



The Impact of Loading and Temperature on the Oxygen Reduction Reaction at Nitrogen-doped Carbon Nanotubes in Alkaline Medium



W.Y. Wong^{a,*}, W.R.W. Daud^{a,b}, A.B. Mohamad^{a,b}, A.A.H. Kadhum^{a,b}, K.S. Loh^a, E.H. Majlan^a, K.L. Lim^a

^a Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

^b Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

ARTICLE INFO

Article history:

Received 3 December 2013

Received in revised form 16 February 2014

Accepted 16 February 2014

Available online 28 February 2014

Keywords:

metal-free catalyst
nitrogen-doped carbon nanotubes
oxygen reduction reaction
catalytic effect.

ABSTRACT

Metal-free nitrogen-doped carbon nanotube (NCNT) catalysts were synthesised via chemical vapour deposition with ethylenediamine and iron phthalocyanine. The electrochemically active NCNT was studied via thin-film rotating-ring disk voltamogram analysis to elucidate the optimum loading of catalysts for oxygen reduction reaction (ORR) in 0.1 M KOH electrolyte. In this study, the activity and stability of NCNT at elevated temperature were investigated. The current limiting plateau was achieved with loading above 500 $\mu\text{g}/\text{cm}^2$ on glassy carbon tip with insignificant change in onset potential (c.a. +0.9 V vs RHE). The highest electron transfer number of 3.90 was obtained and it was found comparable to $n = 3.95$ on 130 $\mu\text{g}/\text{cm}^2$ Pt/C catalysts. The subjection to cell's temperature from 298 K to 343 K showed improved activity and was found stable above 323 K.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

For decades, platinum-based catalysts have been extensively used as the electrocatalysts in fuel cell electrodes due to their excellent catalytic activity and stability under various operating conditions, such as low pH and high temperature [1,2]. Nevertheless, some technical gaps remain that hinder the commercialisation of fuel cell technology in the near future. One of these obstacles is the high cost of the platinum catalysts and Nafion membranes [3]. Intensive efforts have been devoted to combating the technical barriers to inexpensive, efficient fuel cells, and two major approaches have been identified: reducing the platinum loading on the electrodes (for both the anode and cathode) and exploring alternative catalysts to platinum, mainly on the cathode where the oxygen reduction reaction occurs. Recently, some effort has been devoted to inventing new types of fuel cells that use non-noble metal catalyst electrodes [4]. New innovations in material design have opened up the possibility of altering the conventional fuel cell design, which aims to reduce the cost of the fuel cells while maintaining their existing efficiency.

Several types of non-noble metal catalysts, such as metal porphyrins [5,6], chalcogenic compounds [7], macrocyclic

compounds [8–10], and metal oxides [11,12] have been investigated as ORR catalysts, in both acidic and alkaline media. Gradual improvement on the activity was seen with continuous efforts since the last decade. Recent focus on metal-free nitrogen-doped carbon compound such as carbon nanotubes and graphene has shown to exhibit activity on par to those non-noble metal catalysts, although its activity is still lower than that platinum-based catalysts. Nitrogen as a dopant in a carbon matrix has been shown to possess unique characteristics as a metal-free catalyst for the oxygen reduction reaction and was found to be correlated to the uneven electrons distribution over the NCNT surfaces. It was hypothesised that the more electronegative nitrogen (compared to carbon) could induce an unbalanced electron distribution on the carbon matrix surfaces, thus creating active sites for the oxygen to adsorb and subsequently undergo reduction via specific mechanisms [13]. However, the nature of the active sites on the nitrogen-doped carbon catalysts has an unknown effect on the ORR catalysis. The introduction of nitrogen into the carbon matrix forms four main types of bonding: pyridinic-N, quaternary-N, pyrrolic-N and pyridinic-N-oxides [14]. Pyridinic-N and quaternary-N are candidates for the ORR active sites, but their roles are still unclear. To determine these contributions, some effort was devoted to the fundamental understanding of the process through the use of computational methods, such as density functional theory and ab initio studies [15–17]. To the best of our knowledge, these results are still inconclusive.

* Corresponding author. Tel.: +6038921 6084; fax: +6038921 6024.

E-mail address: wramli@eng.ukm.my (W.Y. Wong).

Geng et al. [18] and Chen et al. [19] have shown that nitrogen-doped carbon nanotubes possess the ability to reduce oxygen in both acidic and basic media. NCNT have shown intrinsic activity in acidic media, while an activity comparable to platinum was observed at NCNT in alkaline media under ambient conditions [20]. Edge plane exposure due to the pyridinic-N bonding was assumed to be the active sites for the ORR, although the reaction mechanisms were different in the two media [21]. The uncertain nature of the ORR activity on nitrogen-doped compounds has prevented many researchers from further investigating the kinetic aspects of the materials which have been reported widely on platinum-based and metal-based catalysts. The results of such investigations could show certain impact to understand the underlying reaction mechanisms. On the conventional platinum catalysts and other transition metals, such as iron and ruthenium, the reaction kinetics were improved with increased temperature. However, to the best of our knowledge, there has been no study on this aspect in non-metal catalyst compounds, such as nitrogen-doped carbon nanotubes.

