Highly active nitrogen-doped nanocarbon electrocatalysts for alkaline direct methanol fuel cell

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HIGHLIGHTS

- N-doped nanocarbon cathode catalysts are studied for direct methanol fuel cell.
- Pyrolysis in the presence of dicyandiamide is used for N-doping of carbon catalysts.
- N-doped nanocarbon catalysts have high electrocatalytic activity for ORR in alkaline media.
- N-doped carbon nanotube catalyst shows higher power density compared to Pt/C.

GRAPHICAL ABSTRACT
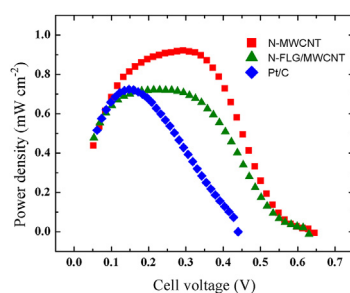
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ABSTRACT

Direct methanol fuel cells are assembled and evaluated using Fumatech FAA3 alkaline anion exchange membrane. Two novel metal-free cathode catalysts are synthesised, investigated and compared with the commercial Pt-based catalyst. In this work nitrogen-doped few-layer graphene/multi-walled carbon nanotube (N-FLG/MWCNT) composite and nitrogen-doped MWCNT (N-MWCNT) catalyst are prepared by pyrolysing the mixture of dicyandiamide (DCDA) and carbon nanomaterials at 800 °C. The resulting cathode catalyst material shows a remarkable electrocatalytic activity for oxygen reduction reaction (ORR) in 0.1 M KOH solution employing the rotating disk electrode (RDE) method. Fuel cell tests are performed by using 1 M methanol as anode and pure oxygen gas cathode feed. The maximum power density obtained with the N-FLG/MWCNT material (0.72 mW cm^{-2}) is similar to that of the Pt/C catalyst (0.72 mW cm^{-2}), whereas the N-MWCNT material shows higher peak power density (0.92 mW cm^{-2}) than the commercial Pt/C catalyst.

1. Introduction

Some of the major topics in the 21st century have been to find solutions to the rapidly growing energy demand and environmental pollution caused by the usage of heavy-duty combustion of fossil fuels. Thereby, a great deal of interest has been added to the research and development of fuel cells as one of the making renewable energy applications [1–4]. Among different types of fuel cells, direct methanol fuel cell (DMFC) has been extensively studied as ideal energy conversion system, which converts chemical energy of methanol directly to electrical energy,

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heat, water and carbon dioxide [5–7]. Compared to pure hydrogen, which is used in most low-temperature fuel cells, methanol possesses several advantages like easy storage, transportation, high solubility in aqueous electrolytes and it can be handled by the existing infrastructure [8–10]. On the other hand DMFC has also few drawbacks like low electrocatalytic activity for the methanol oxidation reaction, CO poisoning of catalysts and low electrocatalytic activity for oxygen reduction reaction (ORR) on cathode catalyst [11]. The slow reaction rate at the cathode side of the DMFC is usually caused by the methanol crossover through the ion exchange membrane or low intrinsic activity of the ORR, which in the end will reduce the efficiency of the fuel cell. Up to now, platinum has been considered as state-of-the-art catalyst for ORR. However, considering that platinum is very expensive and scarce metal then the development of alternative and cheaper non-platinum ORR catalyst materials is significant for widespread marketing of DMFCs [12]. Although some tremendous improvements have been made to replace noble-metal catalysts in fuel cells, several problems still remain unsolved. These include low stability, low reaction rate, high overpotential and low methanol-tolerance. According to literature, most non-Pt catalysts exhibit lower ORR activities than platinum-based catalysts in DMFCs and there are two main reasons why these catalysts have rather poor performance [13]. One of the reasons is that these catalysts are not promoting the direct four-electron pathway of the ORR, but possess mainly 2 + 2 electron transfer mechanism on the fuel cell cathode resulting in the formation of peroxide as intermediate product, which will corrode the carbon support and affect the stability of membranes [14]. Second problem is the methanol crossover in DMFCs which decreases the performance of the fuel cell and the energy conversion efficiency because methanol reacts undesirably at the cathode catalyst resulting immediately in a loss of cell voltage [15–19].

Extensive efforts have been made during the last decades to reduce the cost of noble metal catalysts by reducing the amount of precious metal or to replace them with non-noble metal catalysts. Among the most thoroughly studied non-Pt catalysts are carbon supported transition metal macro-cycles [20]. These catalysts have mainly attracted attention because of their remarkable activity towards the ORR, especially in alkaline media, and their high tolerance to methanol [21–26]. However the price of these metal macro-cycles could still be reduced and the long-term stability has been reported as the major drawback.

