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Catalytically active CNT–polymer-membrane assemblies: From synthesis to application

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ABSTRACT

A new membrane electrode assembly set up for catalytic processes containing carbon nanotubes has been developed. The process includes the nanotube synthesis, sputter deposition of platinum as catalyst and the membrane casting. Aligned nanotube carpets were grown from toluene/ferrocene solutions and sputtered with platinum. Subsequently the assembly was investigated using cyclic voltammetry to confirm a sufficient catalyst activity. A procedure was developed to embed the carbon nanotubes doped with catalyst into SPEEK membranes, while preserving the aligned structure and keeping some surface area of the catalyst-doped nanotubes free of membrane material to allow for easy access to reactants. So far the best results were obtained using an aligned but somewhat loose nanotube structure and a deposition of 0.034 mg/cm^2 Pt, forming a combination of small catalyst clusters and a thin film. The assemblies are optimized in respect to application in fuel cells and functional membranes.

1. Introduction

Embedding carbon nanotubes (CNTs) in polymer matrices has received increasing attention as strategy for membrane development, due to the unique combination of properties: high aspect ratio/high surface area, electron conductivity, superhydrophobicity, frictionless surfaces, simple functionalization and dispersion in organic polymers, capability to enhance mechanical strength with small filler content as well as the potentially close control of pore dimension at the nanometer scale [1]. These characteristics started to be explored in membrane applications for gas and liquid separation [2–6]. Hinds et al. made a pioneering contribution, reporting on the preparation of an aligned CNT membrane for gas permeation and for transport of $Ru(NH_3)_6^{3+}$ ions in aqueous solution [2]. He followed theoretical predictions, which suggest that the diffusivity of light gases inside CNTs with diameter around 1 nm to be orders of magnitude higher than in other porous structures like zeolites [3], due to the inherent molecular smoothness. After the first simulations [5] of water transport in nanotubes, experimental results also demonstrated higher than expected flow rates, making CNT membranes promising candidates for water desalination with the possibility of tailoring the tube diameters to retain salt [6]. CNTs have also been proposed for manufacturing electrodes for water desalination promoting flow through capacitor [7]. Furthermore, they are considered as mechanical support for catalysts [8] and could therefore be an attractive additive in the design of a new generation of catalytic membranes. Their electrical characteristics as well as the high relative surface area encourage their application in catalysis [9]. When used in catalysis they could enable a finer dispersion of catalyst clusters on the nanotubes leading to enhanced catalyst efficiency due to 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.

Recent papers explored the dispersion of catalysts on carbon nanotubes with potential application for fuel cells [10–17]. The catalytically active metal particles may decorate the external walls or be encapsulated in the interior of the nanotubes [10]. Claimed advantages are the large surface area for catalyst dispersion and that CNTs are more resistant to corrosion than carbon black under fuel cell operation conditions [18]. Attempts to prepare optimized membrane electrode assemblies (MEAs) using carbon nanotubes as part of the electrode have been reported recently [18–21]. CNTs

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loaded with catalysts have been deposited or incorporated in the carbon paper or cloth, by dispersion and electrophoretic deposition [19], by growing the CNTs directly onto the carbon paper [20] or alternatively by filtration of a CNT dispersion which is then deposited onto a commercial Nafion® membrane [18,21] and hot pressed with the carbon backing layer. In all cases the MEA was prepared using a commercial Nafion® membrane. However it was demonstrated that the electrochemical performance of PEM fuel cells made with catalyst-coated membranes (CCMs) is superior to those using conventional hot-pressed MEAs with comparable conditions of Pt electrolcatalyst loadings [22]. The CCM method offers higher electrochemical surface area, low cell ohmic resistance and a low charge transfer resistance. The aim of this paper is to propose a method of MEA preparation, combining the advantages of CCM and carbon nanotubes producing a thin integrated MEA, in which aligned CNTs are partially embedded in the polymer electrolyte and partially free for effective contact with the gas reactants and with the catalyst on the CNT surface. For this purpose sulfonated polyetheretherketone (SPEEK) has been chosen as electrolyte, since SPEEK membranes can be easily fabricated from solution [23] and can be integrated in the MEA. In principal the method can be adapted to any other membrane, including commercial Nafion® membranes, which can be fabricated from polymer electrolyte solutions. The first challenge is to prepare the polymer composite with aligned CNTs. This set up may offer advantages for the MEA preparation, due to higher electronic conductivity along the tubes than across them [24]. Additionally other authors [21] predicted a higher gas permeability when the CNTs are aligned. Furthermore the aligned tubes may as well exhibit superhydrophobicity, facilitating a fast removal of water, which is a product of the electrocatalytic cathode reaction. CNT alignment has been claimed to be advantageous in other membrane applications as well and different production strategies have been reported in literature [2,4,10,25]. Hinds et al. [2] obtained a vertically aligned array of multiwalled CNTs grown on quartz by chemical vapor deposition (CVD). The space between the tubes was filled with polystyrene and the membrane was removed from the quartz by treatment with fluoridic acid. Mi et al. [25] grew vertically aligned CNTs directly on a porous alumina support and filled the space between the CNTs with polystyrene as well. Kim et al. [4] fabricated the membrane by orienting functionalized single wall CNTs with a filtration method. Beside the CNTs alignment, when fuel cell applications are concerned, not only an optimized contact between polymer electrolyte and CNT is required, but also free access of catalyst surface to the reactant gases. A method is proposed to address these requirements.

