



Highly efficient cathode catalyst layer based on nitrogen-doped carbon nanotubes for the alkaline direct methanol fuel cell



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ABSTRACT

The performance of a direct methanol alkaline anion-exchange membrane (Fumatech FAA3) fuel cell with Pt-free nitrogen-doped few-walled carbon nanotubes (N-FWCNT) as the cathode catalyst is compared with a commercial supported Pt catalyst. The ionomer content of the N-FWCNT cathode catalyst layer is therefore optimized and it is shown to be 40 wt% of FAA3. Scanning electron microscopy images of the catalyst layer show that the ionomer forms aggregates with N-FWCNTs probably due to their charged nature and that the catalyst layer structure is remarkably open even with high ionomer contents facilitating the mass transfer of reactants and products to the active sites. With oxygen as the oxidant, the maximum power density obtained with our Pt-free N-FWCNTs (0.78 mW cm^{-2}) is slightly higher than with the Pt catalyst (0.72 mW cm^{-2}). However, when more practical air is used as the oxidant, the N-FWCNTs (0.73 mW cm^{-2}) show clearly superior performance compared to the Pt catalyst (0.18 mW cm^{-2}). The lower performance with the Pt catalyst is attributed to the denser electrode layer structure resulting in higher mass transport resistance and to the presence of methanol in the cathode, which poisons the Pt but not the N-FWCNTs.

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1. Introduction

Liquid-fed fuel cells, like the direct methanol fuel cell (DMFC), are very promising candidates for power sources of low-power electronic devices. However, large-scale commercialization requires improvements in the performance, durability and cost of the catalysts [1] and membranes [2]. Many activities are concentrated on the anode where complex and relatively slow methanol oxidation occurs, but the oxygen reduction reaction (ORR) taking place at the cathode is also under active research, especially since all typical fuel cells employ an oxygen reducing cathode. Although ORR is catalyzed relatively well by platinum, large loadings are required (0.4 mg cm^{-2}) due to the complexity of the reaction compared with for example hydrogen oxidation (0.05 mg cm^{-2}) [3]. This contributes greatly to the total cost of the whole system. Platinum nanoparticles used as catalysts also agglomerate during fuel cell use further reducing their activity [4]. In addition with DMFCs, methanol crossover from the anode to the cathode due to unideal

membrane materials causes a mixed potential and poisons the catalyst in the cathode with the intermediate product CO [5].

To solve these problems, alternative catalyst materials for ORR have been researched [6–9]. Recently, nitrogen-modified carbon materials have been shown to have inherent oxygen reduction activity that can reach or even exceed the activity of Pt-catalysts, while being immune to CO and methanol poisoning, and catalyst nanoparticle agglomeration [10–12]. These catalysts show moderate activity toward oxygen reaction in acidic and neutral conditions, and excellent activity in alkaline conditions [13–17]. Generally, they have been synthesized with the help of metal catalysts (e.g. Co or Fe), which had raised the concern that the ORR activity was attributable to the metal-nitrogen complexes as in the well-known case of metal-porphyrins [9]. However, synthesis methods that do not use any metal precursors or catalysts have been recently developed and ORR activity of the catalyst has been preserved [15,18–22].

The exact mechanism of the ORR on nitrogen-modified carbon is not entirely clear at the moment, but the active sites are generally thought to be quaternary nitrogen atoms bonded to three carbons and pyridinic ones bonded to two carbons, or the highly active defect and edge sites present near the nitrogens functionalities [6].

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Also, the more electronegative nature of nitrogen compared to carbon causes a negative charge on the nitrogen atom and positive charges on the surrounding carbon atoms, which should facilitate the adsorption of O_2 on the catalyst surface [11].

Although a large number of metal-free N-modified materials have been synthesized and studied for ORR (e.g. graphene [10,23–33], carbon nanotubes [11,20,21,34–43], carbon nanofibers [12,44–47], mesoporous carbon [15,22], graphitic carbon [48,49], carbon spheres [19,50–53], carbon nanocages [54], flower-like carbon [55], carbon aerogel [56,57], vesicular carbon [58], nanodiamonds [59]) relatively few have been tested in actual fuel cell conditions [58,60–69].

The most popular application target is the acidic polymer electrolyte membrane fuel cell (PEMFC) using hydrogen fuel. Nallathambi et al. [60] showed that metal-free synthesis of N-functional groups containing carbon black improved its ORR activity compared to as-received carbon material. Pyrolysis of the catalyst with a Co–Fe(1:1) chelate complex followed by acid-leaching to remove the metals further improved its performance, while the voltage loss for the catalyst over a 480 h test was $80 \mu V h^{-1}$. Wu et al. [61] found similar results with N-doped graphene nanoplatelets, which contained very little Fe (0.6 at%) and no Co residues on the surface of the catalyst. The catalyst showed somewhat poorer performance than a Pt catalyst (80 mV lower potential at 0.1 A cm^{-2}) and good stability over 400 h (voltage loss of $100 \mu V h^{-1}$). Mo et al. [58] synthesized N-doped metal-free vesicular carbon with a Fe catalyst and showed maximum power density of 200 mW cm^{-2} , while commercial Pt-catalyst produced 550 mW cm^{-2} in the same conditions. Onodera et al. [62] synthesized N-doped carbon on KetjenBlack support, which showed moderate performance in a PEMFC. Oh et al. [63] modified carbon black, carbon nanotubes and carbon nanofibers with nitrogen and showed that the nanofibers performed best in a H_2/O_2 fuel cell due to their high nitrogen content and edge plane exposure. The performance decrease of the fuel cell was $215 \mu A \text{ cm}^{-2} h^{-1}$ over a 120 h test at 0.4 V. Liu et al. [64] studied the nitrogen structure of a N-modified carbon before and after a H_2/O_2 fuel cell test of 100 h and they linked the stability of the catalyst to the quaternary nitrogens, while pyridinic nitrogens protonate under the acidic conditions and become inactive. Similar conclusion about durability was made by Dorjgotov et al. [65] and they also showed performance equivalent of Pt catalyst in H_2/O_2 fuel cell (0.52 A cm^{-2} at 0.6 V).

