



## Fuel cells based on multifunctional carbon nanotube networks

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### ABSTRACT

Highly conducting single wall carbon nanotube (SWCNT) networks are functionalized in different ways to achieve multifunctional electrodes. Such electrode material is used as extreme light and thin gas diffusion electrodes in fuel cells. In contrast to previous work, no other carbon material is part of the electrode. We demonstrate that the performance of such SWCNT gas diffusion electrodes is comparable to regular electrodes, which are based on amorphous carbon (a-C). This allows the entire replacement of these regular carbon electrodes by such multifunctionalized SWCNT networks. This way, extremely thin and light gas diffusion electrodes are realized, potentially fulfilling the demands of light weight power supplies.

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### 1. Introduction

Single wall carbon nanotube (SWCNT) networks have recently been recognized as attractive material for various applications. Their properties and consequently potential applications, however, depend strongly on the density of the SWCNT networks. Thin SWCNT networks combine transparency, flexibility and conductivity allowing the realization of transparent conductive coatings [1–4], transparent thin film transistors [5–8], and transparent flexible sensors [9,10]. In contrast, dense SWCNT networks are highly conductive and offer both a high surface area and high porosity. These properties make dense SWCNT networks a promising material for electrodes in various electrochemical devices. The state of the art material for such electrodes is amorphous carbon (a-C), due to its high surface area and porosity. This powdery material requires binders and mechanical support at the backside, such as a woven carbon cloth or a metallic mesh. Also, the conductivity of a-C is rather poor. In contrast, SWCNT networks form a freestanding film without any additive or support. Such a network structure is also mechanically more robust in terms of bending and abrasion. They also have a significant higher conductivity since the high aspect ratio of the SWCNTs leads to a reduced number of contacts between the individual particles. Therefore, the same conductivity can be achieved with much less material. Taking these advantages into account, SWCNT electrodes seem well suited for use in electrochemical devices where they have the potential to entirely replace both the a-C electrode and the metallic current collector. This has

already been demonstrated in supercapacitors [11–15] and batteries [16–18]. In fuel cells, however, SWCNTs have only been used as support for the catalyst deposited on top of an a-C electrode [19–28]. The reason is that the architecture of the a-C electrodes in fuel cells is more complex and it needs to fulfill various functions. Essentially, the architecture consists of two parts: one part of electrode acts as gas diffusion layer with open pores. Therefore, a wetting with the electrolyte is not desired since pores filled with electrolyte would block the gas flow. This property can be tuned either by larger pore size in combination with a sufficient gas pressure or by mixing of the carbon electrode with a hydrophobic material to make this electrode part hydrophobic and to avoid any wetting [29]. Usually, polytetrafluoroethylene (PTFE) is used for this purpose. The other part of the electrode acts as interface between the gas diffusion layer and the electrolyte. Therefore and in contrast to the first part, the second part needs to be hydrophilic to ensure good wetting with the electrolyte. Also, the catalyst is deposited onto this side having contact to both the gaseous fuel and the electrolyte. This way, a three phase boundary is established which is crucial to operate this type of fuel cells.

In the work presented, we describe the complete replacement of a-C material by SWCNT networks. Following the architecture of regular a-C gas diffusion electrodes, the partially hydrophobic property of the SWCNT electrode has been achieved by mixing with PTFE while the catalyst is deposited on the hydrophilic side. We demonstrate that such multifunctional SWCNT networks provide all functions needed for fuel cell operation such as gas diffusion layer, catalyst support, contact to the electrolyte and current collector. As a result, the manufacturing becomes simpler and less material is required which leads to extreme thin and light gas diffusion electrodes.

