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

**Ivar Kruusenberg^a, Sander Ratso^a, Merilin Vikkisk^a, Petri Kanninen^b, Tanja Kallio^b,
Arunachala M. Kannan^c, Kaido Tammeveski^{a,*}**

^aInstitute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

^bSchool of Chemical Technology, Aalto University, FI-00076 Aalto, Espoo, Finland

^cFuel Cell Laboratory, Polytechnic School, Ira A. Fulton Schools of Engineering, Arizona State University, Mesa, AZ 85212, USA

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.

* Corresponding author. Tel.: +372-7375168; fax: +372-7375181
E-mail address: kaido.tammeveski@ut.ee (K. Tammeveski)

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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, 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 (HRTEM) measurements were performed to characterise N-doped carbon catalysts using a double-aberration corrected JEOL-2200FS microscope equipped with a field emission gun operated at 200 kV.

2.2. Electrode preparation and electrochemical measurements

The rotating disk electrode (RDE) method was used to perform the oxygen reduction measurements. The electrode rotation rate (ω) was varied from 360 to 4600 rpm. The RDE was equipped with CTV101 speed control unit and EDI101 rotator (Radiometer). Electrochemical experiments were carried out at room temperature (23 ± 1 °C) in 0.1 M KOH solution (p.a. quality, Merck) in a three-electrode electrochemical cell. For electrochemical measurements the solutions were saturated with O₂ (99.999%, AGA) or Ar (99.999%, AGA). During the experiments the gas flow was maintained over the solution. Saturated calomel electrode (SCE) served as a reference electrode and all the potentials are referred to this electrode. Pt foil served as a counter electrode and was separated from the solution with a glass frit. The potential was applied using Autolab potentiostat/galvanostat PGSTAT30 (Eco Chemie B.V., The Netherlands) and General Purpose Electrochemical System (GPES) software was used to control the experiments.

Glassy carbon (GC) was used as a substrate material. GC disks (GC-20SS, Tokai Carbon) with geometric area (A) of 0.2 cm² were pressed into a Teflon holder and the electrodes were polished to a mirror finish with 1 and 0.3 μ m alumina slurries (Buehler). After polishing, the electrodes were sonicated in 2-propanol and Milli-Q water for 5 min. The GC disk electrodes were modified with N-FLG/MWCNT and N-MWCNT aqueous suspensions (1 mg ml⁻¹) containing 0.25% FAA3 anion exchange ionomer (12 wt.% FAA3 in N-methyl-2-pyrrolidone (NMP), supplied by Fuma-Tech). The N-FLG/MWCNT and N-MWCNT suspensions were sonicated for 1 h prior electrode modification to form a uniform catalyst ink. After that a 20 μ l aliquot of

the suspension was pipetted onto the GC surface and was allowed to dry in air. Care was taken to cover the surface of GC uniformly with catalyst layer.

For comparison purposes the reduction of oxygen was also studied on Pt/C catalysts deposited on GC. The commercial 60 wt.% Pt catalyst supported on high-surface-area carbon was purchased from Alfa Aesar and dispersed in ethanol (1 mg catalyst ml⁻¹).

Methanol tolerance of the N-doped nanocarbon catalysts was studied in 0.1 M KOH solution containing 3 M MeOH. Both cyclic voltammetry and the RDE experiments were performed.

2.3. MEA preparation

FAA3 membrane (Fumatech) was ion-exchanged in 0.5 M NaOH with stirring for 1 h and washed in deionised water. Before assembling the fuel cell, the membrane was soaked in 1 M MeOH. The cathode catalyst inks were prepared by mixing with isopropanol and 12 wt% solution of FAA3 ionomer in NMP. 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. The resulting slurry was painted on a pre-weighed 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 catalyst loadings on 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.% according to the optimised value reported by Carmo et al. [51] and the Pt loading was 0.5 mg cm^{-2} .

The anode electrodes for the MEAs were fabricated from PtRu supported on high area carbon (Alfa Aesar, 40 wt.% Pt, 20 wt.% Ru) with similar method as the cathodes. The FAA3 ionomer content in this case was 30 wt% and the PtRu loading was $3.0 \pm 0.2 \text{ mg cm}^{-2}$. The MEAs were not hot-pressed due to the sensitivity of the FAA3 membrane to pressure and temperature.

