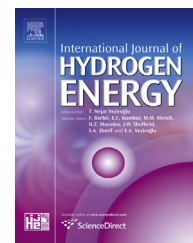




ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Enhanced oxygen reduction reaction activity of nitrogen-doped graphene/multi-walled carbon nanotube catalysts in alkaline media

Sander Ratso^a, Ivar Kruusenberg^a, Urmas Joost^b, Rando Saar^b,
Kaido Tammeveski^{a,*}

^a Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

^b Institute of Physics, University of Tartu, Ravila 14c, 50411 Tartu, Estonia

ARTICLE INFO

Article history:

Received 23 November 2015

Received in revised form

22 January 2016

Accepted 3 February 2016

Available online xxx

Keywords:

Oxygen reduction

Graphene

Carbon nanotubes

Nitrogen doping

Composite catalysts

Electrocatalysis

ABSTRACT

In this work, the electroreduction of oxygen on nitrogen-doped graphene and multi-walled carbon nanotube (MWCNT) composite catalysts is investigated. Acid-treated MWCNTs and graphite oxide were doped using biuret, carbohydrazide and semicarbazide hydrochloride as the nitrogen precursors. The reactants were mixed with carbon nanomaterials and pyrolysed in an inert atmosphere at 800 °C. Scanning electron microscopy was used to characterise the surface morphology of catalysts and X-ray photoelectron spectroscopy (XPS) was used to determine the surface content of the catalysts. XPS revealed different contents of nitrogen gained by using different nitrogen precursors, which were tied to electrochemical activities observed in this work by using the rotating disk electrode (RDE) method. The catalysts revealed high oxygen reduction reaction (ORR) activity even at low loadings and excellent stability over 1000 potential cycles. This indicates their applicability as cathode materials in alkaline anion exchange membrane fuel cells.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Substituting fossil fuels with a sustainable and renewable source of power is one of the key problems in today's society. Traditionally, fuels such as gasoline and diesel are used for automotive purposes, but such engines have low efficiencies and produce unwanted greenhouse gases. Among the promising substitutes for these fuels are hydrogen or methanol, which are converted to electrical energy using fuel cells [1]. The main obstacle to further development of low-temperature fuel cells is the slow oxygen reduction reaction (ORR) on the

cathode side of the fuel cell [2,3]. The ORR can occur either by 2- or 4-electron pathway [4], of which the latter is desired for fuel cell usage. To improve the ORR kinetics on the cathode of fuel cells, precious-metal catalysts, mainly carbon-supported platinum [5–7] or its alloys [8] have been employed, because platinum is a highly active catalyst to facilitate the 4-electron pathway of oxygen reduction. However, platinum is scarce and not available in the amounts needed for the automotive industry. As an alternative, cheap and abundant materials have been used to prepare electrocatalysts with high activity towards the ORR [9–11].

* Corresponding author. Tel.: +372 7375168; fax: +372 7375181.

E-mail address: kaido.tammeveski@ut.ee (K. Tammeveski).

<http://dx.doi.org/10.1016/j.ijhydene.2016.02.021>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Various carbon materials have been used as a starting material to produce electrocatalysts for ORR, such as mesoporous carbon [12–14], carbon aerogels [15,16] and xerogels [17], carbon nanotubes (CNTs) [18–20], graphene [21–23] or their composite materials [24–31]. All these carbon nanomaterials have some common properties, such as high specific surface area, electrical conductivity, chemical stability and good porosity, which makes them good catalyst supports. The porous structure helps with the mass transfer, large surface area is favourable for the creation of a higher number of active sites, electrical conductivity helps to transport electrons needed for O₂ reduction on these active sites and since the materials are also chemically stable, they usually have a long lifetime.

However, since bare carbon nanomaterials are not highly active and mostly catalyse a two-electron reduction of oxygen [32–34], they need to be modified to achieve efficient catalysts. One way for doing this is to dope carbon nanomaterials with heteroatoms, such as nitrogen [12,14,18–23,28–31,35–37]. When nitrogen is substituted to the carbon lattice, the carbon π electrons are conjugated to the lone pair of the N atom [36,38]. This means that nitrogen can donate electrons onto the conjugated orbital and increase the electron-donor properties of the material [39]. The carbon orbital can then donate electrons to the π^* orbital of O₂ molecule, which eases the splitting of the O–O bond and thus increases the ORR activity [24]. Nitrogen species in the carbon lattice also facilitate O₂ adsorption on the carbon material [11].