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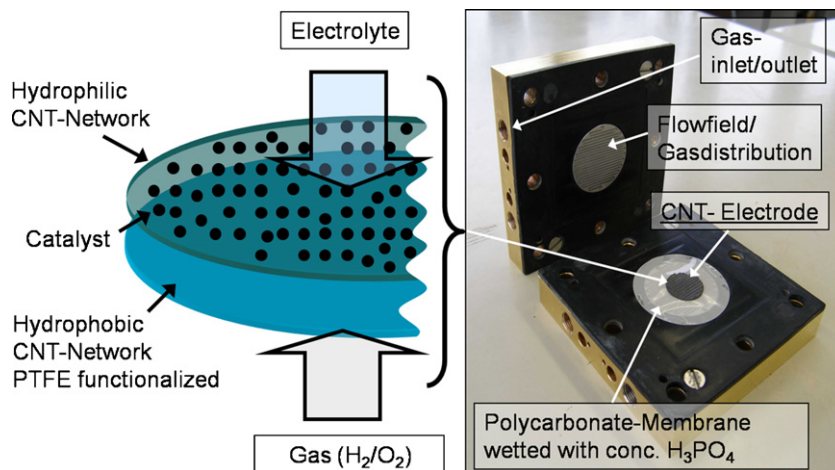


Fig. 1. Sketch of the architecture for the gas diffusion electrode (left) and its placement (right) into a fuel cell. This fuel cell represents our set up.

## 2. Experimental

The SWCNT material [30] was functionalized and doped as reported in detail elsewhere [31]. Briefly, the SWCNT material was sonicated in concentrated  $\text{HNO}_3$  for 3 min. This way, functional groups are introduced acting as dopants and maximizing the conductivity of the SWCNT network. Half of the sonicated SWCNT solution was mixed with PTFE dispersion [32] to a ratio of 2:3. Afterwards, the SWCNT/PTFE solution was filtered through a polycarbonate filter membrane [33] (pore size:  $0.1 \mu\text{m}$ ), using a simple filter flask and moderate vacuum. The SWCNTs and the PTFE par-

ticles remained on the filter forming an entangled hydrophobic network, which serves as the hydrophobic part of the SWCNT gas diffusion electrode. The rest of the SWCNT solution was filtered on top of the PTFE functionalized SWCNT network leading to a hydrophilic top layer. This way, the entire network consists of a both a hydrophobic and a hydrophilic side. After washing thoroughly with water, the catalyst solution ( $0.1 \text{ M H}_2\text{PtCl}_6$  in isopropanol) was cast on top of the hydrophilic side. Then, the entire network was annealed at  $\sim 100^\circ\text{C}$  under  $\text{H}_2$  flow for 1 h to reduce the precursor to metallic platinum. After cooling down, the SWCNT network was left on the filter membrane ready to use. Both anode and cathode

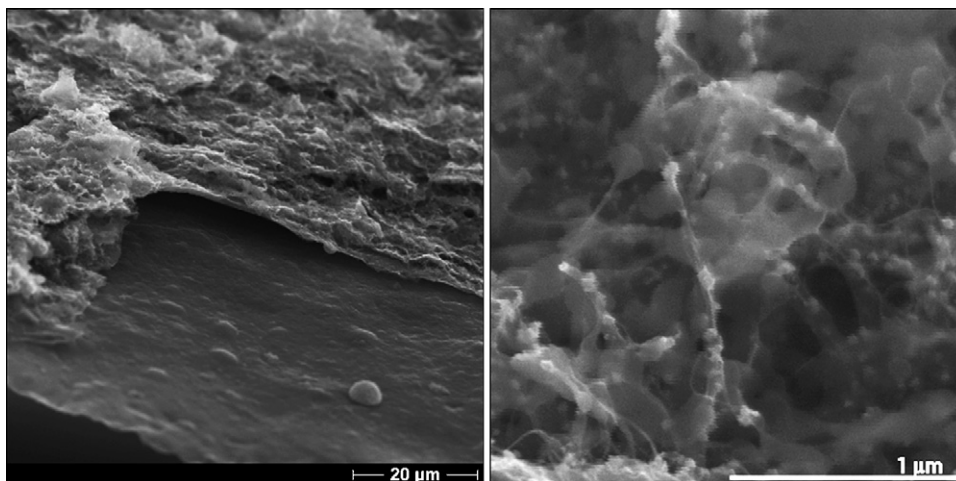


Fig. 2. Scanning electron microscope images of a SWCNT gas diffusion electrode.

