

Short communication

Design of gas diffusion electrodes using nanocarbon

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Abstract

Two types of gas diffusion electrodes (GDE) with nanocarbon as structural component have been prepared and characterised by TEM, SEM, Raman, conductivity studies and fuel cell testing.

The first one combines the well-known properties of carbon cloth and the advantages of carbon nanotubes directly grown on the fibre surface. The second one uses the buckypaper preparation technique which allows a flexible design of layer-type GDEs with tuneable properties (wetting behaviour, catalyst concentration) or gradient materials.

Pt catalyst particles are introduced into the (porous) nanocarbon network in a controlled manner by wet- or dry-chemical platinisation. Appropriate particle size (1.4–5 nm) and distribution (0.2–0.4 mg cm⁻²) are proven by TEM and XRF analysis. The performance of the GDE at high temperature has been tested in a PAFC showing a peak power density of about 220 mW cm⁻² at 150 °C.

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1. Introduction

Amorphous carbon (carbon black, carbon fibres) is commonly used in heterogeneous catalysis as easily processable, inexpensive and chemically stable support. In electrocatalysis, it additionally acts as electrode/current collector. For fuel cells the electrodes further on have to allow fast diffusion of the humidified gases hydrogen and air. To achieve high mass transfer rates these gas diffusion electrodes (GDE) are commonly made from carbon fibres (typically 10–30 μm in diameter) processed as highly porous carbon cloth or paper. Under working conditions extensive accumulation of liquid water has to be avoided because it can block the fuel pathway and reduce the current production. Hence, the size and wettability of the pores are critical material properties. Since water is produced at the cathode side during fuel cell operation, hydrophobic coatings are usually applied at this cell part to decrease the adhesion of the water molecules and to prevent flooding of the cell.

High porosity of the gas diffusion electrode is also a major prerequisite for the electrocatalytical performance of the GDE. Small Pt metal particles with a diameter $2 < d < 5$ nm, acting

as efficient catalysts for the oxidation of hydrogen ($H_2 \rightleftharpoons 2H^+ + 2e^-$) and reduction of oxygen ($(1/2)O_2 + 2e^- \rightleftharpoons O^{2-}$), are introduced into the porous carbon matrix by electrochemical means or reductive treatment of non-metallic Pt-solutions. As suggested, e.g., by transmission electron micrographs (TEM), Ptⁿ⁺ ($n = 2, 4$) is preferentially reduced at carbon defect sites statistically distributed on the surface of the carbon fibre. Typical Pt loadings range from 0.1 to 1 mg cm⁻². The Pt/Carbon composite material is usually hotpressed to the proton conducting membrane, thereby providing triple contacts between catalyst, electronic conductor and ionic conductor, i.e. providing the active centers for the reaction.

The conversion rate will depend on the density of active triple contacts and the kinetics of the reaction. Both quantities are likely to be enhanced when the GDE is build up from nanocarbon. First, the nanocarbons provide higher surface area per unit volume, which is immediately seen if one compares “bulky” conventional C-fibres ($d > 1 \mu\text{m}$) with, e.g., single walled carbon nanotubes (SWNT) ($d \approx 1$ nm). Consequently, more active triple points can be generated in nanocarbon based electrodes. Secondly, the bonding in nanocarbon differs from that in graphite: highly strained sp²-bonds can be formed, which may lead to a more favourable catalyst-support interaction. As importantly, the surface defect density of the nanocarbons can be changed by functionalisation. For example, oxygen defect densities on the

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10% level can be easily introduced by oxidative treatment with HNO_3 . As suggested by Ref. [1] these defects may act as cocatalysts enhancing the fuel cell reaction. Hence, nanocarbon is likely to be more useful in (fuel cell) catalysis than conventional carbon and a higher power output at the same catalyst concentration or a catalyst saving at the same power level is envisaged. According to recent experiments [2–5] the replacement of amorphous carbon by SWNTs or the cheaper multi walled carbon nanotubes (MWNT) leads to an increase by a factor $1 < x < 4$. The uncertainty in the enhancement factor is remarkably high and is mainly caused by the different operation conditions and pretreatments. Further on, the enhancement factor is often derived from the comparison with internal not strictly defined standards. For example, I - V curves obtained with (widely used) E-TEK electrodes as standard can differ markedly, pretending a too large enhancement.

