CNT-SPEEK membrane assemblies for fuel cells: from synthesis to application

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Abstract

A new electrode set up for fuel cell membranes containing carbon nanotubes has been successfully developed including the nanotube synthesis, the electro deposition of platinum and the membrane casting. The nanotube carpets containing different iron loadings were specially grown and adapted for this application. To apply a thin catalyst layer resulting in small clusters, platinum was sputtered on the nanotubes and the assembly was investigated by cyclic voltammetry concerning an improved catalyst utilisation. The so far best combination was found to be an aligned but loose nanotube structure in which a nominal thickness of 16 nm platinum could penetrate conveniently, forming the required small catalyst clusters. This nanotubes could be applied successfully preserving their carpet like structure onto a membrane.

Keywords

nano-composite; nanostructured electrode; multiphase system; electro deposition; electro catalytic activity

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1. Introduction

Polymer electrolyte membrane (PEM) fuel cells are known to be promising alternative power sources, especially for the use in mobile applications. They are known for their environmental friendly reactions with either no or low emission, due to the used reactants, their good energy conversion efficiency and high energy density. Nevertheless one of the technical hurdles for the competitive commercialisation is the use of high cost noble metals as catalyst. In order to decrease the costs, the amount of platinum, which is the mostly used and most efficient catalyst, has to be reduced. An intense research in this field has been carried out over the recent years [1,2]. An important strategy to achieve this is the increase of the utilisation efficiency which is manly depending on the contacts between the catalyst, the proton conductive membrane, the electron conductive material as well as the reactant. There are different ways to prepare the membrane-electrode assembly. Usually the catalyst layer is applied using an ink-process, blending of platinum with carbon particles as electron conductive media and with proton conductive polymers to improve the contact to the membrane. Nevertheless, there are always catalyst particle which are not connected with ether of the materials or isolated from the gaseous reactant. In addition the added polymer leads to a decreased electron conductivity due to separation of carbon particles. Therefore, the utilisation efficiency in commercial fuel cells is still around 30 %, although in the lab scale higher efficiencies are achieved [3,4]. Thus, the optimization of the electrode–catalyst-electrolyte interphase is essential.

For the preparation of the catalysts different fabrication methods are applied, where of the most commonly used also for large-scale production processes are based on precipitation chemistry [5]. Nevertheless, to insert a low content of platinum other methods are also favoured [3]. Sputter deposition is a widely used technique due to the precision and uniform distribution of platinum content and thickness, microstructure morphology, achieved small particle size as well as simplicity of the process and applicability on various materials [6-8].

For very thin layers, O'Hayer et al. found that the performance reaches a maximum at $5-10$ nm respectively $0.014-0.028$ mg/cm² [9]. They claim that smaller sized sputtered platinum particles probably hinders the water transport and a physical weakness of the catalyst layer sputtered directly on the membrane is obtained. On the other hand catalyst particles prepared by chemical methods are reported to have an optimum performance with about 3 nm clusters. Particles smaller than this size tend to be amorphous and have a considerably reduced activity [10].

Carbon nanotubes (CNTs) posses an exceptional molecular structure, which induce remarkable physical and mechanical properties [11]. Particularly their electrical characteristics as well as the high relative surface area lend them to application in catalysis [12]. Concerning the use in fuel cell electrodes this enables a fine dispersion of catalyst nanoclusters along the nanotubes leading to an enhanced catalyst efficiency on account of a higher reactive surface area. Furthermore by choosing nanotubes with suitable electron conductivity and controlling their distribution in the polymer electrolyte, an optimum catalyst-electrode-electrolyte interphase layer could be tailored. In the recent years different methods to apply platinum on carbon nanostructures were intensely studied [13-18]. Nevertheless, only very few studies took into account that also the interphase layer has to be improved in order to enhance the contacts and increase the utilisation efficiency. In order to optimise the electrode structure as well as the catalyst location, CNTs grown in a flowing catalyst CVD process were used [19]. In this widely used production process, aligned CNTs carpets can be formed on substrates. To vary the nanotube length, thickness, carpet density and metal content the different production parameters as reaction time, substrate material as well as catalyst material and concentration can be adapted [20-23]. If then the carpet containing suitable catalyst is partially coated with polymer electrolyte a layer with good electrolyte-catalyst and electron conductive support (electrode) is obtained. If in the same carpet, part of the nanotube contains only catalyst without polymer coating, a free access for the gas reactants, for instance oxygen

in the cathode can be assured. Inserting ferrocene as catalyst and toluene as carbon source in the process, iron containing CNTs are formed. In addition to the designated properties PtFe/C alloys proved to enhance the activity for oxygen reduction in direct methanol fuel cells [24,25]. Therefore the application of CNTs is favourable.

