



A Pt-free Electrocatalyst Based on Pyrolyzed Vinazene-Carbon Composite for Oxygen Reduction Reaction



Akeem Akinpelu^a, Belabbes Merzougui^b, Saheed Bukola^a, Abdul-Majeed Azad^a, Rafil A. Basheer^c, Greg M. Swain^d, Qiaowan Chang^e, Minhua Shao^{e,*}

^a Center of Nanotechnology (CENT), King Fahd University of Petroleum and Minerals, Dhahran, 31261 Eastern Province, Saudi Arabia

^b Qatar Environment and Energy Research Institute (QEERI), Qatar Foundation, Doha, Qatar

^c Materia Chemica LLC, P.O. Box 82342, 511 Old Towne Rd, Rochester, MI 48308, USA

^d Chemistry Department, Michigan State University, 578 South Shaw Lane, East Lansing, MI 48824, USA

^e Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

ARTICLE INFO

Article history:

Received 31 December 2014

Received in revised form 25 January 2015

Accepted 7 February 2015

Available online 10 February 2015

Keywords:

Fuel cells

Non-precious metal electrocatalysts

Vinazene

Methanol tolerance

Oxygen reduction reaction

ABSTRACT

The 2-vinyl-4,5-dicyanoimidazole (Vinazene) was used as a nitrogen precursor to synthesize a promising non-precious metal (NPM) catalyst for oxygen reduction reaction (ORR). Vinazene together with an iron source was impregnated into a carbon matrix and pyrolyzed at 900 °C in N₂ atmosphere. The structure of the resulting Fe–N–C nanocomposite was analyzed by X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray diffraction. Both rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) experiments showed excellent ORR activity for the obtained catalyst with low H₂O₂ formation (~3.0%) in 0.1 M KOH. The catalyst was found to be rich in mesoporous structure along with high percentage of pyrrolic-N function with surface area of about 673 m² g⁻¹ and pore size of 4.2 nm. In addition to its excellent ORR activity, the catalyst showed remarkable tolerance towards methanol oxidation and demonstrates good stability over 10,000 potential cycles (0.6–1.0 V vs RHE). We believe that this N-rich Vinazene molecule will be beneficial to further development of nitrogen doped carbon electrocatalysts.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The mass commercialization of fuel cells is consequent upon development of efficient, stable and cost effective electrocatalysts that could replace completely or at least a large portion of Pt-based catalysts. Platinum and its alloys are known as the most efficient catalysts for oxygen reduction reaction (ORR). However, lack of long term stability, high sensitivity to impurities, intolerance to methanol oxidation, cost and dwindling supply of Pt have been major impediments to the large scale implementation of fuel cells technology [1,2]. To circumvent the aforementioned shortcomings, many approaches have been tailored to develop electrocatalysts based on non-noble metals. The first improvement in performance of non-precious metal (NPM) catalysts towards ORR was made five decades ago following Jasinski's discovery of catalytic nature of cobalt phthalocyanine [3]. Despite their higher tolerance to

methanol oxidation, Pt-free electrocatalysts still exhibit low ORR activity and low stability as compared to commercial Pt-based ones [4]. Recent studies have focused on improving the overall ORR activity by doping carbon support with a heteroatom such as nitrogen, selenium, phosphorus, boron and sulfur [5–10]. Nitrogen doped carbon electrocatalysts with and without transition metals have received a great attention among the researchers owing to their good thermal conductivity, π -delocalization and high electronic conductivity [4]. Studies have shown that incorporation of nitrogen into the carbon matrix plays a significant role in improving the carbon electron-donor capacity which leads to high ORR activity and stability [5,11–13].

In very recent reports, ORR electrocatalysts based on different nitrogen-bearing compounds and non-noble metals, enriched in highly active sites that are benign for ORR activity and stability have been extensively explored. For example, Wang et al. [14] reported a highly active NPM catalyst prepared from melamine as N and C precursor. The excellent ORR activity was attributed to the incorporation of nitrogen atoms into the carbon matrix creating active sites. Similarly, Xie et al. [15] found that N-dopant and metal complexed with N–C sites, achieved through incorporation of

* Corresponding author.

E-mail addresses: bmerzougui@qf.org.qa (B. Merzougui), kemshao@ust.hk (M. Shao).

phenanthroline/melamine into graphene oxide matrix in the presence of transition metal (Fe), were prerequisites for the enhanced ORR activity and stability. Although, there are some reports on metal-free nitrogen doped carbon catalysts that show improved ORR activity [16–18], it is generally believed that transition metal participation by forming M-N_x (metal-nitrogen) sites at the molecular level could induce higher ORR activity and stability [2,19–22]. In this regard, nitrogen precursors that have been effectively studied are polyaniline [2,13,23,24], polypyrrole [25], and imidazolic framework with phenanthroline [26]. It has been established that the type of nitrogen precursor remains a key player in determining the properties of ORR catalysts.

The main objective of this study is to demonstrate the electrocatalytic activity towards ORR of a NPM catalyst derived from a new nitrogen precursor 2-vinyl-4, 5-dicyanoimidazole (named Vinazene) as shown in Fig. 1. Vinazene is a derivative of imidazole that can undergo thermal polymerization. Its high nitrogen content (39 wt. % and 26 atom %) along with the intrinsic stability of the imidazole ring system, imparts to it better flammability inhibition, higher softening temperatures and greater char yield [27]. As a very strong electron acceptor, vinazene has also been used in organic solar cells [28,29]. We envisage that such a favorable electron acceptability of vinazene could be exploited to develop a composite catalyst based on metal-nitrogen doped carbon aiming to achieve a good catalytic activity towards ORR.