2.4. Direct methanol fuel cell (DMFC) measurements

The fuel cell was assembled with a FAA3 membrane, painted electrodes and Teflon® gaskets. The cell was then clamped together with eight screws and tightened to a torque of 10 Nm. The active area of the fuel cell was 5.29 cm² and the temperature 40 °C. Cell voltage and current were controlled by a Metrohm Autolab PGSTAT20 potentiostat with a BSTR10A booster. The flow rate of 1 M MeOH was 2.0 ml min⁻¹ and for O₂ the flow rate was 200 ml min⁻¹. Once the open circuit voltage (OCV) stabilised, polarisation curves were measured with a voltage sweep from the OCV to 0.05 V at a scan rate of 2 mV s⁻¹. After measurements, the samples for scanning electron microscopy (SEM, JEOL JSM-7500FA) were cut from the MEA.

3. Results and discussion

3.1. Physical characterisation of N-FLG/MWCNT and N-MWCNT samples

The surface morphology of N-FLG/MWCNT and N-MWCNT samples was characterised by high-resolution transmission electron microscopy (HR-TEM). The TEM images reveal that the surface modification was performed without introducing major defects into the N-FLG/MWCNT and N-MWCNT catalyst materials. This is crucial for keeping the anticipated properties of the N-doped carbon catalysts. The TEM micrographs of the N-FLG/MWCNT and N-MWCNT samples are presented in Figures 1a and 1b, respectively. It is observable from the micrographs that no larger amorphous carbon particles or other impurities are visible. Two-dimensional materials like graphene tend to stack together through π - π interactions, which could cause the blocking of catalytically active sites on the N-doped nanocarbon catalysts [52]. Agglomeration of the graphene nanosheets in N-FLG/MWCNT is not evident as well. Even if minor restacking effect is visible from the image (Figure 1a) then large-scale agglomeration has been avoided by surface masking of graphene layers with MWCNTs. Figure 1a shows that

carbon nanotubes are randomly deposited on the graphene layers, indicating a self-assembled structure of the catalyst. Similar quality has been observed also for N-MWCNT catalyst from Figure 1b.

Figure 1. HR-TEM image of (a) N-FLG/MWCNT and (b) N-MWCNT material.

The elemental composition and chemical surrounding of nitrogen species in N-doped nanocarbon materials was characterised by X-ray photoelectron spectroscopy (XPS) and the

results have been presented in a previous paper [53]. The XPS analysis showed clearly that nitrogen doping was successful and four different types of nitrogen species were identified on the surface of carbon materials, from which the main component was pyridinic nitrogen. In N-FLG/MWCNT samples the overall N content was found to be approximately 4 at.%.

3.2. Electrochemical characterisation of catalysts

The electrochemical reduction of oxygen on N-FLG/MWCNT and N-MWCNT catalyst materials was investigated using the RDE method. Figure 2a and 2b presents the RDE polarisation curves for oxygen reduction on different N-doped nanocarbon catalyst modified GC electrodes in O₂-saturated 0.1 M KOH solution. The onset potential of the ORR for both catalyst materials is approximately -0.1 V vs. SCE. A high reduction current was evident for these electrocatalysts, which is plausibly caused by the effective N-doping of the nanocarbon materials and the formation of electrocatalytically active sites. The good ORR activity is consistent with previous results [54]. Despite the vast research done to investigate different nitrogen-doped carbon materials, the exact nature of electrocatalytically active nitrogen species is still under debate. Previous literature reports are contradictory regarding the electrocatalytic effect of various nitrogen species on the ORR. Some investigators claim that quaternary nitrogen is responsible for the enhanced catalytic activity, but several other groups state that it is the pyridinic nitrogen which could be the reason for the electrocatalytic activity of N-doped catalysts [55-57]. According to the XPS results the total nitrogen content was found to be approximately 4 at.%, from which pyridinic N constitutes 50 at.%, quaternary N 15 at.%, pyrrolic N 26 at.% and pyridine-N-oxide 9 at.%. The XPS analysis presented clearly that all four different type of nitrogen species were present on the surface of N-doped carbon catalyst, from which the main component is pyridinic nitrogen [53]. Based on the RDE and XPS results, we can conclude that pyridinic nitrogen could play the major role in enhancing the ORR activity

of the N-FLG/MWCNT and N-MWCNT materials.

