by Wiesener in 1986 [11] assumes that the iron or cobalt served as a catalyst in the formation of the active sites during heat treatment, although neither of them served as the active site directly. This contradiction on active sites is still under discussion; however, the consensus obtained so far can be summarized by the following two points. (i) The presence of iron or cobalt during at least one heat-treatment step can contribute to the enhancement of the ORR activity of the resulting catalyst even if these metals were finally removed at a level below the detection limit of X-ray photoelectron spectroscopy (XPS), which has been often used for the characterization of surface species. (ii) Nitrogen atoms are necessary in the carbon matrix for enhancing ORR activity.

Recently, boron atoms have been reported as either an agent for enhancing the ORR activity of a nitrogen-doped carbon catalyst, which belongs to the type (3) group in both acid [36,37] and alkaline media [42], or an active site itself in boron-doped, nitrogen-free carbon nanotubes in alkaline media [60]. Ozaki et al. [36] performed simultaneous doping of boron and nitrogen into a carbon matrix by polymerizing furfuryl alcohol mixed with both boron trifluoride methanol and melamine. Although the ORR activity of the resulting catalysts was quite limited compared with that of the state-of-the-art non-platinum-group metal catalysts for use in PEMFCs [23,25,28,29,31,34,35], this finding was the first to report the boron and nitrogen-codoped carbon catalysts' ORR activity in acid media. Wang et al. [42] synthesized vertically aligned carbon nanotubes codoped with boron and nitrogen by a thermal chemical vapor deposition with the use of melamine and boric acid as precursors and silicon oxide/silicon substrate sputter-coated with nickel/iron as a substrate for the nanotube growth. In alkaline media, the catalyst showed high ORR activity comparable to that of Pt-C. In both works [36,42], the ORR activity of carbon catalysts codoped with boron and nitrogen has been reported to be higher than those solely doped with boron or nitrogen. Although the ORR is generally more facile in alkaline media compared with its acid counterparts [61], the codoping of boron and nitrogen into a carbon matrix has the potential to produce ORR catalysts with high activity in acid media. Knowledge of this new type of catalyst is quite limited compared with that of nitrogen-doped carbon catalysts. In particular, the effect of iron species on the activity of boron and nitrogen codoped-carbon catalysts has never been reported. The purpose of this work was to devise a strategy to improve the ORR activity of carbon catalysts codoped with boron and nitrogen in acid media. An inexpensive sol–gel route recently developed to produce $CO_2$ adsorbents by Raidongia et al. [62] was modified for the synthesis of the present catalysts. Various amounts of iron acetate were added in the precursor dispersion, and in one case, the obtained catalysts were washed with concentrated sulfuric acid and heated in an Ar atmosphere to investigate the effect of iron species on their ORR activity. Their surface morphology, crystal structure, and surface composition and chemical states were evaluated by field-emission transmission electron microscopy (FE-TEM), X-ray diffraction (XRD) analysis, and XPS, respectively. The ORR activity and selectivity were evaluated by obtaining cyclic voltammograms (CVs) and rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) voltammograms.

## 2. Experimental

### 2.1. Synthesis of catalysts

The catalysts were synthesized via a sol–gel route developed by Raidongia et al. [62] with the following modifications: the addition of iron acetate to the precursor dispersion, the use of different types of activated carbon, and the use of different heating processes.

First, 0.3 g of boric acid, 3.6 g of urea, and various amounts of iron(II) acetate [95% $Fe(CO_2CH_3)_2$, Sigma–Aldrich Co.] were dissolved in 100 $cm^3$ of distilled water by stirring. The mass ratio of boric acid used to the base case value of 0.3 g, $r_B$, was varied from 0 to 3 in some cases. Unless otherwise stated, $r_B$ was 1. Second, 1 g of an activated carbon powder (Taiko SA1000, Futamura Chemical Co.) was dispersed into the solution followed by heating the dispersion with continuous stirring to 333–343 K to form a thick slippery liquid. A product of the mass fraction of iron in the activated carbon powder and iron times 100, $\chi_F$, was varied from 0 to 3. Third, the obtained liquid was allowed to cool to room temperature and then placed in an alumina boat and set in a horizontal quartz tube furnace that was slowly evacuated and purged with $N_2$ gas. Fourth, the liquid was heated from room temperature to 1173 K at 500 K $h^{-1}$, maintained at this temperature for 10 h, and cooled to room temperature at an uncontrolled rate under flowing nitrogen with a flow rate of 1000 standard cubic centimeters per minute (sccm; 1 sccm = $1.67 \times 10^{-8}$ $m^3$ $s^{-1}$) to obtain $B_xC_yN_z$ catalysts. Fifth, the precursor powders were heated again from room temperature to 1223 K at 500 K $h^{-1}$, maintained at this temperature for 3 h, and cooled to 773 K at ~200 K $h^{-1}$. The cooling rate was not controlled below 773 K. The flowing gas was $N_2$ with 1000 sccm and $NH_3$ with 200 sccm when the temperature was below and above 773 K, respectively. For simplicity, $B_xC_yN_z$ catalysts before and after the $NH_3$ treatment are hereafter denoted with $\chi_F$ values as $\chi_F$Fe–$B_xC_yN_z$ and $\chi_F$Fe–$B_xC_yN_z$–$NH_3$, respectively. When $\chi_F = 0$, they are denoted as $B_xC_yN_z$ or $B_xC_yN_z$–$NH_3$. In the case of $\chi_F = 0$ and $r_B = 0$, that is, $x = 0$, they are denoted as $C_yN_z$ or $C_yN_z$–$NH_3$. Only some 1.4Fe–$B_xC_yN_z$–$NH_3$ catalyst powders were further leached in 0.5 mol $dm^{-3}$ sulfuric acid for 7 h with stirring, sonicated for another 1 h in the same dispersion to remove iron species, and then washed with water several times followed by drying overnight at 363 K. The dried powders were then heated again in the quartz tube