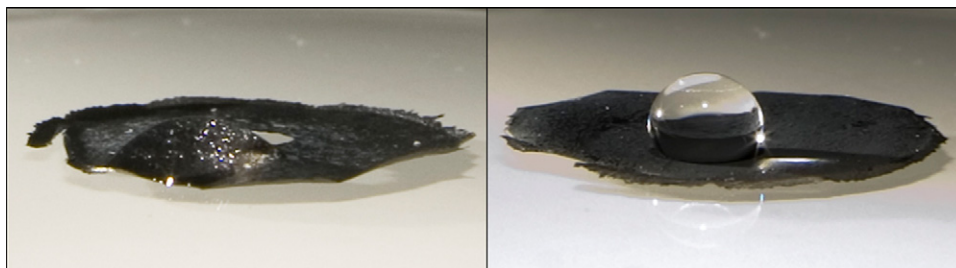


Fig. 3. Wetting of water to the hydrophilic (left image) and hydrophobic PTFE functionalized side of the gas diffusion electrode. The diameter of the SWCNT electrode is  $\sim 5 \text{ cm}$ .

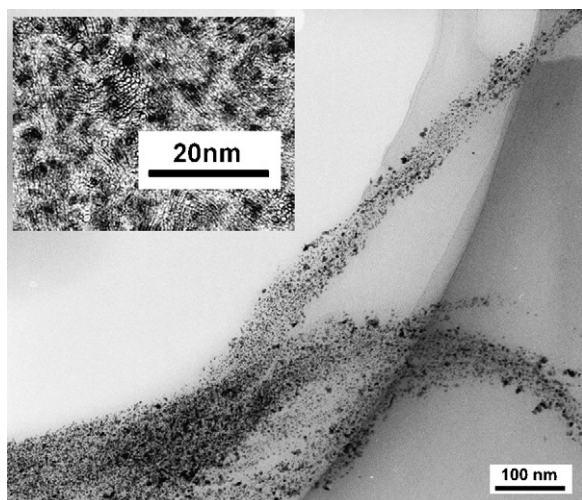


Fig. 4. TEM image Pt particles on SWCNTs.

were prepared the same way. For the fuel cell testing, the SWCNT electrodes are placed in a home-built fuel cell consisting of bipolar plates, gas in- and outlet and flow fields for gas distribution. The SWCNT gas diffusion electrodes were placed with the hydrophobic side facing the flow fields and the hydrophilic side covered with the filter membrane facing the other electrode. The filter membranes were thoroughly wetted with the electrolyte (conc.  $\text{H}_3\text{PO}_4$ ) before the fuel cell was sandwiched together. In Fig. 1, a sketch of the electrodes architecture and the fuel cell set up is shown.

### 3. Results and discussion

#### 3.1. Characterization of the SWCNT electrode

The electrode is characterized by means of scanning electron microscope (SEM), transmission electron microscope (TEM), wetting behavior and size analysis of the catalyst particles. In Fig. 2, SEM images of the CNT gas diffusion electrode are presented.

The left image clearly shows the layered structure with the hydrophilic side on the bottom and the hydrophobic side on top. The right image shows an enlarged part of the hydrophobic PTFE functionalized side. The PTFE appear as individual particles distributed along the SWCNTs rather than as a closed layer. But the overall behavior is still hydrophobic. This is demonstrated in Fig. 3 using simply a water droplet.

It is obvious from the contact angle that the water droplet wets the one but not the other side of the sample and that the SWCNT gas diffusion electrode indeed provides both a hydrophobic and a hydrophilic side. TEM was used in order to characterize the Pt particles. In Fig. 4, typical TEM images of our samples are presented.

Based on the TEM pictures, a detailed analysis of the particle size distribution was done showing that the size distribution of the Pt particles is mainly around 2–3 nm (Fig. 5). This is within the optimum range proposed for Pt particles used as catalyst [34,35] and comparable to the size distribution found in commercially available electrodes [35].