Figure 2. RDE voltammetry curves for oxygen reduction on (a) N-FLG/MWCNT and (b) N-MWCNT modified GC electrodes in O₂-saturated 0.1 M KOH. $\nu = 10 \text{ mV s}^{-1}$, $w =$ (1) 360, (2) 610, (3) 960, (4) 1900, (5) 3100 and (6) 4600 rpm.

Even if the mechanism of oxygen adsorption and the ORR process on the N-doped carbon materials is not completely clarified, it has been proposed that oxygen molecules chemisorbed to the carbon atoms in the N-doped carbon material mainly because of the different nitrogen functionalities and their different electronic properties [58].

It is believed that carbon atoms together with nitrogen dopants will have a considerably high positive charge density to counterbalance the strong electronic affinity of the nitrogen atom. The conjugation effect of the nitrogen lone-pair electrons on the nitrogen and carbon π -system leads to increase in the bulk electrical conductivity and the density of states at the Fermi level [59,60]. It is also believed that the above mentioned charge delocalisation could alter the adsorption behaviour of carbon material towards O_2 molecules and thereby effectively weaken the O-O bond to facilitate the electroreduction of oxygen [31,61].

The number of electrons transferred per O_2 molecule (n) was calculated from the Koutecky-Levich (K-L) equation [62]:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} = - \frac{1}{nFAkc_{O_2}^b} - \frac{1}{0.62nFAD_{O_2}^{2/3}n^{-1/6}c_{O_2}^b w^{1/2}} \quad (1)$$

where I is the measured current, I_k and I_d are the kinetic and diffusion-limited currents, respectively, k is the rate constant for O_2 reduction, A is the geometric electrode area, F is the Faraday constant (96485 C mol^{-1}), w is the rotation rate (rad s^{-1}), D_{O_2} is the diffusion coefficient of oxygen ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) [63], $c_{O_2}^b$ is the concentration of oxygen in the bulk ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$) [63] and n is the kinematic viscosity of the solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$) [64].

Figure 3a and 3b presents the K-L plots obtained from the RDE data on oxygen reduction for the N-FLG/MWCNT and N-MWCNT catalysts in 0.1 M KOH. The intercepts of the extrapolated K-L lines were close to zero, which shows that the process of O_2 reduction is almost entirely under the diffusion control [62]. The inset of Figure 3a and 3b compares the n values calculated from the K-L equation at various potentials. For both N-doped carbon nanomaterials the n value was close to four in the range of potentials studied. This indicates the superiority of the N-FLG/MWCNT and N-MWCNT catalyst and their great potential as DMFC cathode catalyst.

Figure 3. Koutecky-Levich plots for oxygen reduction on (a) N-FLG/MWCNT and (b) N-MWCNT electrodes in 0.1 M KOH solution. Inset shows the potential dependence of n . Data derived from Figure 2.

A comparison of the RDE data on oxygen reduction recorded on GC electrodes modified with different catalyst materials is presented in Figure 4. The electrocatalytic behaviour and the ORR

polarisation curves of N-FLG/MWCNT and N-MWCNT are similar and rather positive onset potentials with high reduction currents are in evidence for both nitrogen-doped carbon catalysts. The RDE results of N-doped catalysts are compared with the commercial carbon-supported Pt catalyst (60 wt.% Pt/C), which shows almost 0.1 V positive shift of the onset potential compared to the N-doped nanocarbon catalyst. Such high electrocatalytic activity towards the ORR is related to the high loading of platinum. The RDE voltammetry curve of bare GC has been also added for comparison purposes.

Figure 4. Comparison of RDE results of O_2 reduction on bare GC, N-FLG/MWCNT, N-MWCNT and Pt/C modified GC electrodes in O_2 -saturated 0.1 M KOH. $v = 10 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$.