In recent years nitrogen-doped nanocarbon materials such as N-doped carbon black [27], N-doped carbon nanotubes [28] and N-doped graphene [29] have attracted utmost importance as electrocatalysts for ORR. In particular, these N-containing catalysts are mostly inactive to the adsorption and oxidation of methanol, which means that they are excellent methanol-resistant catalysts and have a great potential to replace platinum in DMFCs cathode side [13,30]. The electrocatalytic activity of nitrogen-doped carbon materials has been extensively studied [31–34]. These researches point out the importance of the bonding configuration of N-atoms incorporated to the surface of carbon nanomaterials for the electrocatalytic activity towards the ORR. Typical bonding configurations of nitrogen on the surface of nanocarbons are N atoms in six-member ring (pyridinic-N), N atoms doped into graphene basal plane (graphitic-N), N atoms in five member ring (pyrrolic-N) and N atoms bonded with O atoms (oxidised nitrogen species). Despite the extensive study of N-doped carbon materials, the exact mechanism of the ORR on these catalysts remains still unclear [35].

It has been also found that all these catalytic aspects, the amount of nitrogen in the catalyst material and the nature of nitrogen functionalities are dependent on the particular nitrogen source used and the pyrolysis temperature [36]. The heat-treatment of carbon materials in the presence of nitrogen precursor has been usually carried out at temperatures between 700 and 1000 °C, which has been found to be optimum temperature for N-doping [37]. Alike to undoped carbon materials, the ORR activity of N-doped carbons is much lower in acidic media than in the solutions of high pH [38].

Along with the other N-doped carbon materials, nitrogen-doped graphene has attracted a great deal of attention in recent years [39–41]. Graphene has unique structure and morphology, which provides both diffusion channels for O₂ and active sites on the edge planes for oxygen reduction [42]. Qu et al. were the first who reported a remarkable electrocatalytic activity of N-doped graphene for ORR [43]. Chemical doping of graphene with nitrogen atoms can improve the performance of this material in various applications, such as fuel cells, supercapacitors and batteries by improving the electronic properties, by providing more active sites and by enhancing the interaction between carbon structure and other molecules [44]. Agglomeration of graphene has been reported to be a major problem in the application of this material in fuel cell electrocatalysis [45]. Restacking of graphene, which is inflicted by van der Waals forces, reduces the active surface area and the number of electrocatalytically active sites of graphene catalyst and thereby resulting in decreased electrocatalytic activity. Carbon nanotubes (CNTs) can be used as spacers to prevent restacking of graphene layers. The formation of graphene/CNT assembly will create space for effective transport of reactants and CNTs will act as circuits between the graphene layers to provide better electron transfer [46].

In this work a pyrolytic approach was used for nitrogen doping of carbon nanomaterials. Graphene oxide was mixed with acid-treated multi-walled carbon nanotubes (MWCNTs) and with dicyandiamide followed by high-temperature pyrolysis to prepare N-doped few-layer graphene/MWCNT catalyst. Plain N-doped MWCNTs without graphene has been also used as the comparison material. The electrocatalytic activity of these nitrogen-doped cathode catalysts for ORR has been studied in alkaline media using a rotating disk electrode. With the DMFC experiments we demonstrate that the N-doped FLG/MWCNT and N-doped MWCNT cathode catalyst exhibit superior performance compared to a commercial carbon-supported Pt.

2. Experimental

2.1. Nitrogen doping of carbon nanomaterials

Dicyandiamide (DCDA) was purchased from Aldrich and was used as nitrogen precursor for N-doping of carbon nanomaterials. The graphene oxide (GO) material used in this work was synthesised from graphite powder (Graphite Trading Company) by a modified Hummers' method [47,48]. Multi-walled carbon nanotubes (MWCNTs) (Nano-Lab, Inc., Brighton, MA, USA) were acid-treated according to a published procedure [49]. First GO and MWCNTs were mixed in ethanol in ratio 1:1. Then polyvinyl pyrrolidone (PVP) and nitrogen precursor were added. Two N-doped materials were prepared from GO/MWCNT/DCDA and MWCNT/DCDA with mass ratios of 1/1/20 and 1/20 respectively according to the previously reported procedure [50]. All the mixtures were sonicated for 2 h and after that dried at 75 °C in vacuum. Next, the materials were pyrolysed in flowing argon atmosphere at 800 °C for 2 h. After maintaining the temperature for 2 h, the furnace was cooled down to room temperature and the final black product was collected. The synthesised catalyst materials are designated as N-FLG/MWCNT and N-MWCNT.

High-resolution transmission electron microscopy (HR-TEM) measurements were performed to characterise N-doped carbon catalysts using a double-aberration corrected JEOL-2200FS