In this work the preparation of membrane-electrode-assemblies starting from nanotube carpets is evaluated aiming the application for fuel cell. First, an adapted CNT carpet was grown on a silicon substrate given the specific over all structure for the electrode. Then a low content of platinum was sputtered on the nanotube tips. The membrane was formed via a lift of process and a modified drop casting to retain the carpet structure and obtain the desired catalyst location. In this work, not only the process route was evaluated and the functionality was analysed. Furthermore, the influence of the iron content inserted in the CVD process was investigated.

2. Experimental

2.1. CNT growth

The CNTs were grown in an apparatus adapted from Singh et al. [23]. In the CVD-process toluene was used as the solvent and carbon source to which 2 wt% or 8 wt% ferrocene was added. These ferrocene-toluene solutions were inserted into the preheated zone (200 °C) of a two-stage oven via a syringe pump. Both materials typically vapourise under these conditions, given vaporisation temperatures of 175 °C for ferrocene and 110 °C for toluene. In the reaction zone of the oven (760 °C) ferrocene decomposes to iron particles which then act as catalyst for the nanotube growth while the toluene acts as carbon feedstock. A mixture of argon and 10 % hydrogen was used as carrier gas with a total flow rate of 750 ml/min while the injection rate was set to 5 ml/h. A reaction time of 1 hour respectively 45 minutes was chosen to gain nanotubes of a certain length. In this process CNTs were grown from both

silicon substrates and the surrounding tube to result in aligned CNTs, commonly known as "carpets". Figure 1 pictures produced aligned CNT carpets on a silicon substrate.

2.2. Sputtered Pt deposition

Pt was magnetron sputtered from a 3 inch target Cu film using an ION'X-2UHV planar-magnetron sputter source (Thin Film Consulting, Germany). The samples were mounted on a rotatable sample holder in an UHV chamber with a base pressure of 10^{-7} mbar. Pt a total nominal thickness of 16 nm respectively 8 nm were obtained by using rotation of the carbon nanotube samples at room temperature. The deposition rate and nominal thickness were monitored by a quartz crystal microbalance. A low sputter rate at only 8 Watt ensures a relatively probability for homogeneous nucleation on the surface of the carbon nanotubes at room temperature, and therefore a formation of nanosized Pt Clusters. Deposition at elevated temperatures (up to 400 °C) led to an undesired Pt distribution, as too much material in the form of thin films was found at the tips of the tubes.

2.3. Membrane fabrication

Sulfonated poly (ether ether ketone) (SPEEK) was used as polymer electrolyte for the membrane preparation. SPEEK with 56 % sulfonation degree was prepared in the laboratory as previously described in other papers [26]. To establish an improved catalyst – electrode – electrolyte assembly it is essential to partly preserve the aligned structure of the CNTs. Therefore, a drop cast process with SPEEK dissolved in DMSO was used. The solution can infiltrate the carpet and while drying keep the array of nanotubes together. However, preliminary experiments have shown that the SPEEK - DMSO solution penetrates and wets the CNTs so well that the carpet was overall covered in polymer given no desired reaction zone. Thus, a modified production process was developed (Figure 2).

In a first step a polystyrene foil was hot pressed on the CNT tips that previously were covered with platinum via sputter deposition with the nanotubes still attached to the substrate. Taking the CNT – PS – layer of the substrate the nanotubes ends were still uncoated. On this side the polymer electrolyte solution containing 10 wt% SPEEK was applied via drop casting. After evaporating the DMSO at 70 °C in the last step the PS was dissolved using toluene mixed with 10 wt% acetyl acetate. This process led to a one sided electrode membrane on which a second electrode acting as anode could be pressed or applied elsewise on the other side. The achieved set up and application is depicted in Figure 3.