Recently, alkaline anion-exchange membrane fuel cells (AAMFC) have been studied to replace the expensive Nafion membrane, reduce the corrosion in the fuel cell system and facilitate the catalysis of the electrode reactions [70,71]. Because of the higher ORR activity and stability of the N-modified carbon materials in alkaline conditions [13–17], they have recently been investigated as AAMFC cathodes.

Rao and Ishikawa [66] fabricated N-doped carbon nanotubes with an aluminum template and studied them in an H_2/O_2 AAMFC. The performance of their catalyst was approximately 60% of a Pt catalyst in terms of maximum power density and it was stable for a 30-h test at a constant current. Higgings and Chen [67] synthesized self-standing, acid-washed N-doped carbon nanotube thin films with an Fe catalyst. The catalyst was tested in a H_2/O_2 AAMFC and showed 34% higher maximum power density than carbon supported Pt catalyst.

Although N-modified carbon materials could be highly beneficial for the DMFC due to their tolerance to methanol and CO poisoning [72], there have been only two tests in an actual DMFC. Kim et al. [68] studied nitrogen-doped carbon nanofibers in an acidic DMFC cathode and could generate moderate electrical current. Sun et al. [69] co-doped cheap carbon black materials with nitrogen and fluorine and used them as ORR catalysts in a direct methanol AAMFC. They demonstrated better performance than

commercially Pt/C at same catalyst loading ($15 \text{ vs } 13 \text{ mW cm}^{-2}$) and stable performance for 24 h. In another similar study, Mazin et al. [73] used Co and Fe supported on nitrogen-modified carbons in a direct ethanol AAMFCs. They did not report on the performance of the catalyst after acid-leaching to remove the Co and Fe particles.

Other type of fuel cells where metal-free N-modified catalysts have been used as cathodes are microbial fuel cells in neutral conditions resulting in better performance than with Pt [74,75] and intermediate temperature ($75\text{--}250^\circ\text{C}$) fuel cells based on metal oxide electrolytes in both acid and alkaline mode [76].

In this study, we have fabricated MEAs for a direct methanol AAMFC with Pt-free, nitrogen-doped few-walled carbon nanotubes (N-FWCNTs) that have been proven to be very active for ORR in rotating disk electrode measurements [77] as the cathode catalyst and have optimized the ionomer content of the cathode electrode layer. After optimization, we demonstrate that our AAMFC with the N-FWCNT cathode catalyst shows superior performance compared to a commercial carbon supported Pt, both with oxygen and air as the oxidant.

2. Experimental

2.1. Catalyst preparation

A detailed description of the synthesis is given in [77]. Briefly, few-walled carbon nanotubes (FWCNT) were synthesized via decomposition of CH_4 diluted with H_2 at 950°C on CoMo–MgO catalyst [78]. The FWCNTs were purified by washing in HCl followed by rinsing with deionized water. Nitrogen doping of the FWCNTs was accomplished by first coating them with a layer of polyaniline (PANI) deposited by in situ chemical polymerization of aniline in acidic media and subsequent carbonization of the PANI-coated FWCNTs at 900°C for 1 h in Ar gas flow, according to a method previously reported for carbon black [79], producing the nitrogen-doped FWCNTs (N-FWCNTs).

High-resolution transmission electron microscopy (HRTEM) was performed on the N-FWCNTs using a double-aberration corrected JEOL-2200FS microscope equipped with a field emission gun operated at 200 kV.

2.2. MEA preparation

FAA3 membrane (Fumatech) was ion-exchanged in 0.5 M NaOH with stirring for 1 h and washed in deionized water. Before assembling the fuel cell, the membrane was soaked in 1 M methanol. The cathode catalyst inks were prepared by mixing the synthesized N-FWCNTs with isopropanol and 12 wt% solution of FAA3 ionomer in N-methyl-2-pyrrolidone (NMP). The amount of FAA3 was varied so that its weight percentage of the total cathode mass (ionomer + N-FWCNT) was 21.7, 30.6, 42.0, 51.1 and 60.5 wt% in each case. The MEAs fabricated from the above inks were labeled as MEA20, MEA30, MEA40, MEA50 and MEA60, respectively. The components were first mixed by a magnetic stirrer for 45 min, then subjected to 10 min of sonication and finally mixed by a magnetic stirrer overnight. Isopropanol ($400\text{--}600 \mu\text{l}$) was added to the ink during mixing until the viscosity of the ink was suitable for air brush painting: the more FAA3 solution in the ink, the less isopropanol was needed for good viscosity. The resulting slurry was painted on a pre-weighted gas diffusion layer (GDL) with a microporous layer (FuelCellEtc GDL-CT) by an air brush and dried in a vacuum oven at 40°C for 1 h. The GDL was then weighed to determine the weight of the dry catalyst layer. The N-FWCNT loadings of the cathodes were $2.2 \pm 0.3 \text{ mg cm}^{-2}$. The same procedure was used to fabricate a reference MEA with Pt supported on a high surface area carbon (Alfa Aesar, 60 wt% Pt). The FAA3 content in this case was 30 wt%

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