In order to be able to improve the electrode structure as well as the catalyst location, CNTs grown in a flowing catalyst CVD process were applied [26]. In this widely used production process, aligned CNT 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 [27–30]. Inserting ferrocene as catalyst and toluene as carbon source in the process, iron containing CNTs are formed. Nevertheless, since Pt–Fe proved to enhance the activity for oxygen reduction in direct methanol fuel cells, additional iron is favourable and has no negative effect on the reactions [31,32].

To preserve the nanotube structure sputter deposition was chosen for inserting platinum as catalyst. This technique is widely used 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 [33–35]. Depending on the process parameters and surface area of the materials thin films or small particles are formed. For very thin layers, O'Hayer et al. observed that the performance reaches a maximum for a particle size 5–10 nm, respectively 0.014–0.028 mg/cm^2 [36]. They claim that smaller sized sputtered platinum particles probably hinder the water transport and a strong interfacial adherence on the membrane is obtained. On the contrary, 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 [37].

In this work a novel preparation technique of membrane electrode assemblies starting from nanotube carpets is presented. First, an adapted CNT carpet was grown on a silicon substrate as to give it the structure dimension used in the electrode. Then a small amount of platinum was sputtered onto the nanotube tips. The membrane was formed via a lift of process and a modified drop casting to retain the carpet structure and to obtain the desired catalyst location. In this work, the process route was evaluated, and additionally the functionality in terms of electrochemical activity of the platinum sputtered CNTs was analysed.

2. Experimental

2.1. CNT growth

The CNTs were grown in an apparatus adapted from Singh et al. [30]. In the CVD process toluene was used as the solvent and carbon source to which 2 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 vaporise 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 vol.% 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 h, respectively 45 min 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". Fig. 1 shows one of these aligned CNT carpets on a silicon substrate.

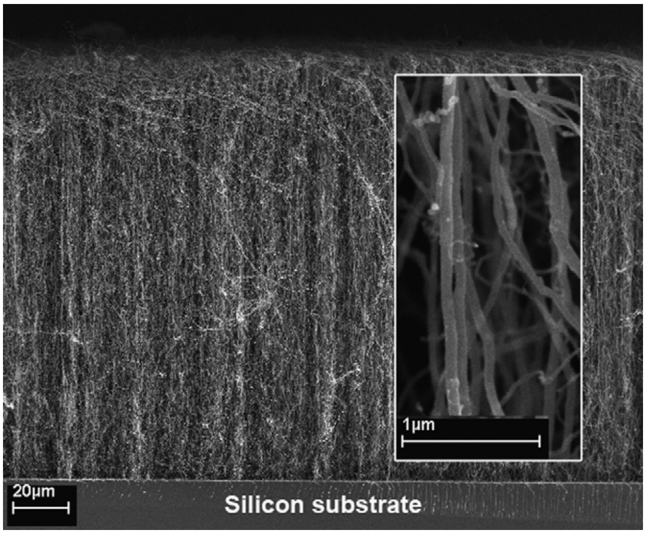

Fig. 1. SEM picture of an aligned CNT carpet on a silicon substrate, including CNT image with higher resolution.