Tafel analysis is performed in order to obtain more information about the ORR kinetics on N-FLG/MWCNT and N-MWCNT materials. Tafel plots for oxygen reduction on both catalyst materials are presented in Figure 5. Two linear regions of distinct slope could be observed in the Tafel plots. Namely, in the low current density region (in the potential range from -0.15 to -0.2 V) the slope values are -0.069 and $-0.084 \text{ V dec}^{-1}$ for N-FLG/MWCNT and N-MWCNT catalysts, respectively. In the high current density region (between -0.2 and -0.3 V) higher slope

values (b) are in evidence ($b = -0.139 \text{ V dec}^{-1}$ for N-FLG/MWCNT and $b = -0.141 \text{ V dec}^{-1}$ for N-MWCNT). Small difference in slope values could be attributed to the difference in porosity and surface area and it is worth mentioning that similar Tafel behaviour has been observed for N-doped carbon catalysts by other groups as-well [58,65,66]. From the practical point of view it is of utmost importance to determine the values of mass activity (I_m - kinetic current normalised to catalyst mass) at low overpotentials. The E vs. $\log I_m$ plots are shown in Figure 5b. As can be seen from the Figure the mass activity values are rather high for both catalysts indicating good electrocatalytic properties of these N-doped nanocarbon materials.

Figure 5. Mass-transfer corrected Tafel plots for oxygen reduction on N-FLG/MWCNT and N-MWCNT catalysts in 0.1 M KOH. (a) E vs. $\log I_k$ and (b) E vs. $\log I_m$ plots. $\omega = 1900 \text{ rpm}$. Data derived from Figure 4.

3.3. Methanol tolerance of N-doped nanocarbon catalysts

Methanol tolerance is an extremely important performance criterion for cathode materials in direct methanol fuel cells and also known as a shortfall of Pt-based catalysts. Therefore the methanol tolerance of N-FLG/MWCNT and N-MWCNT modified GC electrodes was investigated in 0.1 M KOH solution containing 3 M MeOH by the RDE method at 10 mV s^{-1} (Figure 6a and 6b, respectively). Inset to Figures 6a and 6b shows cyclic voltammograms in the

same solutions at a scan rate of 100 mV s^{-1} . According to these testing results both N-FLG/MWCNT and N-MWCNT N-MWCNT catalysts possess good methanol tolerance and thus afford a promising non-precious metal cathode catalyst for DMFC.

Figure 6. RDE voltammetry curves for oxygen reduction on (a) N-FLG/MWCNT and (b) N-MWCNT modified GC electrodes in O_2 -saturated 0.1 M KOH solution with and without 3 M MeOH. $\nu = 10 \text{ mV s}^{-1}$, $\omega = 960 \text{ rpm}$. Inset shows the cyclic voltammograms recorded at a scan rate of 100 mV s^{-1} .

3.4. DMFC performance of N-FLG/MWCNT and N-MWCNT catalysts

The catalysts were then tested in a direct methanol alkaline anion-exchange membrane fuel cell using a FAA3 membrane (Fumatech GmbH). The polarisation and power density curves are presented in Figure 6a and 6b, respectively. It is immediately clear that both the N-doped nanocarbon catalysts perform even better than a commercial carbon-supported Pt catalyst. The maximum power densities reached with each catalyst are: 0.92 (N-MWCNT), 0.72 (N-FLG/MWCNT) and 0.72 mW cm⁻² (Pt/C). The open circuit voltages (OCV) achieved with the N-doped catalysts (~0.64 V) are much higher than that achieved with Pt/C (~0.44 V) due to their high tolerance towards methanol. As a consequence, the maximum power density is reached at higher potential than with the Pt/C catalyst, which is important as electronic devices require high operating voltages. The methanol tolerance of the cathode catalyst also improves the performance because permeating methanol does not react on the cathode eliminating CO poisoning and competition towards the active sites for ORR [67]. These results show that the N-doped carbon nanomaterials are suitable replacements for Pt-based catalysts in alkaline fuel cells. With N-MWCNT, the power densities reached are even higher than with the nitrogen-doped few-walled carbon nanotubes (0.78 mW cm⁻² at 50 °C) [68] or commercial Pt/C (0.32 mW cm⁻² at 30 °C) [69] studied in similar systems based on FAA membranes. The performance is also in the same range as with a radiation-grafted ETFE anion-exchange membrane based alkaline DMFC with 4 mg cm⁻² catalyst loading (1.5 mW cm⁻² at 50 °C) [70]. Despite the good performance of the N-MWCNT, the power densities of alkaline membrane based direct methanol fuel cells are still low and not comparable to the proton exchange membrane based direct alcohol fuel cells [11]. This is mainly due to the low conductivity of hydroxide ion and