2. Experimental

2.1. Chemicals and Materials

Vinazene was purchased from Vinazene Inc. and Ketjen Black EC-300 was obtained from AKZO Nobel. Acetonitrile, Isopropanol (IPA) and potassium hydroxide were purchased from J T Baker, Fisher Scientific, and Prolabo VWR, respectively. All chemicals were used without further purification. MilliQ UV-plus water (Millipore) was used throughout the experiments.

2.2. Synthesis of vinazene based electrocatalyst

200 mg of carbon black (Ketjen Black EC-300) was dispersed in a mixture of acetonitrile (ACN) and isopropyl alcohol (IPA) by sonication for 30 min. Approximately 100 mg of vinazene was then added to the mixture and left under stirring for 48 hr in an enclosed system at room temperature to prevent solvent evaporation and to allow proper impregnation of vinazene into the carbon matrix. Then, 170 mg of FeCl₃·6H₂O (10 wt. % Fe) was added to the mixture and stirred for another 24 hr. The solvent was then allowed to evaporate and the solid was vacuum dried at 70 °C.

2.3. Heat treatment of the synthesized powdered sample

Sample pyrolysis at high temperature is a crucial step in catalysts development for ORR. The active sites are created on the catalyst surface during the heat treatment step. In a typical procedure, the obtained powdered sample was placed in an alumina crucible and transferred to a quartz tube in a MTI furnace (OTF-1200X-S). The temperature was ramped from room

temperature to 100 °C for 30 min and held at this temperature for another 30 min while flowing N₂ gas at a rate of 100 mL min⁻¹. This step is important in order to purge out absorbed oxygen and water. Then, the temperature was ramped to 900 °C at a rate of 5 °C min⁻¹ and held for 60 min. The system was allowed to cool down under ambient condition. The obtained powdered sample was denoted Fe-N-C.

2.4. Spectroscopy Characterization

A Perkin Elmer Phi 5400 ESCA system with a Mg K α X-ray source was used for XPS characterization. Sample was analyzed at pressures between 10⁻⁹ and 10⁻⁸ torr with pass energy of 29.35 eV and a take-off angle of 45°. The spot size is roughly 250 mm². All peaks were referenced to the signature C1s peak for carbon at 284.6 eV. Raman spectra were taken on an iH320Horiba spectrometer with charge-coupled device (CCD) using monochromatic laser (300 mW, 532 nm), grating of 1200 cm⁻¹ and an aluminum substrate. X-ray diffraction (XRD) patterns were collected using a Rigaku Miniflex II instrument with a monochromator of Cu K α 1 (1.5406 Å) at 30 kV, 15 mA. The XRD patterns were recorded in the static scanning mode from 5° to 60° (2 θ) at a detector angular speed of 2° min⁻¹ and step size of 0.02°. Field emission scanning electron microscope (FESEM, Tescan-Lyra-3) and energy dispersive X-ray spectroscopy (EDX, Oxford-Xmax) were used to provide images and elemental composition. Surface area analysis and porosity measurements were done on ASAP 2020 by micromeritics. High resolution transmission electron microscopy (HR-TEM) images were collected on a JEOL JEM-2100F at 200 kV.

2.5. Electrochemical measurements

Electrode preparation involves dispersion of 5 mg of Fe-N-C catalyst in a mixture of water and isopropyl alcohol (30% V/V). 37 μ l of 1.66 wt. % Nafion[®] (prepared from 5 wt. % Nafion[®] solution, Aldrich) was added and the mixture was sonicated for 15–20 min to obtain a homogeneous ink. The working electrode was prepared by depositing a certain volume of the catalyst ink on a pre-cleaned glassy carbon rotating disk electrode (RDE, 5 mm in diameter, Pine Research Instrument) to achieve a catalyst loading of 0.6 mg cm⁻². To determine the yield of H₂O₂, a rotating ring-disk electrode (RRDE) was also used in this study. It consists of a 0.2475 cm² glassy carbon electrode and a Pt ring of 0.1866 cm² (Pine Research Instrument). Commercial Pt (20 wt. %)/Vulcan, denoted as Pt/C was used for comparison. The Pt loading was kept at 30 μ g cm⁻².

The electrochemical experiments were carried out in a three-electrode electrochemical cell at controlled temperature (25 °C) using a circulating bath. A platinum mesh or carbon cloth was used as counter electrode during the electrochemical evaluations. A calomel electrode with 3.0 M KCl, and calibrated against reversible hydrogen electrode (1.004 V vs RHE in 0.1 M KOH) was used as a reference electrode. It is important to mention, that carbon cloth was used as the counter electrode during durability studies to avoid any contamination of catalyst sample by Pt during potential cycling. Potential measurements were converted to RHE. Potentiostat Voltalab PGZ 402 from Radiometer Analytical was used for all the electrochemical measurements.

3. Results and discussion

3.1. Structural analyses of Fe-N-C Vinazene derived catalyst

Fig. 2a is the scanning electron microscopy (SEM) image of the synthesized catalyst that shows porous structure. To further

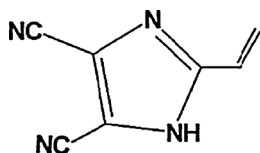


Fig. 1. Structure of 2-vinyl-4, 5-dicyanoimidazole (Vinazene).

Download English Version:

<https://daneshyari.com/en/article/184187>

Download Persian Version:

<https://daneshyari.com/article/184187>

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