2.4. Characterisation

The single production steps were examined in a field emission gun scanning electron microscopy (Leo FE-SEM 1530). The CNTs structure as well as the distribution of iron and platinum on the CNTs were investigated by transmission electron microscopy (TEM) using a Philips EM 400 at 120 kV acceleration voltage and a Jeol 2000FX-II at 200 kV acceleration voltage. The element contrast imaging was obtained in a Tecnai G^2 200kV transmission electron microscope operating at 200 kV with a post-column Gatan Imaging Filter. Two images were obtained, one using only electrons with zero energy loss and another using electrons with energy loss corresponding to the Fe L2,3 ionization edge.

Cyclic Voltammetry (CV) test were performed to gain informations on the catalytic activity of the different CNT – Pt formation. For the electrochemical measurements, 2 mg the CNT samples sputtered with nominal 16 nm Pt (8 wt% respectivily 2 wt% ferrocene in toluene, 1 hr reaction time) were dispersed in an ultra sonic bath in a solution containing 2 ml of water, 1 ml of ethanol and 1 ml of acetone. 80 μl of this suspension were then pipetted on a glassy carbon support and dried in a nitrogen stream. 20 μl of aqueous Nafion solution were then dropped on the catalyst film and the water was removed in a nitrogen stream, leaving Nafion on the surface to prevent that the catalyst is washed away in the electrolyte. The

sample was then installed in an electrochemical flow cell with an electrolyte flow rate of about 50 μl/s. All measurements were performed in 0.5 M H_2SO_4 and the potentials are given versus the reversible hydrogen electrode (RHE).

To compare the iron and platinum concentration on the nanotubes, the platinum sputtered CNTs as well as on the finished electrode-membrane were investigated by energy dispersive X-ray analysis (EDX) in the SEM.

3. Results and discussion

3.1. CNTs

In the applied CVD process aligned multiwalled CNTs were grown on a silicon substrate as shown in Figure 1. The dimension of the produced nanotubes are depending on the catalyst concentration in the feedstock as well as reaction time [23]. Therefore, the CNTs length is different for the three prepared samples. For the nanotubes grown with 8 wt% ferrocene in toluene for 1 hr the average length was about 300 μm where the 2 wt% solution lead to a length of about 150 μm. The third carpet grown with 2 wt% solution for 45 minutes was even shorter with an average length of 65 μm. The length also vary along the substrate due to the flow field in the reactor. Likewise the outer diameters differ in the carpets. For the 1 hour reaction the 8 wt% solution the average is about 65 nm and for the 2 wt% CNTs about 45 nm, where for the shorter reaction time it is 30 nm in average (Figure 4 and 5). Furthermore, the CNT yield is equally related to the catalyst concentration given a higher rate for higher ferrocene concentrations which indicates along with the different nanotube dimensions a reduced carpet density for the low ferrocene concentration.

The nominal platinum thickness was chosen to be 16 nm for the two CNT samples grown for 1 hr with 8 wt% respectively 2 wt% solutions and 8 nm for the CNTs grown with 2 wt% for 45 min. Despite this differences for the same sputter rate the platinum coated the CNT similarly with close-packed clusters, though the low platinum content gave a less dense

structure even at the nanotube tips (Figure 4). Nevertheless, for all samples the cluster size was found to be in average 3 - 5 nm, but larger accumulations up can be found at the upper part getting more dense to the tip of the CNTs with the high platinum content. However, the penetration depth in the two carpets sputtered with 16 nm platinum was different and found to be with about 19 μm to 14 μm increased for the 2 wt% less close grown nanotubes (Figure 6). For the low platinum content the depth of penetration was even smaller with about 10 μm. Thus, the possible reaction area in the CNT carpet sputtered with 8 nm is noticeable smaller, due to the high surfaces area provided by the nanotubes.

Due to the use of ferrocene as catalyst for the CNT growth iron can be found all over the nanotubes (Figure 5). Given a base growth mechanism in the applied production process iron cluster are located at the ends as well as in the centre between the nanotube walls [23]. This can be found in both at low and high ferrocene concentration grown CNTs. Especially with the high concentrations also iron clusters covered with carbon can be found on the nanotubes (Figure 5. b). Furthermore, via element contrast imaging small amounts of iron could be shown embedded in the wall structure of the nanotubes. Despite the low ferrocene concentration of 2 wt% in toluene and the short reaction time of 45 minutes, the iron was clearly detectable (Figure 5. d).