We have therefore started investigations in which the two most commonly used electrode preparation techniques – the buckypaper route and the direct growth of nanocarbon on carbon fibres (cloth, paper) – are followed in parallel and where the samples are tested under the same conditions. In the following our first results on buckypaper-type GDEs and the growth of MWNTs on commercial C-fibre gas diffusion layers are reported.

2. Experimental

The experimental section presents detailed information about the cleaning and processing of nanocarbon, mainly SWNTs. MWNTs have been primarily grown on carbon cloth in a CVD process; SWNTs can be tightly anchored as well on such cloths. MWNTs are currently favoured on commercial reasons.

2.1. Preparation of nanocarbon and nanocarbon/fibre substrates

2.1.1. Growth of CNTs on carbon fibres

A thin film of Ni (or Co) is magnetron-sputtered on a $5\text{ cm} \times 5\text{ cm}$ sheet of carbon cloth (B-1/A, DeNora/E-TEK). Thermal treatment at 500°C leads to the formation of small (1 nm) catalyst particles. Growth of carbon nanotubes/carbon fibres is established by a CVD process at 700°C with 475:475 sccm $\text{C}_2\text{H}_2:\text{H}_2$ for 25 min. The CVD process takes place in a quartz tube inside a furnace (Carbolite). SEM/TEM and Raman measurements are used for the analysis of the growth products [6].

2.1.2. Buckypapers + CNT networks (spray-drying)

Twenty milligram of single wall CNTs from HiPCo are mixed with 15 ml of concentrated nitric acid and treated with ultrasound (Hielscher UP 100H) for about 10 min. This treatment creates functional groups ($-\text{OH}$, $-\text{C}=\text{O}$, $-\text{COOH}$) on the CNT surface and renders the material hydrophilic. Simultaneously, impurity concentrations (Ni, Co growth catalyst particles, amorphous carbon) are reduced to $<1\text{ wt.}\%$. The solution is diluted with 50% DI-water. Addition of a PTFE suspension increases the hydrophobicity of the electrode. After vacuum-filtration

over a polycarbonate membrane (Osmotics, $0.4\ \mu\text{m}$ pore size, $d=47\text{ mm}$), rinsing with DI-water and drying the remaining paper-like solid (“buckypaper”) is characterised by conductance measurements and AFM/SEM. Alternatively, spray-drying can be used to deposit thin CNT-films on various substrates. The purified CNTs (as described above) are suspended in diluted isopropanol and airbrushed on the substrate. The spray dried films show conductivity values higher than the ionic conductivity of the membrane material (Nafion 117). The conductivity of the buckypaper ($\sim 1800\ \text{S cm}^{-1}$, measured by four-point-method) exceeds that of graphite [7].

2.2. Catalyst preparation

Two different methods are applied to generate catalyst particles tightly anchored to the nanocarbon surface. The dry and wet synthesis of nanosized Pt particles is described in the following. Pt–Ru particles have been simultaneously prepared.

2.2.1. Dry platinisation of SWNTs

An aqueous solution (1:3) of 1 mol H_2PtCl_6 and isopropanol is applied on a buckypaper and allowed to dry for 30 min. After heating for 1 h to 100°C reduction to metallic Pt particles with average size of 1.4 nm is obtained by H_2 addition. The statistical catalyst distribution is verified by TEM-imaging and XRD. According to the EDX data, Pt loadings from 20 to 40 wt.% are obtained. For a typical buckypaper weight of $1\ \text{mg cm}^{-2}$ this corresponds to a Pt loading of $0.2\text{--}0.4\ \text{mg cm}^{-2}$.