poor overall performance of the membrane. To elucidate the MEAs performance the SEM micrographs of the catalyst layers were taken from the N-FLG/MWCNT and N-MWCNT MEAs (Figure 8a and 8b, respectively). In Figure 9 a close-up on the finer structure of the catalyst layer is shown.

Figure 7. Fuel cell performance of the catalysts in 1 M MeOH at 40 °C showing (a) polarisation curves, and (b) power density curves.

Firstly, the thicknesses of the different catalyst layers can be determined as follows: for N-FLG/MWCNT 109 μm , for N-MWCNT 76 μm and for Pt/C 19 μm . Considering that the total catalyst loading (Pt+C) is 0.83 mg cm^{-2} for Pt/C and 2.2 mg cm^{-2} for the N-doped materials indicating 2.7-fold increase, it is clear that the N-doped materials form thicker catalyst layers as the increase in thickness is 5.5-fold for N-FLG/MWCNT and 4-fold for N-MWCNT compared to Pt/C. This is due to the large cracks visible in the catalyst layers of the N-doped materials (Figures 8a and 8b), while the Pt/C catalyst layer (Figure 8c) is more uniform and tightly packed. These cracks can facilitate transport of O_2 and water in the layer thus explaining the improved performance of the N-doped catalyst materials in the DMFC even though these catalyst layers are 4-5 times thicker than the Pt/C catalyst layer increasing the mass transfer distances. The close-ups in Figure 9 show that the fine structures of the catalyst layers are also different. In N-FLG/MWCNT (Figure 9a), the walls of the cracks are smooth, while there are small pores in the N-MWCNT structure (Figure 9b) much like in the commercial Pt/C (Figure 9c). This suggests the fact that N-MWCNT performs the best in the DMFC is related to mass transfer: the large cracks helps to distribute O_2 through the whole catalyst layer efficiently and facilitate water flow out of the catalyst layer and the smaller pores allow access to a high number of active Pt catalyst sites. On the other hand, in the N-FLG/MWCNT layer efficient pathways to the catalyst particles are blocked, and for Pt/C, O_2 and water is forced to travel through small pores the whole way to the catalytic sites and out of the layer.

As a conclusion, it can be summarised that the excellent performance of the N-doped carbon catalysts compared to the commercial Pt/C in the DMFC is the combined result of their methanol tolerance, high catalytic activity for ORR and the favourable porous catalyst layer structure.

Figure 8. SEM micrographs of the tested (a) N-FLG/MWCNT, (b) N-MWCNT and (c) Pt/C covered MEAs. The cathode catalyst layer is indicated with green lines.

Figure 9. Close-up SEM micrographs of the finer structure of the (a) N-FLG/MWCNT, (b) N-MWCNT and (c) Pt/C cathode catalyst layers.

4. Conclusions

High electrocatalytic activity for oxygen reduction reaction was achieved by annealing of few-layer graphene/multi-walled carbon nanotube composite and pure MWCNT material in the presence of dicyandiamide. The reduction of oxygen was studied in 0.1 M KOH on GC electrodes modified with the metal-free nitrogen-doped nanocarbon catalysts employing the RDE method. The RDE results and comparison with a commercial Pt/C catalyst showed that the nitrogen-doped FLG/MWCNT and MWCNT catalysts are highly active for ORR in alkaline media and therefore could be used as an alternative cathode catalyst for the Pt-based materials in alkaline membrane fuel cells. Membrane electrode assemblies (MEA) were fabricated using a catalyst coated Fumatech (Fumatech FAA3) membrane and were compared with 60 wt.% Pt/C catalysts covered MEAs. The catalysts were tested in alkaline membrane direct methanol fuel cell and the performance of the MEAs with N-doped FLG/MWCNT and N-doped MWCNT as cathode catalyst was found to be better than Pt/C.

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