The activity measurements of two different samples using CV are shown in Figure 7, in which a) pictures the cyclic voltamogram of the 8 wt% ferrocene CNTs grown for 1 hr, given a blank glassy carbon electrode as a reference. The CV shows the features of Pt, namely the H_{UPD} region at potentials between 0.06 and 0.3 V and the Pt oxidation (0.8 to 1.3 V)/reduction (0.9-0.6 V), although they are only weakly resolved. The oxidative current at around 0.6 to 0.8 V in the positive going potential scan is most likely attributed to the oxidation of Fe or Fe^{2+} [27].

For comparison Figure 7. b) shows the CV of the electrode prepared from CNTs grown with 2 wt% ferrocene and sputtered with nominal 16 nm platinum. (Again the blank glassy

carbon electrode is included as reference). In this CV the typical features of a polycrystalline Pt Electrode [28] are well resolved, confirming a successful loading of the CNT´s by platinum sputtering. In comparison with the first sample of longer as well as more dense grown CNTs with the same amount of deposited platinum the active surface area of the 2 wt% CNTs calculated from the electrochemical measurements by integration of the Hupd-region, is more then ten times higher compared. To rate this, the different yield of the produced CNTs per area has to be taken in account. Since it was estimated to about 1 : 2.5 (2 wt% . 8 wt%), the higher active surface area can be understood by a deeper penetration of the Pt particles in-between the CNTs during the Pt sputtering, resulting in a better separation of the Pt-particles. Agglomeration of Pt particles results in a smaller active surface area for the same mass of Pt.

Furthermore, CO_{ad} stripping experiments were performed on the 2 wt% CNT sample (Figure 1c). Therefore the Pt surface was first saturated with CO at a constant potential of 0.06 V and after removal of CO by rinsing the cell with 0.5 M H_2SO_4 for about 20 minutes the potential was scanned between 0.06 and 1.3 V in 0.5 M H_2SO_4. The oxidation of adsorbed CO results in two well resolved current peaks, centered at 0.65 and 0.8 V, respectively. The appearance of two peaks in a CO stripping experiment is commonly interpreted as oxidation of CO adsorbed on large Pt-particles (0.65V) and Pt nanoparticles (about 3 nm) (0.8V) [29]. This result agrees well with the observation on TEM images, were it was found that Pt agglomerations are formed on the tips of the CNTs, where else Pt particles of 3 to 5 nm are formed on the nanotubes.

3.2. Membrane

The membranes were set up as described in 2.3. SEM images of the fabrication steps are shown in Figure 8. In this process the aligned structure of the CNT carpets kept in good order for the first production steps, the sputtering of platinum as well as the hot pressing of the polystyrene foil and the stripping of the substrate. Nevertheless, the dissolution of the

polystyrene deranged the structure partly. However, a loose assembly that seem suitable for an electrode setup can still be found. While in a few parts of the membrane the CNTs were even covered with the electrolyte closer to the tips, in most areas the needed reaction interfaces are available.

Due to the production process sulfonated PEEK as well as platinum can be found at the membrane surface. EDX measurements point out, that platinum was still on the CNTs after the processing while the iron clusters on top of the CNTs seemed to be "washed of" the nanotube tips (Figure 9). Since iron was also found to be embedded in the wall structure, small amounts of iron under the detectable range of the EDX must still be present. Also a high sulphur peak can be found that is related to the sulfonated polymer and indicates the close combination of platinum and the electrolyte. This supports further the suggestion of a good fuel cell reaction area on the membrane surface.

4. Conclusions

This paper describes a new way to tailor CNT/polymer nanocomposites with potential use for fuel cell application. A procedure starting with the CNT growth in a carpet array, deposition of catalyst and assembling in a set up which integrates polymer electrolyte membrane, catalyst and conductive CNT array as electrode is reported.

The structural analyses of the nanotubes as well as the sputtered platinum give the informations on the differences due to varied ferrocene concentrations in toluene used for the growth. They reveal a small iron content in all kinds of CNTs and a lower carpet density as well as CNTs length and diameter for the lower concentration. Thus, a better platinum penetration can be achieved and furthermore probably more small clusters of 3 – 5 nm can be formed, given a higher surface area. Also the electro chemical measurements have confirmed that the Pt loading of the CNTs was successful and resulting in a better separation of the Pt particles when Pt is evaporated on the less densely packed CNTs prepared with 2 wt%

ferrocene. Nevertheless, large platinum particles can be found decreasing the potential maximum activity. Further experiments with half of the amount sputtered platinum reveal that with only 8 nm nominal thickness the penetration depth is noticeable decreased and the nanotubes only partly covered with clusters. Thus, leading to further needed investigation applying in between quantities to gain an optimal platinum utilisation. Anyhow, it could be shown that CNTs prepared in widely used processes and applied to membrane using an adapted membrane casting process are well qualified for the application in polymer electrolyte fuel cells.

