



## Research paper

# Insights into oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) active sites for nitrogen-doped carbon nanostructures (CN<sub>x</sub>) in acidic media



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## ARTICLE INFO

## Article history:

Received 16 January 2017

Received in revised form 2 June 2017

Accepted 28 July 2017

Available online 5 August 2017

## Keywords:

ORR

OER

CN<sub>x</sub>

Active sites

Regenerative fuel cells

## ABSTRACT

This study demonstrates promising bifunctionality of nitrogen-doped carbon nanostructures (CN<sub>x</sub>) for ORR and OER in acidic medium. Although CN<sub>x</sub> catalysts are not as active as Pt/C in ORR and Ir/C in OER, they exhibit significantly lower combined overpotential for ORR and OER relative to those shown by the two commercial catalysts, which are highly active only for one of the two reactions, but not both. The effect of various nitrogen functionalities on the ORR and OER activity of CN<sub>x</sub> catalysts was also studied. CN<sub>x</sub> samples with higher pyridinic-N site density exhibited higher ORR and OER activity.

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## 1. Introduction

Oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) are becoming increasingly important electrochemical reactions due to growing emphasis on sustainable power generation technologies [1,2]. An example of this class of technologies is a proton exchange membrane (PEM) fuel cell where hydrogen (fuel) is oxidized at the anode producing protons which are transported through the electrolyte (membrane) to the cathode where oxygen is reduced forming water. The low temperature of operation (<80 °C) and slow kinetics of hydrogen oxidation and particularly oxygen reduction necessitate Pt-based electrocatalysts [3,4]. Similarly, oxygen evolution reaction (OER), relevant from the point of water electrolysis employs ruthenium or iridium-based catalysts [5,6]. Thus, both reactions use precious metal-based electrocatalysts which are expensive and available only in limited reserves making a strong case to develop low-cost, active and stable electrocatalysts for the two reactions. Furthermore, bifunctionality for ORR and OER is important and extremely relevant for regenerative fuel cell systems. Nitrogen-doped carbon nanostructures or “CN<sub>x</sub>”

are considered as promising alternatives [7–15]. As an example, CN<sub>x</sub> materials can be synthesized using chemical vapor deposition of a C and N source (such as CH<sub>3</sub>CN) over a metal-doped support (such as MgO, SiO<sub>2</sub>, or Al<sub>2</sub>O<sub>3</sub>) followed by an acid-washing step to remove the exposed metal and the oxide support [16,17]. Thus, the metal merely acts to initiate growth of CN<sub>x</sub>, and is not accessible on the surface where electrocatalysis occurs. Though these CN<sub>x</sub> materials have been shown to exhibit both ORR and OER activity, the nature of their active sites still remains disputed. There are contradicting reports in the literature suggesting the role of various nitrogen species in imparting catalytic activity to these materials [7,10–13,18–27]. Though techniques such as Mössbauer spectroscopy or X-ray Absorption Spectroscopy (XAS) are widely used to reveal active sites and compute their density for metal-centered catalysts [28,29], they are of little use in the case of CN<sub>x</sub> due to the absence of a metal-center. In-addition, absence of poisoning using well-known probes such as CO, CN<sup>-</sup> and H<sub>2</sub>S [10,15,30,31] makes identification and quantification of active sites in these materials even more challenging.

With this motivation, we have recently focused on devising strategies that can help reveal the active sites in CN<sub>x</sub> materials. One of these is related to identification of a probe molecule which poisons these CN<sub>x</sub> catalysts and thus provides insights about their active sites [32]. We recently demonstrated, for the first time,

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that ORR active sites in CN<sub>x</sub> catalysts can be probed using phosphate anion poisoning. The loss in pyridinic-N site density was observed to be correlated to the loss in ORR activity. Based on these results, we hypothesized two possible active site models namely i) pyridinic-N sites and ii) C atoms next to pyridinic-N. The former would be rendered inactive by protonation whereas the latter by a site blocking effect of the phosphate ions which would also stabilize the pyridinic-NH sites [32]. Another useful approach is to modify the pyrolysis conditions such that the amount of various nitrogen species on the surface can be controlled. This latter approach is also the focus of this work. The first part of the study aims to evaluate the bifunctional characteristics of these CN<sub>x</sub> catalysts for ORR and OER. Comparisons with the state-of-the-art catalyst materials for ORR and OER are also presented. In the second part of the study, CN<sub>x</sub> catalysts were synthesized using different pyrolysis temperatures, but the same C, N source. This allowed us to control the distribution of various nitrogen functionalities in the synthesized materials. ORR and OER activities of these samples were then correlated to the amount of each of these nitrogen species. Results from characterization experiments using X-ray Photoelectron Spectroscopy (XPS) and Laser Raman Spectroscopy (LRS) are also presented.

## 2. Experimental

### 2.1. Materials

The growth substrates for the CN<sub>x</sub> catalysts were prepared through incipient wet impregnation technique on MgO (Aldrich) support by using 2 wt% iron (from iron (II) acetate, Aldrich) dissolved in deionized water, the volume of which was decided based on the pore volume of the support. The sample was then kept overnight in an oven for solvent evaporation and then ball-milled at 200 rpm for 3 h using a rotary ball-mill. The ball-milled substrate then went through an acetonitrile pyrolysis step for 2 h at 900 °C for the carbon growth process. The resulting sample was then subjected to an acid-washing step in 1 M HCl for 1 h at 60 °C and then vacuum-filtered, washed and dried in an oven at 80 °C. The final product collected from the oven is denoted as CN<sub>x</sub>. Similarly, CN<sub>x</sub> was also synthesized using pyrolysis temperatures of 750 °C, 800 °C and 850 °C respectively. 10% Pt/C (Etek) and 20% Ir/C (Premetek Co.) were used as received as the state-of-the-art catalyst materials for ORR and OER, respectively.

