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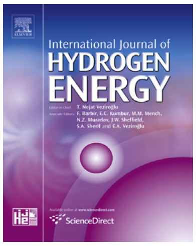

Effect of temperature on the oxygen reduction reaction kinetic at nitrogen-doped carbon nanotubes for fuel cell cathode

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ABSTRACT

One of the technical challenges in commercializing proton exchange membrane fuel cell (PEMFC) technology in this century is related to cost reduction of the fuel cell components especially the cost of the electrochemical catalysts, which are normally noble metals such as Pt. Nitrogen doped carbon nanotubes (NCNT) made by doping nitrogen as an *n*-type dopant in carbon nanotubes, have been shown to possess catalytic activity towards oxygen reduction reaction (ORR). Functionally modified NCNT can become a cheaper alternative electrochemical catalyst that is as good as the noble metals such as Pt. Since the efficiency of the fuel cell is dependent on cell temperatures, this study looks at the effects of the temperatures towards ORR over the temperature range of 298–343 K in 0.5 M H_2SO_4 on the metal-free NCNT using a thin-film rotating-ring disk electrode (RRDE). The NCNT catalysts were synthesized via chemical vapour deposition with ethylenediamine and iron phthalocyanine and post-treatment process was carried out prior to the analysis. The results showed that the optimum ORR activity in NCNT was achieved at 50 °C, beyond which, the ORR activity decreased. In order to increase ORR activity beyond this temperature, the NCNT should be modified by compositing it with other metal or non-metal to improve its activity at higher temperature.

Introduction

Although proton exchange membrane fuel cell (PEMC) technology using hydrogen fuel is hailed as the energy conversion technology of choice because it is a green, clean and sustainable way of generating electrical energy but its deployment is hindered by its high manufacturing cost. Extensive efforts have been conducted by many researchers from all over the world to reduce the manufacturing cost of its

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components. The high cost is attributed to high material costs of its components: electrochemical catalyst, proton exchange membranes and bipolar plate. The most dominant cost is the Pt-based electrochemical catalyst.

Thus, reduction of Pt catalysts' loading and the search for alternative catalysts to Pt are two of the key research areas for fuel cell components in recent years. The catalytic activity of transition metals and metal-free catalysts [1,2] have been shown to exhibit high activity towards the oxygen reduction reaction at the cathode of PEMFC. However, a significant drawback of transition metals catalysts is their low stability in PEMFC because of their tendency to dissolve in electrolyte membrane over a long period [3]. Metal-free catalysts such as nitrogen-doped or boron-doped carbon-based compound have also shown reasonable activity although they are still far lower than the platinum-based catalysts [2,4]. Past studies although still unclear, has revealed some possible mechanisms and active sites on organic compound [5–7]. Coupling organic compound with transition metal ion, the metal-N_4 moiety have also shown to be active towards oxygen reduction reaction (ORR). Hence, suitably modified organic compound has great potential to be used as ORR catalysts.

Nitrogen-doped carbon nanotubes (NCNT) that has been synthesized in our previous work has shown to be active towards ORR. As PEMFC normally operates at temperature range between 60 and 80 °C, the stability of the catalysts used in the fuel cell remain a vital aspect to be investigated. Thus, this paper focuses on investigating the effect of operating temperatures towards the ORR activity on NCNT in acidic electrolyte to mimic the PEMFC environment.

Experimental and procedures

The synthesis of the active NCNT in this study was described in our previous work [8] using the chemical vapour deposition (CVD) method. The nitrogen and carbon source is ethylenediamine, the catalyst for the growth of NCNT is iron (II) phthalocynanine and the gas carrier is nitrogen. The NCNT sample was characterised using transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) to investigate the NCNT morphology and nitrogen bonding environment, respectively. Cyclic voltammetry and rotating-ring disc voltammetry techniques were employed to investigate the ORR activity on our sample of NCNT in 0.5 M H_2SO_4 electrolyte and was measured on an Autolab PGSTAT128N potentiostat. Potential scan range was set from 1.0 V to −0.2 V vs Ag/AgCl. A background scan in nitrogen-saturated condition was performed prior to each scan in oxygen-saturated condition to measure the oxygen reduction activity. A heating jacket was used to vary the electrolyte's temperature from 298 K to 343 K.

Results and discussion

Fig. 1 shows the TEM image of NCNT with bamboo-like structures and irregular surface morphology which is highly corrugated. The high degree of surface defect on NCNT as compared to pristine CNT was attributed to the presence of nitrogen dopant in the carbon aromatic rings that disrupted its structure by forming sp^2 or sp^3 hybridisation with carbon atoms adjacent to it [2]. The presence of nitrogen dopant in the nanotubes was confirmed by the XPS study. In our previous report [8], it was confirmed that no iron traces was found on the surface of NCNT and thus the activity of NCNT for oxygen reduction in this study is believed to be originated from the active sites on the NCNT. In the narrow scan for N 1s in XPS showed in Fig. 2, there are four main nitrogen–carbon bonding nature that could be deconvoluted, namely pyridinic-N (31.0%), pyrrolic-N (4.0%), quaternary-N (36.0%) and pyridinic-N-O (28.0%). The pyridinic-N-O whose oxygen atom was added by possible oxidation during exposure to the atmosphere, shows similar molecular structure to pyridinic-N. The higher proportion of occurrence of pyridinic-N (31.0%) and pyridinic-NO (28.0%) bonding natures compared to that of quaternary-N bonding natures is attributed to the high surface defect of the NCNT that also causes the corrugation on the nanotubes [9,10], which is in good agreement with our previous report [11].

Fig. 1 – TEM image of NCNT at magnification of 35,000 × .

Cyclic voltammetry (CV) technique was employed as the initial step to investigate the catalytic activity of the as-produced NCNT for ORR activity qualitatively. In order to

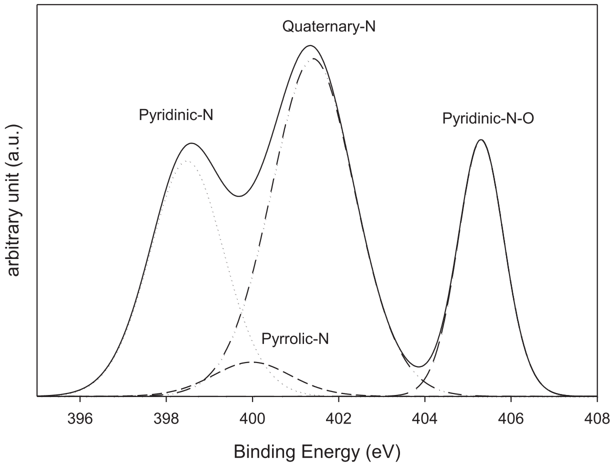

Fig. 2 – XPS spectrum of NCNT in N 1s region.