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Figures
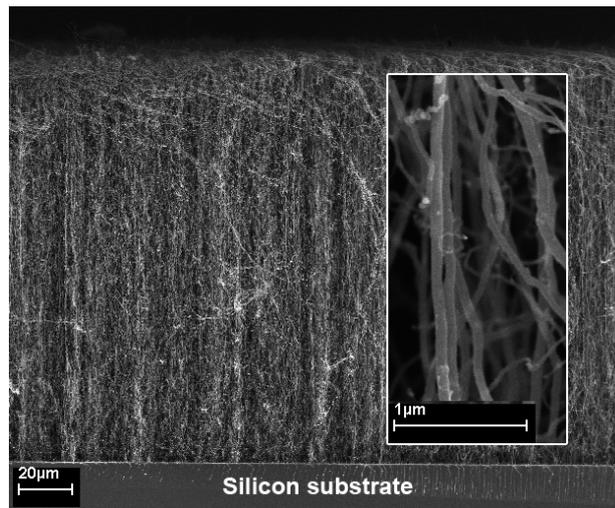
Figure 1. SEM picture of an aligned CNT carpet on a silicon substrate, including CNT image with higher resolution.
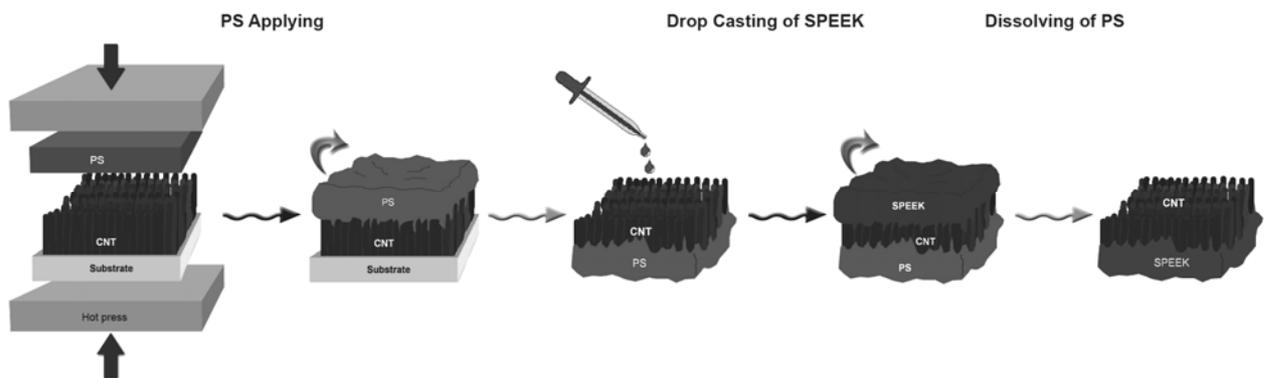

