Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

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

Evaluation of ORR active sites in nitrogen-doped carbon nanofibers by KOH post treatment

Navaneethan Muthuswamy[a], Marthe E.M. Buan[a], John C. Walmsley[b], Magnus Rønning[a,*]

[a] *Department of Chemical Engineering, Norwegian University of Science and Technology, 7491 Trondheim, Norway*
[b] *SINTEF Materials and Chemistry, Høgskoleringen 5, 7465 Trondheim, Norway*

ARTICLE INFO

Keywords:
Nitrogen-doped carbon
Carbon nanofiber
KOH treatment
Carbon electrocatalysis
Oxygen reduction reaction
Active site

ABSTRACT

Oxygen reduction on N-doped carbon nanomaterials is believed to take place at either N-centered active sites (C-N_x) or Fe-centered active sites (Fe-N_x). In this work the origin of the oxygen reduction on nitrogen-doped carbon nanofibers (N-CNFs) is investigated by removing nitrogen and iron from the N-CNF surface using high temperature KOH treatment. The activities for the oxygen reduction reaction (ORR) in 0.5 M H_2SO_4 are correlated with the XPS results and discussed with respect to the contribution from C-N_x and Fe-N_x active sites. Increasing the time and temperature of the KOH treatment decreased the iron and nitrogen content at the N-CNF surface. The contribution from Fe-N_x active sites was found to be minor compared to the C-N_x active sites as the KOH-treated N-CNFs with no iron in the surface still showed considerable ORR activity. Furthermore, the activity was maintained when the fraction of pyridinic-N was greatly reduced compared to quaternary-N. Finally, even when no iron or nitrogen could be detected by XPS, 50% of the initial oxygen reduction activity of the N-CNFs persisted. It is therefore suggested that there are active sites not originating from iron or nitrogen atoms, but rather from a distinct carbon environment.

1. Introduction

Developing novel, highly active, and cheap catalysts for the oxygen reduction reaction (ORR) in acidic electrolyte is crucial to take the PEM fuel cell technology to market [1–4]. In this objective, several new catalytic materials have recently been developed through rational design, and shown promising catalytic performance for the oxygen reduction [4–6]. One of the most promising materials is nitrogen doped carbon nanomaterials prepared in the presence of Fe, hereafter called Fe-N-C, which have opened a new opportunity to replace the costly Pt-based catalysts currently used [7–13]. However, a PEM fuel cell assembled with state-of-the-art Fe-N-C catalysts generate lower current density than the state-of-the-art Pt-based catalysts [2]. In turn, this increases the capital cost for the Fe-N-C fuel cell stack as the required electrode area increases, thereby increasing the requirements of other fuel cell components such as the bipolar plates. Lowering the capital cost of the Fe-N-C fuel cell can be achieved if the number of active sites in the Fe-N-C catalysts is increased so that higher current densities can be obtained. In this case it is important to perform fundamental studies to identify the key active site for the ORR on Fe-N-C catalysts and find suitable synthesis conditions to achieve more active sites.

Substantial efforts have recently been made to determine the key active sites on Fe-N-C catalysts using sophisticated instruments. Two main active sites have been hypothesized; one consisting of non-metallic sites in a carbon graphitic structure (C-N_x) and another consisting of an active metal center stabilized by nitrogen ligands (Fe-N_x) [5,14–20].

In C-N_x, nitrogen doping could lead to unique electron-donor nitrogen-atom-centered active sites [21–23]. In addition, the nitrogen can modify the electronic density of the adjacent carbon atoms creating electron-acceptor carbon-atom-centered active sites [8,24–26]. This will introduce electrophilic and nucleophilic character to the surface, and consequently affect the interaction with oxygen and intermediate reaction products [8,27]. Various types of nitrogen-groups are found in N-doped carbon nanomaterials with the three most common types being pyridinic, pyrrolic and quaternary nitrogen [23,26,28,29]. It has been proposed that the presence of pyridinic nitrogen on graphitic edge planes may be playing a more important role for the ORR activity compared to the other nitrogen groups [23,28].