2.2.2. Wet chemical platinisation

Six hundred milligram of Elicarb[®] WetCake (Mixture of 3% SWNT and water, Thomas Swan Inc., UK) is purified and oxidised with concentrated nitric acid as described above. Filtered and rinsed, 2/3 of the cleaned SNWTs are cooked under reflux conditions for 2 h with 20 ml ethene-1,2-diol, 10 ml DI-water and about 10 mg of K_2PtCl_6 which is reduced to metallic Pt particles with average size of 3 nm (170°C) to 5 nm (140°C). Buckypaper is formed by vacuum-filtration of 1/3 PTFE-doped SWNTs followed by filtration of 2/3 of platinised SWNTs (preparation see above). XRF-analysis of the vaporised filtrate shows no traces of Pt^{n+} indicating complete conversion or nearly 100% yield, respectively. Accordingly the Pt loading corresponds to 20 wt.% ($=0.4\ \text{mg Pt cm}^{-2}$).

2.3. GDE/MEA preparation

Two different preparation routes have been followed, the hot pressing of preformed GDEs onto the polymer membrane and the direct formation of GDEs on the membrane itself.

Nafion 117 (Dupont) serves as membrane in all investigations.

2.3.1. Hot pressing

A $5\text{ cm} \times 5\text{ cm}$ -Nafion 117-sheet is embedded between two Pt doped buckypapers, the platinised side adjacent to the membrane. At 140°C , the package is hotpressed between two

coplanar PTFE-coated plates for 5 min at a pressure of approximately 1 MPa.

2.3.2. Spray drying

A suspension of platinised SWNTs, isopropanol, water and 1 wt.% of Nafion solution is homogenised by ultrasonic treatment for 5 min. A wet sheet of Nafion 117 (5 cm × 5 cm) is heated to 110 °C. To avoid warping while drying, the nafion sheet is pulled to the support by means of vacuum. The SWNT/Pt suspension is airbrushed on the heated sheet, allowing each thin layer to dry separately.

2.4. Fuel cell testing

The SNWT-GDE (buckypaper, dry platinisation, Pt loading $\sim 0.4 \text{ mg cm}^{-2}$) has been tested first as anode in a PAFC at 150 °C [7] with dry H_2/O_2 as fuels. A standard Elat-electrode (1 mg Pt cm^{-2}) from E-TEK Inc., served as cathode. A thin ($< 10 \mu\text{m}$) porous membrane saturated with concentrated phosphoric acid as electrolyte separates both electrodes. *I/V*-curves have been taken in the potentiostatic mode. Tests in a PEFC (DMFC) are currently underway.

3. Results and discussion

3.1. Growth of MWNTs on commercial carbon cloth

Although the main properties of GDEs made from amorphous carbon (electrochemical stability, metallic conductivity, density, structure (pore size and distribution)) have been optimised for long time, there is still room for improvement by the deposition of nanocarbon increasing the surface area and the density of triple contacts, respectively. Chemical vapor deposition (CVD) has been chosen as preparation method allowing high throughput and upscaling. As importantly, the direct growth of nanocarbon on the fibre surface, here commercial B-1/A carbon cloth from E-TEK Inc., provides the best possible contact between carbon fibre and nanocarbon.

Samples with standard size for fuel cell testing (5 cm × 5 cm) have been prepared by the Cambridge group using Ni or Co clusters as growth catalysts. Fig. 1 presents a typical SEM image of (two crossing) carbon fibres that are completely covered with nanocarbon ($d \approx 40 \text{ nm}$). According to the Raman analysis mainly MWNTs have been grown [6]. BET analysis of the surface area and subsequent deposition of Pt onto the MWNT floor is in progress.

3.2. Characterisation of Pt catalyst

GDEs require well-dispersed nanosized catalysts, usually Pt particles of 2–5 nm size. In order to allow reasonable comparison between conventional and nanocarbon-based GDEs, catalyst loading and size-distribution should be very similar. Therefore, we have carefully checked the density and size of the deposited Pt by XRF-analysis (see Section 2.2.2) and TEM. Fig. 2 shows a TEM-image of SWNT bundles platinised via the wet chemical route. Statistical analysis of the particles, obtained by the