**Figure 2.** Steps of the membrane processing.
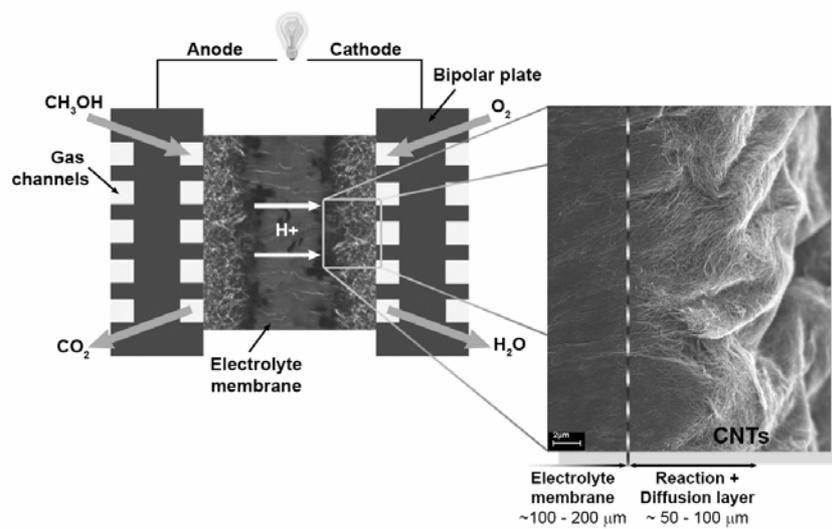

Figure 3. Fuel cell model with CNTs.
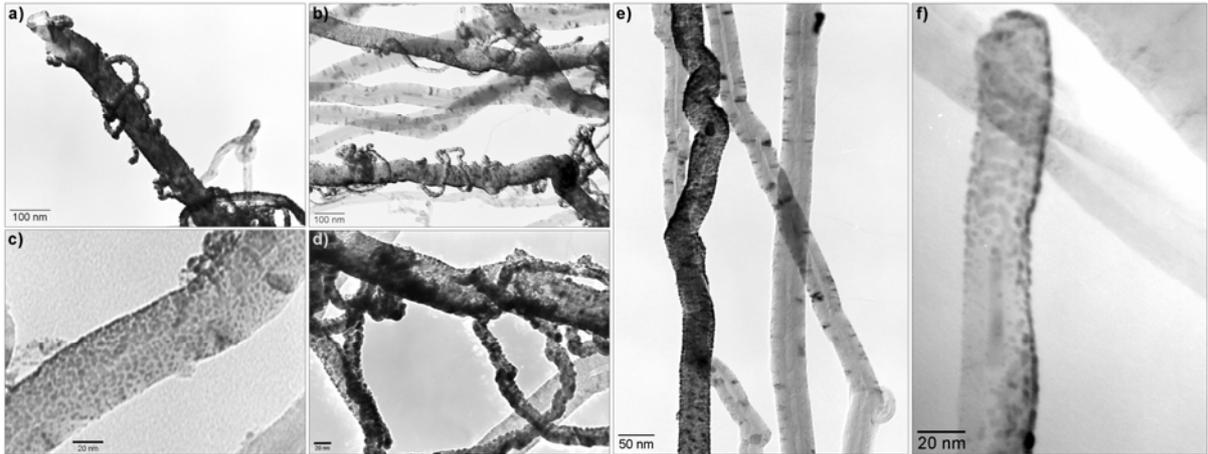
Figure 4. TEM picture of CNTs sputtered with platinum, a) tips of a CNT grown with 8 wt% ferrocene in toluene for 1 hr, 16 nm nominal platinum thickness b) and c) 8 wt%, 16 nm Pt CNTs further down, d) and e) part of CNTs 2 wt%, 1 hr, 16 nm Pt and f) tip of a CNT 2 wt%, 45 min, 8 nm Pt.
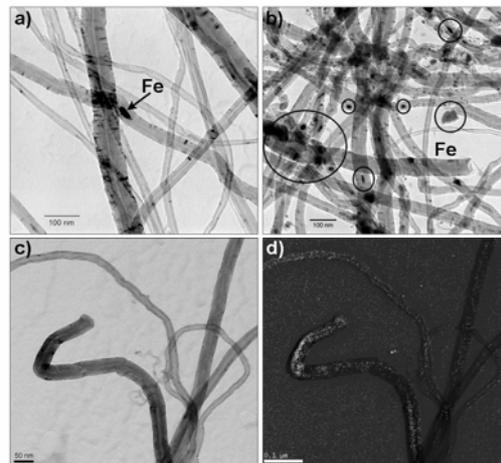

