Carbon 116 (2017) 591–598

Contents lists available at ScienceDirect

Carbon

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

Synergistically enhanced oxygen reduction activity of iron-based nanoshell carbons by copper incorporation

Takafumi Ishii [a], Takuya Maie [a], Mikiya Hamano [a], Takeaki Kishimoto [b], Mayumi Mizushiri [b], Yasuo Imashiro [b], Jun-ichi Ozaki [a], *

[a] *International Research and Education Center for Element Science, Faculty of Science and Technology, Gunma University, 1-5-1, Tenjin-cho, Kiryu, Gunma, 376-8515, Japan*
[b] *Nisshinbo Holdings Inc., 1-2-3 Onodai, Midori-ku, Chiba, Chiba, 267-0056, Japan*

ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form
9 February 2017
Accepted 11 February 2017
Available online 14 February 2017

ABSTRACT

This study reports the synergistic improvement of the oxygen reduction reaction (ORR) activity of a carbon catalyst prepared from a phenol–formaldehyde resin by simultaneous incorporation of Cu and Fe phthalocyanines. This carbon catalyst exhibited higher ORR activities than those prepared with either Cu or Fe phthalocyanines, with an approx. 28-fold maximum ORR current enhancement observed when Cu/Fe = 75:25 was incorporated into the carbon precursor. Surface and structural characterizations of these catalysts suggested that the incorporated Cu played a role in suppressing the catalytic activity of Fe, forming the reported nanoshell structure, and in keeping more nitrogen atoms attached to carbons. The incorporation of Cu in the carbon catalyst provided a doping effect for nitrogen into the carbon structure and inhibited catalytic graphitization caused by Fe species. These effects resulted in a distinctive carbon structure in the nanoshell. These multiple effects of Cu incorporation were considered key factors in the enhancement of ORR activity caused by Fe and Cu incorporation.

1. Introduction

The development of a high-performance Pt-free electrocatalyst to accelerate the oxygen reduction reaction (ORR) is crucial for the widespread commercialization of polymer electrolyte fuel cells (PEFCs). Carbon catalysts are some of the most promising candidates for cathode catalysts [1]. Much effort has been directed towards developing a high-performance carbon catalyst by using various transition metals, such as Fe, Co, and Ni [2–7], with the intention to produce metal–nitrogen complexes on the carbon surfaces.

It is widely accepted that carbon structures vary widely in the presence of transition metals that alter the carbonization processes [8]. Peng et al. reported that the effects of transition metals on these structures, including the nitrogen content, vary depending on the metal used [9]. In our previous study [10], a distinctive structure was observed in carbon derived from a phenol–formaldehyde resin with a transition metal species, which was produced by the catalytic action of the incorporated transition metal species altering the carbonization process. The distinctive carbon structure was shell-like, consisting of a few dozen graphene sheets, and referred to as a nanoshell. These prepared carbons were therefore named nanoshell-containing carbons (NSCCs), of which some had high catalytic activities for the ORR. Our previous studies investigated NSCCs produced using one metal, such as Fe or Co [10–14]. Among them, Fe-NSCC, which was derived from a phenol–formaldehyde resin with Fe phthalocyanine, showed excellent ORR activity [14]. The ORR activities of NSCCs were not only influenced by the metal species, but also by the presence of doped nitrogen atoms. In order to maximize the ORR activities of NSCCs, tuning the carbon structure and nitrogen doping levels is critical [14].

Simultaneous incorporation of different transition metals into the preparation would be a useful method to produce NSCC while controlling the structure and nitrogen content. Although such a cooperative approach would still require further detailed investigation because interactions between doped metals are complicated, it is considered to have potential as a pathway to optimizing and enhancing catalytic activity. Copper has attracted attention as a metallic element that promotes surface catalytic action and deposits graphene on its films or particles under certain deposition

---

* Corresponding author.
E-mail address: jozaki@gunma-u.ac.jp (J.-i. Ozaki).

http://dx.doi.org/10.1016/j.carbon.2017.02.035
0008-6223/

conditions [15], whereas it does not cause catalytic carbonization [8]. The simultaneous incorporation of Fe and Cu into the preparation of NSCC has not yet been examined. In this paper, we report a study conducted to incorporate another additive, Cu, to the abovementioned precursor of Fe-NSCC, to control the carbon structure and nitrogen doping level. We also attempted to elucidate the rules of ORR activity provided by nanoshell and nitrogen atoms in NSCC prepared by the simultaneous incorporation of Fe and Cu.

2. Experimental

2.1. Sample preparation

Carbon precursors were obtained by incorporating Fe phthalocyanine (FePc) and Cu phthalocyanine (CuPc) into a phenol–formaldehyde resin, where the Cu ratio in the total amount of Cu and Fe varied from 0 to 1, by fixing the total amount of metal species at 5 wt%. The precursors were carbonized at 800 °C for 1 h in a N_2 stream, followed by sequential ball milling and washing with HCl solution. The acid wash was included to remove residual metal species from the surface of the carbon catalysts. Hereafter, carbons prepared using only FePc or CuPc are referred to as 100Fe-C and 100Cu-C, respectively, while carbons prepared using CuPc and FePc together are referred to as *x*Cu-Cs, where *x* is the mixing ratio ($0 < x < 100$) of the two metals. Controls were also prepared by carbonizing the precursors, in which CuPc was replaced with metal-free phthalocyanine (MfPc). The molar amount of MfPc was adjusted according to that of CuPc used in *x*Cu-Cs, and the controls were named as *x*Mf-Cs, where x stands for the value as used in that of *x*Cu-Cs.