For Fe-N_x active sites it is believed that the Fe atom coordinated to nitrogen atoms plays an important role in the oxygen reduction reaction. The Fe atom can be involved directly in the ORR by facilitating O_2 adsorption [30–32], or it functions as a bi-functional active site by providing favorable reaction intermediates for the ORR.

---

* Corresponding author.
E-mail address: magnus.ronning@ntnu.no (M. Rønning).

http://dx.doi.org/10.1016/j.cattod.2017.03.045
Received 30 November 2016; Received in revised form 14 March 2017; Accepted 24 March 2017

Please cite this article as: Muthuswamy, N., Catalysis Today (2017), http://dx.doi.org/10.1016/j.cattod.2017.03.045

However, some studies have suggested that Fe is not directly involved in the ORR, but merely facilitates the growth of N-doped carbon with a distinct microstructure or surface chemistry suitable for oxygen reduction [5,18,28,33–35]. The presence of carbon edges has been found to be beneficial for the oxygen reduction without contribution from any dopant or metal atoms [36,37]. First principle calculations have shown that defects in CNT or graphene surfaces activate the adsorption and dissociation of O_2 [38,39]. Chu et al. reported a correlation between oxygen reduction and the amount of edge sites in carbon fibers [40].

Several research groups have deliberately poisoned their Fe-N-C catalysts with carbon monoxide, cyanide and sulphur to determine whether Fe is present in the active site for the oxygen reduction [41,42]. The poisoning experiments were based on evidence that Fe-porphyrins (Fe-N_4) have higher affinity for CO or CN^- than for oxygen [41]. However, the attempts of deactivating the Fe-N-C catalyst were unsuccessful. For Ozkan's research group no difference was observed in the linear sweep voltammetry (LSV) in O_2-saturated electrolyte and in an electrolyte with a mixture of O_2 and CO showing that the active site was totally inert to any interaction with CO.

In this work, we have deliberately removed both nitrogen and iron from our Fe-N-C catalyst by KOH and subsequent H_2SO_4 treatment to investigate the involvement of C-N_x and Fe-N_x active sites for the oxygen reduction reaction.

2. Experimental

2.1. Synthesis and KOH treatment

Nitrogen-doped carbon nanofibers supported on expanded graphite (EG) were prepared following the same method as described in previous reports [12,13]. In brief, the growth catalyst (0.5–0.5 g, 20 wt% Fe/EG) was loaded in the reactor and reduced in an H_2/Ar flow (40/160 ml/min, 5.0/5.0, AGA) while heating the furnace up to 650 °C. Subsequently, N-CNFs were grown at 650 °C using a synthesis gas mixture of CO/NH_3/H_2 (150/6.5/20 ml/min, 3.7/3.6/5.0, AGA). The synthesis time was 44 h giving a total weight of 2.2 g N-CNF/EG after synthesis.

Alkaline treatment was performed by grinding the N-CNF sample (0.4 g) with KOH pellets (1.6 g) and ethanol (96%). The mixture was then placed on a stainless-steel holder and loaded into a vertical reactor. To remove air present in the reactor, Ar was flushed for 30 min before the N-CNF/KOH mixture was heated at 10 °C/min to 800 °C or 900 °C in Ar. The temperature was kept for 30 or 60 min before cooling the reactor to room temperature. Thereafter the samples were washed with 1 M H_2SO_4 (95–97% H_2SO_4, Sigma Aldrich), DI-water and ethanol, and dried at 100 °C overnight. Subsequently, a heat treatment in Ar for 1 h at 900 °C was employed to remove excess oxygen groups introduced on the surface. The obtained samples were named “800KOH-0.5h”, “800KOH-1.0h” and “900KOH-0.5h” indicating the temperature and duration of the KOH treatment.

2.2. Physicochemical characterization

The specific surface area of the N-CNFs was calculated by the Brunauer-Emmet-Teller (BET) method from N_2-adsorption measurements performed in a Micromeritics TriStar II 3020. The specific pore volume (2–300 nm) was obtained by Barret-Joyner-Halenda analysis of the desorption isotherm and the specific micropore volume was determined using the t-plot model.