Figure 5. TEM picture of CNTs picturing the iron content, a) iron cluster in a CNT grown with 2 wt% ferrocene in toluene for 45 min, b) exemplary iron clusters in CNTs grown with 8 wt% ferrocene for 1 hr, c) tip area of CNTs grown with 2 wt% ferrocene in toluene for 45 min and d) element contrast image showing the iron content in the CNTs pictured in c).
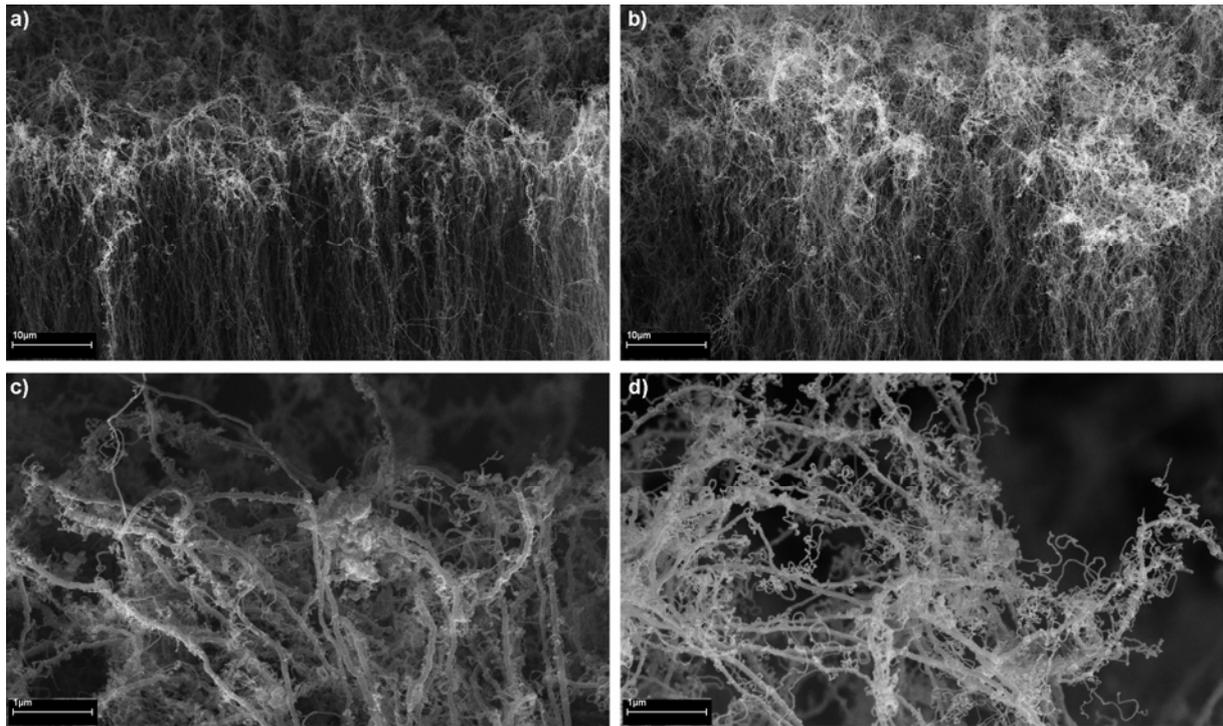
Figure 6. SEM picture of aligned CNT carpet sputtered with 16 nm platinum. a) and c) different magnifications of CNT tips grown with 8 wt% ferrocene in toluene for 1 hr, b) and d) tips of CNTs grown with 2 wt% for 1 hr.
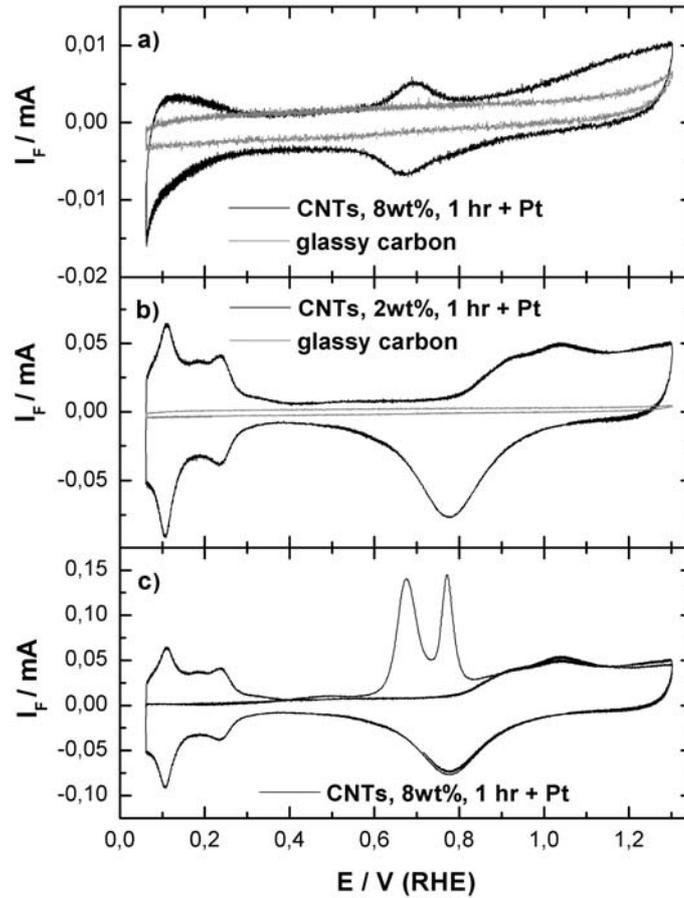