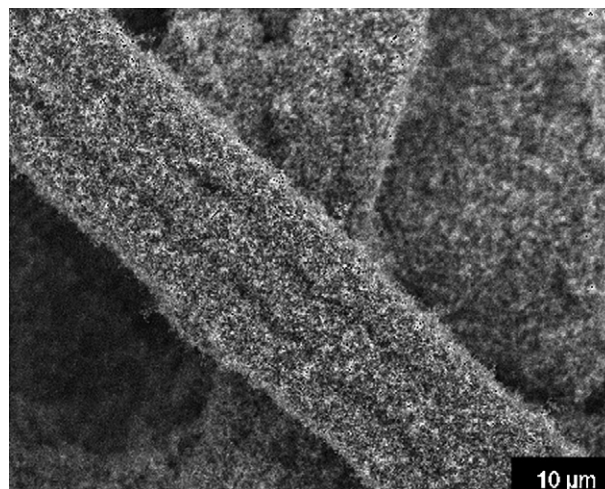


Fig. 1. SEM of MWNTs grown on carbon cloth.

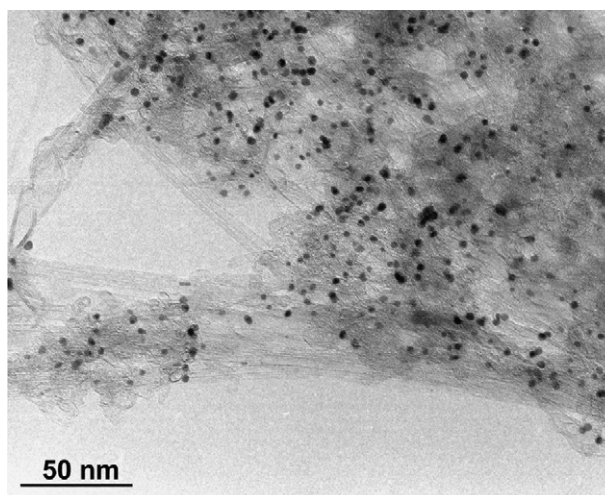


Fig. 2. TEM of platinised SWNTs (wet chemical route).

dry or wet chemical route, yield mean particle sizes of 1.4 to 5.0 nm. The particles are distributed randomly; the envelope drawn in Fig. 3 corresponds to the expected lognormal distribution.

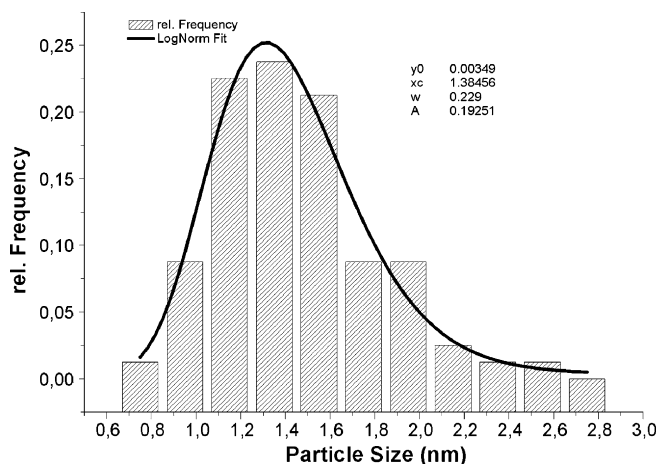


Fig. 3. Size distribution of Pt particles (dry chemical route).

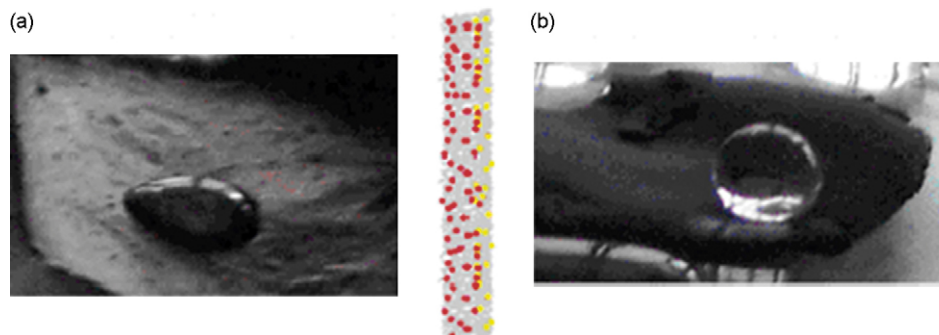


Fig. 4. (a) Wetting behaviour of buckypaper-GDE (hydrophilic side). (b) Wetting behaviour of buckypaper-GDE (hydrophobic side).