The microstructure and morphology of the N-CNFs was observed using a Hitachi S-5500 scanning transmission electron microscope (S(T)EM). Transmission electron microscopy (TEM) using a Jeol JEM-ARM200F was employed to characterize the nanostructure of the N-CNFs. Both the S(T)EM and TEM samples were prepared by dispersing N-CNFs in isopropanol by ultra-sonication. A drop of the dispersion was then deposited on a holey carbon film supported by a copper grid and dried at room temperature.

X-ray photoelectron spectroscopy (XPS) measurements were carried out in a Kratos Axis Ultra DLD spectrometer using monochromatic Al Kα radiation (hν = 1486.58 eV). Sample preparation was done by covering carbon tape with an even layer of catalyst powder. Survey spectra were collected using fixed analyzer pass energies of 160 eV while the high-resolution spectra were collected at pass energies of 20 eV. Data analysis was performed using the CasaXPS software. The elemental composition was calculated after the subtraction of Shirley-type backgrounds for the high-resolution spectra. The N 1s region was deconvoluted using Gaussian-Lorentzian line shapes with 30% Lorentzian weighting.

2.3. Electrochemical characterization

The electrochemical characterization was conducted in a conventional three-electrode setup using a reversible hydrogen electrode (RHE) as reference electrode and a platinum wire as counter electrode. All potentials reported in this paper are given versus the RHE. A rotating ring disk electrode (RRDE, disk: 5 mm ϕ, ring: Pt with 20% collection efficiency) was used as working electrode. The N-CNF catalysts were deposited on the glassy carbon disk electrode using the method described by Schmidt et al. [43]. The catalyst suspension was prepared by sonicating 3.0 mg of N-CNFs in a mixture of 500 μL Millipore H_2O, 200 μL ethanol (100%), 200 μL isopropanol and 100 μL of 0.5 wt% Nafion® (DuPont™ DE521, Ion Power,Inc) for one hour. About 16 μL of the suspension was placed on the glassy carbon disk and dried under a N_2-flow giving approximately 245 μg/cm^2 of N-CNF catalyst on the electrode surface.

Before performing ORR the electrolyte was saturated with Ar and the electrodes were cleaned using cyclic voltammetry between 1.2 V and 0 V at different scanning rates. The background current was then measured by linear sweep voltammetry (LSV) from 1.10 V to 0.01 V at 5 mVs^{-1} in the Ar-saturated electrolyte. Oxygen reduction experiments were carried out in O_2-saturated 0.5 M H_2SO_4 (95–97% H_2SO_4, Sigma Aldrich) at room temperature. The potential range of the ORR was 1.10 V–0.01 V, the scan rate 5 mVs^{-1} and the rotational speed 1600 rpm. The third cathodic scan after background subtraction is reported for all catalysts. Onset potentials for the oxygen reduction (E_{ORR}) were determined by comparing the LSV curve obtained in Ar with the ORR measurement.

In order to detect the amount of H_2O_2 produced on the working electrode during the ORR, a constant potential of 1.2 V vs. RHE was applied to the Pt ring electrode. The H_2O_2 yield was calculated from the ring current (I_R), the disk current (I_D) and the collection efficiency of the Pt ring (N) using the following equation [44]:

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

3. Results and discussion

Treatment of the N-CNFs with KOH was performed at high temperatures (800 and 900 °C) for 30 or 60 min. Following a cleaning and drying procedure, the samples were heat treated once more to remove oxygen functional groups introduced by the KOH. Only characterization of the N-CNFs after both heat treatment steps will be presented. To indicate the temperature and duration of the KOH treatment the N-CNFs are named “800KOH-0.5h”, “800KOH-1.0h” and “900KOH-0.5h” after treatment.

3.1. Structure and porosity

SEM and TEM images of the as-prepared N-CNFs on graphite and KOH treated counterparts are shown in Fig. 1a and b respectively. The as-prepared N-CNFs consist of well dispersed, loosely bound and ordered crystalline fibers. Whereas in the case of KOH treated N-CNFs,