Assuming that the Pt particles are spherical and evenly distributed on the sample, the surface area of the Pt particles  $A_{\text{Pt}}$  can be calculated according to  $A_{\text{Pt}} = 6 \times 10^3 / \rho_{\text{Pt}} \times D_{\text{Pt}}$ , where  $\rho_{\text{Pt}}$  is the density of Pt particles and  $D_{\text{Pt}}$  their diameter [36]. Using the size distribution analysis from the TEM image (Fig. 5), we estimated a surface area of  $A_{\text{Pt}} = 100\text{--}140 \text{ cm}^2 \text{ g}^{-1}$ , which is in very good agreement to values found in commercially available electrodes [37].

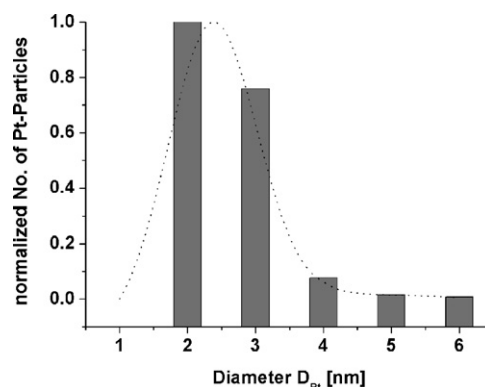


Fig. 5. Pt particle size distribution coated on SWCNTs.

In summary, we have a highly conductive SWCNT network with a tuned wetting behavior and highly distributed small diameter catalyst particles, thus, all requirements for a gas diffusion electrode in fuel cell applications are fulfilled. The advantages of using SWCNT networks become very obvious when its basic properties such as conductivity  $\sigma$ , thickness  $d$  and mass  $m$  are directly compared to a commercially available a-C electrode (Table 1). The conductivity is improved by more than two orders of magnitude whereas thick-

Table 1

Basic properties of gas diffusion electrodes based on either a-C (E-Tek<sup>37</sup>) or on SWCNT networks

Material	$\sigma$ ( $\text{S cm}^{-1}$ )	$d$ ( $\mu\text{m}$ )	$m$ ( $\text{mg cm}^{-2}$ )
E-Tek	$\sim 2$	400	$\sim 24$
SWCNT	2000	10–20	$\sim 0.7$

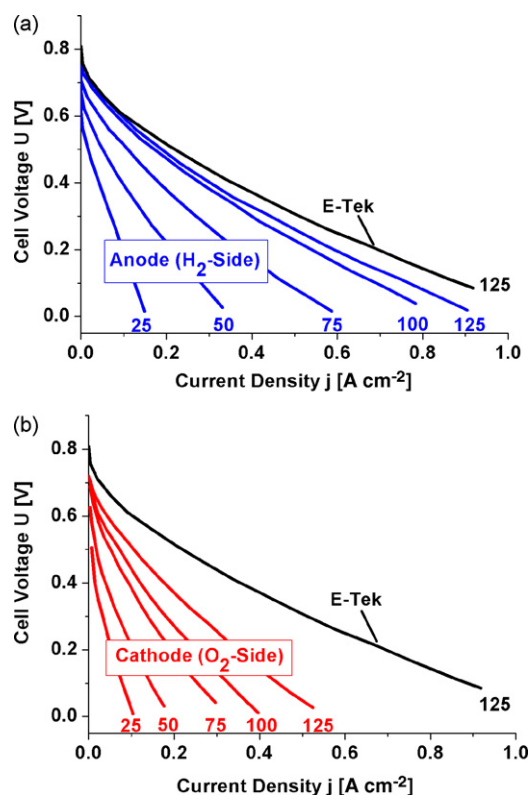


Fig. 6.  $I/V$  curves for a fuel cell where either the anode (upper curves) or the cathode (lower curves) is replaced by a SWCNT network. The numbers indicate the different temperatures in  $^{\circ}\text{C}$ .