A major drawback of the non-noble metal or metal-free ORR catalysts is related to its low active site density affecting the decrease in fuel cell performance over a period of time due to the mass transport limitation [22]. Optimizing the catalyst loading is expected to raise and maximize the active site density and thus provide a stable performance to the fuel cell system. As a part of our continuing effort, the viability of nitrogen-doped carbon nanotube catalysts for alkaline fuel cells was investigated in this study at different electrolyte temperatures to simulate the intermediate cell temperature environment. Concerning the unknown active site density on NCNT, the effect of catalysts loading on the GC electrode was studied prior to the subsection of the cell to elevated temperature aiming to obtain the optimum catalyst loading with true current limiting plateau. Experiments have previously been performed in the laboratory to search for suitable precursors that produce highly active NCNT. The most active NCNT produced was used in this study [23]. This study observed a dissimilar trend with temperature in the catalytic activity of ORR than for the metal catalyst. It was found that the ORR activity was shown to increase and was found relatively stable above 50 °C. Besides, no lost in activity after cooling down.

2. Experimental

2.1. Preparation of Nitrogen-doped Carbon Nanotubes

Nitrogen-doped carbon nanotubes were synthesised via a chemical vapour deposition (CVD) method in a flow furnace (Carbolite, U.S.) using ethylenediamine as the precursor and iron (II) phthalocyanine as the nanotube growth catalyst. Briefly, iron (II) phthalocyanine was placed at the opening of the furnace. Then, the ethylenediamine liquid was bubbled with nitrogen carrier gas and transported into the furnace in the gas phase. A small quartz tube served as the substrate for the NCNT growth. The NCNT growth temperature was set at 850 °C for 30 min and was allowed to cool to room temperature under the continuous flow of nitrogen. The metal residue on the collected NCNT was removed using excess 0.5 M H₂SO₄ under reflux conditions for 6 hours. The solution was filtered, and the NCNTs were dried in the oven for 1 hour before being removed for analysis.

2.2. Physical and chemical characterisations

The nanotube diameters and morphologies were characterised using a Philips CM 12 transmission electron microscope (TEM) operated at 80 kV. The samples were dispersed in excess ethanol by sonicating for 30 min before placing the samples on a 200-mesh copper grid support for TEM analysis. The specific surface area of the

samples was measured and calculated by BET method (Micromeritics ASAP 2020) using N₂ adsorption at -195.82 °C. Prior to the analysis, the samples were degassed at 350 °C for 8 hour to desorb any impurities and moisture present. The nitrogen content on the surfaces of the samples were determined using a Krato Axis Ultra DLD X-ray photoelectron spectrometer (XPS) operated at 14 kV. The XPS data were collected using a dual anode X-ray source with Mg K radiation at an energy of 1253.6 eV. A survey scan was performed from 1200 to 0 eV on each of the samples, followed by a narrow scan specifically on the C 1s, N 1s and O 1s regions. The data were analysed using XPS data analysis software. Quantitative analysis was performed to obtain the composition of the nitrogen-carbon functional groups in the samples. The sensitivity factors were taken into account.

2.3. Electrochemical characterisation

The activity of the NCNT samples in the oxygen reduction reaction in alkaline condition was analysed in electrolyte solution consisting of 0.1 M KOH and was evaluated on an Autolab PGSTAT128 N potentiostat through cyclic voltammetry and rotating ring-disk electrode measurements (Gamry Instruments, Inc.). A conventional water-jacketed three-electrode cell was used with a 5 mm glassy carbon (GC) as the working electrode with a Pt ring placed apart externally to the GC separated by a teflon casing. Pt wire was used as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. All potentials reported in the following section were referred to the reference hydrogen electrode (RHE) potential (a correction of +0.99 V vs SCE in 0.1 M KOH [24] was made). The cell was soaked overnight in concentrated H₂SO₄ and rinsed thoroughly several times with high-purity water before it was filled with the electrolyte. The background potential scan was performed in a N₂-saturated electrolyte over the potential window from 0.0 V to -1.0 V (vs SCE), prior to the potential scan in the O₂-saturated condition. The cyclic voltammograms were considered successful when the voltammogram features were stable for three consecutive cycles. The electrolyte temperature was varied by heating the water jacket and was controlled by measuring the temperature with a clean thermometer. The hydrodynamic voltammograms were obtained after each cyclic voltammetry measurement at different rotation speeds with a scan rate of 5 mV/s in the negative direction over the same potential window. The NCNT used for the measurement was blended into an ink solution consisting of 8.8 mg of the NCNT sample, 0.1 ml of a 0.5 wt% Nafion solution and 0.7 ml of deionised water. Different loading of NCNT ink varying from 0.05 mg/cm² to 0.8 mg/cm² were tested in the same condition. The NCNT catalyst ink was deposited onto the GC electrode surface with a micropipette. The ink paste was allowed to slowly dry at ambient conditions for three hours. The electrode was rinsed with high-purity water before the measurements were performed.

3. Results and Discussions

3.1. Properties of the NCNT catalysts

As shown in the TEM micrograph in Fig. 1, the as-synthesised NCNT displayed tube diameters of 20 - 40 nm with a highly corrugated surface structure, very thin walls of 3-4 nm and wide inner hollow tubes. The segmented, bamboo-like structures in the NCNT were attributed to the defects in the six-membered carbon rings in CNT, which resulted from the five- and seven-member ring formation due to the nitrogen doping in the graphite network [13,25,26]. The BET specific surface area of the NCNT obtained was 164.72 m²/g which is appreciably high and was found comparable to CNT (176

Download English Version:

<https://daneshyari.com/en/article/185925>

Download Persian Version:

<https://daneshyari.com/article/185925>

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