2.2. Electrochemical measurements

The catalytic activity of the prepared carbons in the ORR was evaluated by linear sweep voltammetry employing an oxygen saturated 0.5 mol dm^{-3} H_2SO_4 aqueous solution. The working electrode was prepared by covering the glass-like carbon disk electrode with a mixture of the prepared carbon and Nafion®, where the amount of loaded carbon sample was kept to 200 μg cm^{-2}. Voltammograms were obtained by sweeping the potential from 1.0 V vs. reversible hydrogen electrode (RHE) to 0 V vs. RHE at 1 mV s^{-1} by rotating the electrode at 400–2500 rpm. Double layer capacitance was compensated for by subtracting the voltammogram obtained in nitrogen-saturated electrolyte from the obtained ORR voltammogram.

The current observed in rotating electrode voltammetry consisted of kinetic current (i_k) and diffusion current (i_d). The kinetic current, i_k, can be separated by applying the Koutecky–Levich equation to the obtained voltammograms, given in Fig. S1. The plots of $1/i$ against the square root of rotation speed for the samples prepared here exhibited a linear relationship, as shown in Fig. S2. Extrapolating the rotating speed to infinity gave the kinetic current, i_k. The number of participating electrons, n, was calculated from the slope of the plots using $D_{O2} = 1.40 \times 10^{-5}$ cm^2 s^{-1}, $\nu = 1.00 \times 10^{-2}$ cm^2 s^{-1} from Ref. [16] and $C_{O2} = 1.20 \times 10^{-6}$ mol cm^{-3} given by our experimental determination using optical oxygen meter (FireStingO$_2$, Pyro science GmbH).

2.3. Characterization techniques

Samples were subjected to transmission electron microscopy (TEM) observation and X-ray diffraction (XRD) analysis to investigate their carbon structures. For TEM observation, the sample was ground in ethanol and sprayed over a Cu microgrid. Sample lattice fringes on the microgrid were observed using a 200 kV transmission electron microscope (JEM-2010, JEOL Ltd.). XRD analysis was performed using an X-ray diffractometer (XRD-6100, Shimadzu Corp.) with Cu-Kα radiation. The surface areas and pore structures of the samples were evaluated using nitrogen adsorption–desorption measurements (BELSORP mini, MicrotracBEL Corp.) at −196 °C. Surface composition analyses of the elements contained in the samples were performed using X-ray photoelectron spectroscopy (XPS, AXIS NOVA, Shimadzu Corp.).

3. Results

3.1. Electrochemical properties of carbon catalysts

Fig. 1a shows the ORR voltammograms of the prepared carbon catalysts obtained in an oxygen-saturated 0.5 mol dm^{-3} H_2SO_4 aqueous solution. ORR voltammograms defined by kinetic current i_k are also shown in Fig. 1b. The voltammograms had different onset potentials and shapes depending on the types of metal species. ORR activity is represented by the onset potential, E_{O2}, as defined by the potential at $i_k = -10$ μA cm^{-2} (shown in Fig. 1b), as used in our previous studies [11,14]. The E_{O2} values of the samples are lower than that of Pt/C electrocatalyst (E_{O2} = ~0.95 V) but to examine their activities is important for understanding catalytic actions occurred on the surface of carbon catalysts. The dependence of E_{O2} on the

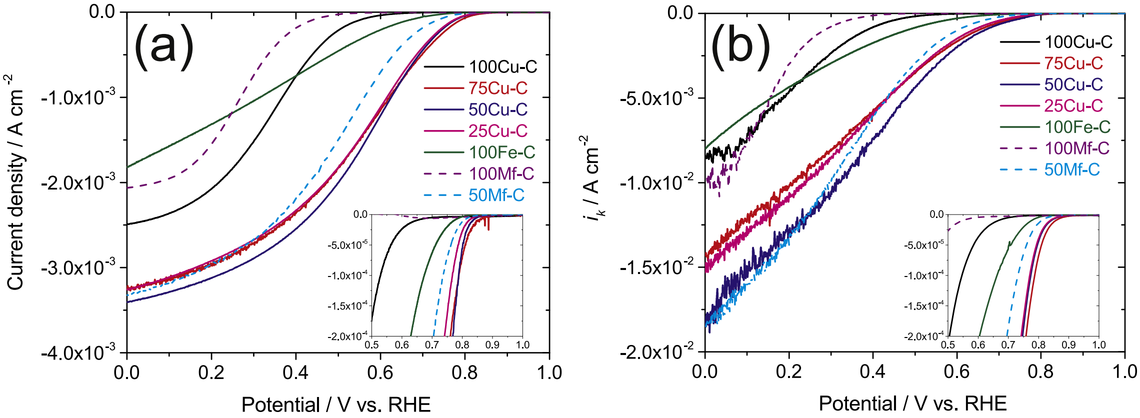

Fig. 1. (a) ORR voltammograms of the prepared carbon catalysts obtained at a rotating speed of 1600 rpm and (b) voltammograms represented in terms of i_k. (A colour version of this figure can be viewed online.)