### 2.2. Electrochemical testing

Oxygen reduction reaction (ORR) activity was measured in a standard three-electrode system comprising of a working electrode (glassy carbon disk, 5.61 mm and 0.2472 cm<sup>2</sup>), a hydrogen reference electrode (ET070 Hydroflex) and a counter electrode (Pt coil). The electrolyte used was 0.1 M HClO<sub>4</sub>. To prepare the CN<sub>x</sub> catalyst ink, 95 μL of 5 wt% Nafion<sup>®</sup> solution and 350 μL ethanol (200 proof) were added to 10 mg of catalyst weighed in a 2 mL vial. The vial was then kept for ultrasonication in an ice bath until the catalyst was well-dispersed. A 9 μL aliquot of the ink was then pipetted onto the glassy carbon disk which corresponded to a catalyst loading of about 800 μg/cm<sup>2</sup><sub>geometric</sub>.

The catalyst ink preparation procedure was similar for Pt/C and Ir/C and the catalyst loading (including the mass of carbon) was about 200 μg/cm<sup>2</sup><sub>geometric</sub> for these samples.

Cyclic voltammograms (CVs) were first collected at 50 mV/s from 1.2 V to 0 V to 1.2 V with the working electrode rotating at 1000 rpm until reproducible CVs were noted in the oxygen saturated electrolyte. Slow CVs at 10 mV/s were then collected at 400, 800, 1000, 1200 and 1600 rpm on the disk again from 1.2 V to 0 V

to 1.2 V. CVs were also collected in an argon saturated electrolyte serving as a blank.

ORR performance was evaluated by comparing (i) potential at a background-subtracted current density of -0.1 mA/cm<sup>2</sup>, (ii) half-wave potential (E<sub>1/2</sub>), (iii) specific kinetic current (i<sub>k</sub>) at 0.7 V. Calculation of specific kinetic current for ORR was made using the Koutechy-Levich equation Eq. (1).

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{lim}} \quad (1)$$

where *i* is the measured current density,

*i<sub>k</sub>* is the kinetic current density defined by  $i_k = nFkC_{O_2}$   
and *i<sub>lim</sub>* is the limiting current density defined by  $i_{lim} = 0.62nFD^{2/3}C_{O_2}\nu^{-1/6}$ .

Here, *n* is the number of electrons transferred per molecule of oxygen, *F* is the Faraday's constant (96485 C/mole of electrons), *k* is the rate constant for ORR, *C<sub>O<sub>2</sub></sub>* is the bulk concentration of oxygen (1.18 × 10<sup>-6</sup> mol/cm<sup>3</sup>) [33,34], *D* is the diffusion coefficient of oxygen (1.93 × 10<sup>-5</sup> cm<sup>2</sup>/s) [33–35], *ν* is the kinematic viscosity of the electrolyte (1.009 × 10<sup>-2</sup> cm<sup>2</sup>/s) [33,35].

In-addition, Tafel analysis was performed to gain insights into the rate-determining step for ORR using Eq. (2).

$$V = V_0 + b \log \frac{i_k}{i_0} \quad (2)$$

where *V<sub>0</sub>* is the equilibrium potential (1.23 V), *b* is the Tafel slope and *i<sub>0</sub>* is the exchange current density.

To evaluate OER activity, linear sweep voltammograms (LSVs) were collected from 0.0 to 2.0 V in an argon-saturated electrolyte with the catalyst-coated electrode rotating at 1600 rpm. The scan rate used was 10 mV/s. The capacitive current was subtracted from the measured total OER current. The current observed below 1.3 V was assumed as the capacitive contribution and was consequently subtracted from the overall measured current. Potential at an OER current density (after subtracting the capacitive component) of 10 mA/cm<sup>2</sup><sub>geometric</sub> was considered as a measure of OER activity.

All potentials referred to in this work are referenced with respect to a reversible hydrogen electrode (RHE) scale.

### 2.3. Characterization

X-ray Photoelectron Spectroscopy (XPS) was used to analyze the composition of the surface species. A Kratos Axis Ultra DLD Spectrometer was used with Al Kα monochromatic X-ray radiation (1486.6 eV). The spectra were collected at room temperature with 20 eV pass energy. Binding energy (B.E.) values were referenced to the standard C 1s binding energy of 284.5 eV. CasaXPS program was used for data analysis and curve fitting. Shirley-type background and Lorentzian-Gaussian combination were used for data processing.

Laser Raman Spectroscopy experiments were performed at room temperature using a LabRAM HR Raman microscope system from Horiba Scientific. All measurements were performed at room temperature using 514.5 nm laser and a 50x objective. Before collecting the spectra, calibration was made using a silicon reference at 520.7 cm<sup>-1</sup> and white light at 0 cm<sup>-1</sup>. The spectrograph uses a grating of 1200 lines/mm. Multiple spectra were collected and averaged to improve the signal to noise ratio. The peak assignments were based on the literature. Data analysis and curve fitting were performed using MagicPlot program.

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