The effects of nitrogen doping can vary. The two most important factors are the amount of nitrogen doped into the carbon material and also the types of nitrogen present [40]. Nitrogen can form four types of groups when doped into carbon: pyridinic N, pyrrolic N, graphitic N (quaternary N), and pyridinic N⁺–O[–]. Among these, pyridinic N and graphitic N are typically considered as the active groups for ORR in alkaline medium, while pyrrolic N and pyridinic N-oxide are stated to be inactive [11,41,42]. It has also been recently suggested that graphitic nitrogen can be divided into two subtypes of nitrogen according to its placement in the carbon lattice with the different types having different activities for ORR [43,44]. However, since there has not yet been demonstrated a way to achieve only a single type of nitrogen species on a catalyst, there is no way to properly determine the activity of each group and thereby there are controversial studies which assert pyrrolic N to be active instead [45,46] and pyridinic N to catalyse the 2-electron reduction of oxygen [47]. Surface nitrogen contents have been shown to increase the ORR activity in both acidic [48,49] and alkaline conditions [49,50], as the number of active sites on the surface is proportional to the amount of nitrogen.

A wide range of methods have been harnessed to obtain nitrogen-doped carbon materials, for example doping directly during synthesis via arc-discharge [19] or chemical vapour deposition (CVD) [20,43,51] and the so called post-treatment methods, such as treatment of existing carbon materials with NH₃ [52–55] or pyrolysis in the presence of a nitrogen precursor [18,23,25,56–59]. Compared to the other synthesis methods, pyrolysis of a carbon material-nitrogen precursor mixture, has been found to be a cost effective and quick method, granted that the materials used are cheap and

contain a large quantity of nitrogen [60,61]. For this purpose, a number of organic compounds have been used: pyridine [31], melamine [57,62], polyaniline [63], dicyandiamide (DCDA) [23,25], urea and its derivatives [37,64].

We have recently studied post-treatment doping using urea and DCDA as nitrogen precursors [18,23,25,65]. In this work, we show a quick and easy one-step synthesis method of N-doped nanocarbons using graphene and MWCNTs as carbon base materials and different nitrogen-containing substances to obtain electrocatalytically active composite catalysts for ORR. All the nitrogen precursors used (biuret, carbonylhydrazide and semicarbazide hydrochloride) are derivatives of urea and therefore the main motivation of this research is to compare the electrocatalytic properties of the N-doped composite materials with that of the urea-derived composite studied previously [25]. The N-doped carbon nanomaterials are physically characterised by scanning electron microscopy and X-ray photoelectron spectroscopy. The electrochemical characterisation of N-doped nanocarbon catalysts was performed using a rotating disk electrode.

Experimental

Materials and composite catalysts preparation

The graphene oxide (GO) material used in this work was synthesised from graphite powder (Graphite Trading Company) by a modified Hummers' method [66,67]. Firstly, 50 ml of concentrated sulphuric acid and 2.0 g of graphite powder were mixed in a 250 ml beaker at room temperature. Then, the mixture was sonicated for 1 h. Next, sodium nitrate (2.0 g) and potassium permanganate (6.0 g) divided to smaller portions were slowly added into the beaker in a sequence. At the same time the mixture was stirred on a magnetic stirrer. Afterwards, the mixture was heated at 35 °C for 18 h. When the heating was completed, the beaker was put into an ice bath and 80 ml of deionised water was added into the solution. After few minutes, 20 ml of H₂O₂ (30%, Merck) was added. The mixture was then washed few times with 10% HCl solution and with water on a vacuum filter. Finally, the obtained brown solid was dried in vacuum at 75 °C.

Multi-walled carbon nanotubes (MWCNTs, Nano-Lab, Inc., Brighton, MA, USA) were treated in acids using a previously published procedure [68]. After the treatment, the nanotubes were sonicated in ethanol until a homogenous dispersion was achieved. GO was weighed and added so that the amount of GO would correspond to the weight of the nanotubes. Then either biuret, carbonylhydrazide or semicarbazide hydrochloride as nitrogen precursors (see Scheme 1 for chemical structures of these compounds) and polyvinyl pyrrolidone (PVP) as a dispersing agent were added. In what follows, these catalyst materials are designated as NG/NCNT-BR, NG/NCNT-CH and NG/NCNT-SC accordingly. The amount of nitrogen precursor was 20 times that of carbon nanomaterial, similarly to our previous studies [23,25]. The final mixture was further sonicated for 2 h and then dried at 75 °C in vacuum. The material was gathered into a quartz boat and pyrolysed in flowing argon atmosphere at 800 °C for 2 h. After that the furnace was

Download English Version:

<https://daneshyari.com/en/article/5147268>

Download Persian Version:

<https://daneshyari.com/article/5147268>

[Daneshyari.com](https://daneshyari.com)