3.3. Design and performance of free-standing SWNT-GDE

The processing from liquid suspensions allows a variety of layer-type arrangements with close contacts between layers having very different properties (e.g., layers differing in porosity, hydrophobicity, catalyst doping, etc.) or arrangements with rather similar properties leading to a gradient material. In our case, the buckypaper and spray drying technique have been used to prepare (free-standing) GDEs with the catalyst confined in a narrow zone adjacent to the membrane and for GDEs with strongly differing wetting properties. A GDE which combines both properties results from the following design: In step one a buckypaper of thickness 5–30 μm is generated by filtration of an aqueous CNT/PTFE solution. As shown in Fig. 4, the hydrophobicity of the buckypaper can be substantially increased by the addition of μm -sized PTFE particles. In step two, SWNT/Pt solution is deposited on the wet paper and vacuum-filtrated. Depending on the SWNT/Pt concentration and the volume deposited, a narrow ($100\text{ nm} < x < 10\ \mu\text{m}$), uniform catalyst boundary zone of defined loading is created. Since the Pt particles are rather strongly bonded to the SWNT surface catalyst loss by diffusion or water drag during fuel cell operation should be less pronounced than in conventional designs.

The performance of the SWNT-GDE has been tested under working conditions at elevated temperature in a phosphoric acid fuel cell (PAFC). Fig. 5 presents the characteristic I/V -curve at

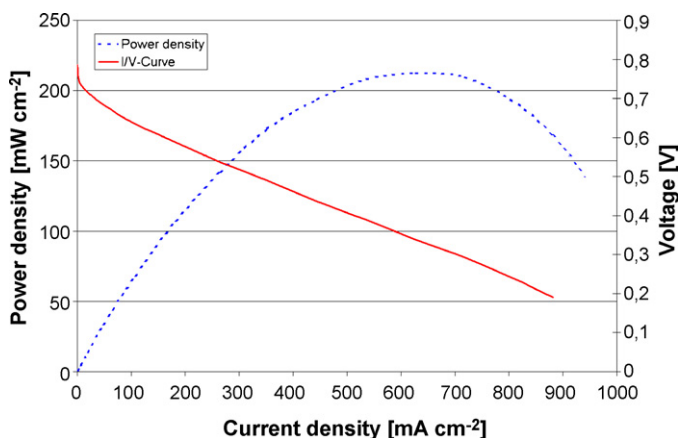


Fig. 5. I/V characteristic curve and power density of PAFC at 150 °C; $\sim 0.5\ \text{mg Pt cm}^{-2}$.

150 °C with hydrogen and oxygen as fuels. The power density of this non-optimised arrangement is comparable to that of a PAFC with conventional electrodes [8,9]. Performance tests in a PEFC and DMFC are in progress.

4. Summary

Microporous GDEs that combine the well-known properties of carbon cloth and the advantages of CNTs have been prepared by direct growth of CNTs on the fibre surface. According to the Raman analysis mainly MWNTs have been attached resulting in a floor-like structure with significantly increased surface. A second type of nanocarbon based GDEs has been prepared by the buckypaper- and spray-drying technique. The preparation technique has been extended to tune the wetting behaviour and catalyst distribution adjacent to the membrane. Deposition of Pt particles suitable for fuel cell operation (2–5 nm size) has been accomplished by wet- and dry-chemical routes. The performance of the GDE at high temperature has been tested in a PAFC showing a peak power density of $220\ \text{mW cm}^{-2}$ at 150 °C. Resuming shortly, the possibility to achieve higher power densities and the flexible design are two key points stimulating further work, necessary to securely establish nanocarbon based GDEs.

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