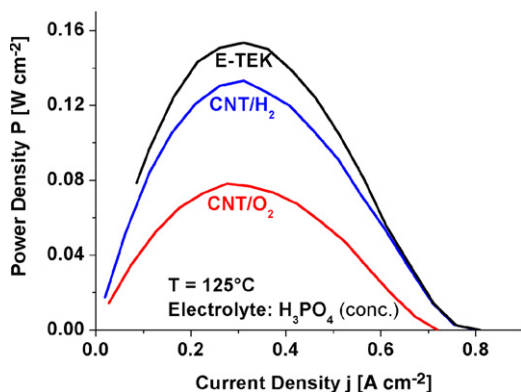


Fig. 7. Power density for a fuel cell at 125 °C, where either the cathode (lower curve) or the anode (middle curve) is formed by a SWCNT network. For the upper curve commercially available a-C electrodes are used on both sides.

ness and mass are decreased by more than one order of magnitude. Therefore, extremely thin and light gas diffusion electrodes can be realized when using SWCNT networks.

#### 4. Fuel cell testing

The proposed SWCNT gas diffusion electrodes were tested in a home-built fuel cell. Pure H<sub>2</sub> and O<sub>2</sub> gases were used without any humidification. We replaced the a-C electrode either on the cathode or the anode side. *I/V* curves are taken at several temperatures ranging from RT to 125 °C. For comparison, a fuel cell using only commercially available a-C gas diffusion electrodes (E-Tek) was tested as well. The results are presented in Fig. 6.

The current density increases with temperature, as expected, due to improved kinetics. At the same temperature, the performance of the anode (H<sub>2</sub> side) is already comparable to the commercial a-C electrode (for clarity, only shown for 125 °C). The performance of the cathode (O<sub>2</sub> side), however, is appreciably lower and only 2/3 of the anode performance is achieved. That can be explained by a different activity of the catalyst and a complex 4e<sup>-</sup> process [29]. Consequently, also the power density  $P$  ( $P = I \times U$ ) is lower for the cathode side, as shown in Fig. 7.

The power density is limited by the internal resistance of the cell which is in our set up dominated by the H<sub>3</sub>PO<sub>4</sub>-wetted filter membrane. It was used with focus on simplicity of the set up rather than on performance since the filter membrane was also used for the preparation of the SWCNT network. It can be expected that optimizations of the electrolyte may increase the power density significantly. Also, it should be pointed out that the commercial electrodes used were highly optimized whereas our electrodes were rather meant as a proof-of-concept. Nevertheless, we believe that the difference in performance observed is rather a question of the catalyst preparation than of the carbon material used. In fact, an elemental analysis of the SWCNT electrode after fuel cell testing using electron diffraction spectroscopy (EDX, spectra not shown here) revealed that the Pt precursor (H<sub>2</sub>PtCl<sub>6</sub>) was not fully converted to elementary Pt. Hence, some of the Pt remained inactive, which explains the rather poor overall-performance of our devices. Consequently, optimizations towards catalyst preparation and the use of other catalyst materials should overcome this problem and are also part of ongoing/future work.

#### 5. Conclusion and outlook

It has been demonstrated that partial functionalization with platinum and PTFE leads to a multifunctional SWCNT network

which can be used as extreme thin and light gas diffusion electrodes. Their performance in a fuel cell has been demonstrated to be competitive to commercial a-C electrodes. This way, a-C electrodes can be entirely replaced by such multifunctionalized SWCNT networks. The light and thin architecture of such material opens the door for a new generation of light weight power supplies, which potentially fulfills the demands of future portable devices.

However, to move beyond the proof-of-concept status towards mass production, some general achievements are still required. The filtration method applied here is not suitable for large scale production, but both the SWCNT and the PTFE/SWCNT suspension can also be processed as inks using various printing techniques such as transfer-printing, spraying or roll-to-roll manufacturing. This has already been demonstrated for thin SWCNT networks [38–41] as well as for a-C [41]. In terms of costs, it can be expected that SWCNT material will probably always be somewhat pricier than a-C. But the price for SWCNT materials is continuously decreasing and eventually, it can be expected that the costs of a SWCNT-fuel cell will be dominated by factors other than the SWCNT material itself.

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