Figure 7. Cyclic Voltamograms of the two different CNT types sputtered with nominal 16 nm platinum and as reference the glassy carbon substrate, a) CNTs grown with 8 wt% ferrocene in toluene for 1 hr, b) CNTs grown with 2 wt% ferrocene in toluene for 1 hr and c) CO_{ad} stripping experiment on the sample shown in b).
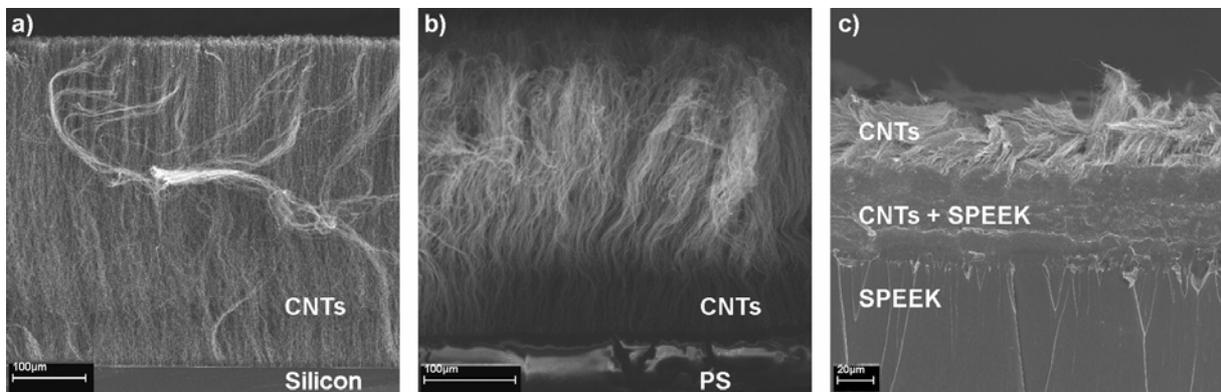
Figure 8. Process steps of the membrane fabrication. a) CNTs on a substrate, b) CNTs partly covered with PS, c) completed membrane with SPEEK.
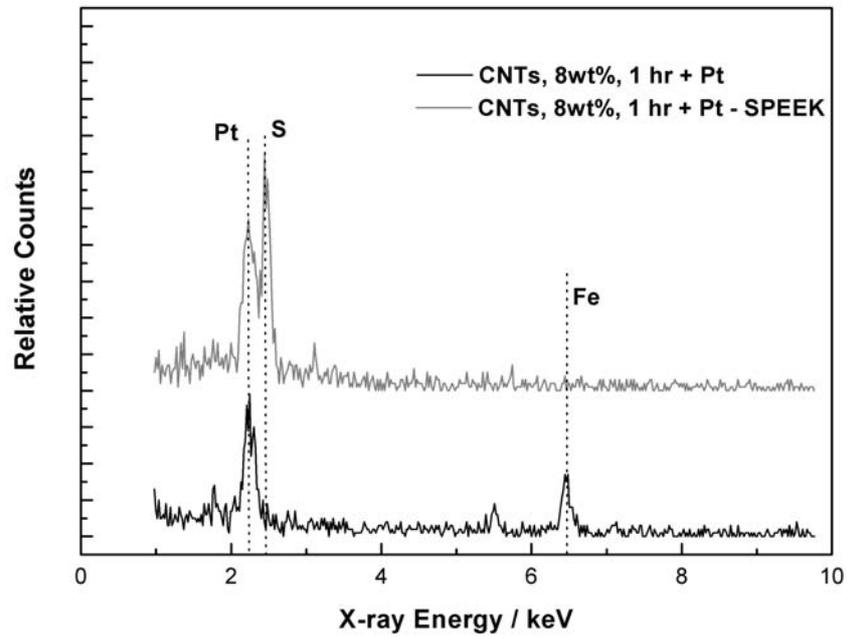
Figure 9. EDX Graphs of CNTs grown with 8 wt% ferrocene in toluene covered with 16 nm platinum as grown and after processing to a membrane with SPEEK.