

Preparation and characterisation of a self-supported SWCNT anode for the DMFC

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Introduction

The direct methanol fuel cell (DMFC) has attracted considerable attention as electrochemical power source because of its simple system design, low operating temperature, and convenient fuel storage and supply. Major limitations of the DMFC are related to the low power density, which is a consequence of the poor kinetics of the methanol oxidation reaction (MOR), poisoning of the catalyst by reaction intermediates, and methanol crossover. The principle of a DMFC is depicted in Figure 1.

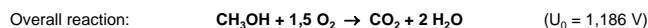
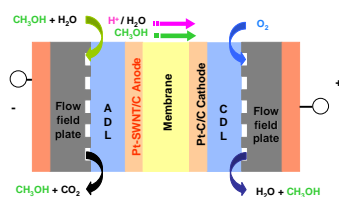


Figure 1: Scheme of the DMFC

Objectives

This project aims at the development of a new type of Membrane-Electrodes Assembly (MEA) on the basis of carbon nanotubes (CNTs) as catalyst support material at the anode and a membrane with low permeation rate for methanol. A particular aim of this project focuses on the development of a self-supported 100 μm thin anode exclusively made of single-walled nanotubes that should improve the electronic conductivity and reduce the transport resistances of methanol and carbon dioxide within the reaction layer.

Preparation of the single-walled CNTs

The single-walled CNTs were prepared by the carbon arc discharge method. The reaction took place in a reaction chamber (A) equipped with a 6 mm graphitic rod anode (C) mixed with 4:1 Ni:Yi catalyst and a graphite cathode (B). The reactor was pressurised with helium at 500 mbar. The current amounted 100 A and the voltage 50 V. The reaction products are visible on picture E and consist in a mixture of carbon nanotubes, amorphous carbon and residual catalysts.

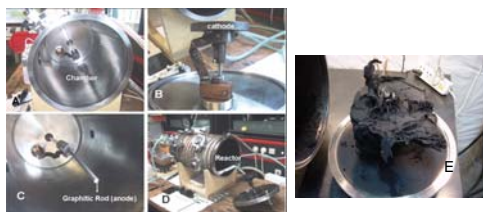


Figure 2: Reaction chamber with graphite electrodes (a, b, c, d) and reaction products (e)

Preparation of the self-supported anode

First, a purification process of the pristine SWCNTs was carried out in order to remove residual catalyst (Ni/Y) and amorphous carbon. In this work, dry and wet chemical or both oxidative methods were used. During this treatment, the SWCNTs undergo a defect functionalization based on the conversion of carboxylic groups and other oxygenated sites that should enhance the specific area and promote the further catalyst deposition such as PtRu. The development of the self-supported anode was based on two successive sedimentation processes of the SWCNT diffusion and PtRu-SWCNT reaction layer, respectively in a 1 wt% sodium n-dodecyl sulfate surfactant solution in the glass apparatus shown in Figure 3. For this filtration process, a 0.40 μm cellulose ester membrane was used. The carbon nanotubes were previously dispersed with the help of a high energy ultrasonic device (Branson), in which a titanium rod was immersed in the mixture. 20 wt% PTFE was added to both suspensions in order to create hydrophobic sites and bind up the different structures. The as-prepared bucky paper with incorporated reaction layer was peeled off with precaution from the membrane and sintered at 130°C for 1 h.



Figure 3: a) Apparatus for the preparation of the self-supported SWCNT anode with vacuum pump

Characterisation of the self-supported SWCNT electrode

The structure of the as-prepared SWCNT gas diffusion layer is shown in figure 4a, c&d. One recognizes a highly compact structure compared to that of a common gas diffusion electrode with carbon fibres in figure 4b. A good connection of the reaction layer with the diffusion layer and uniform distribution of the catalyst within the reaction layer was achieved as well.

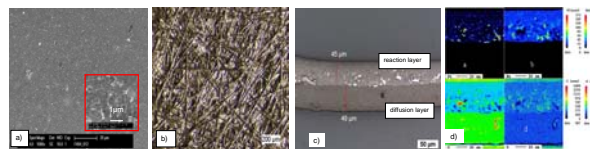


Figure 4: SEM pictures of a) the self-supported SWCNT electrode and b) Toray carbon paper. c) cross-section of an as-prepared self-supported anode with d) Pt, Ru, C and O particle distribution.

Figure 5 shows a cross section of a membrane-electrodes-assembly (MEA) with the novel anode structure.

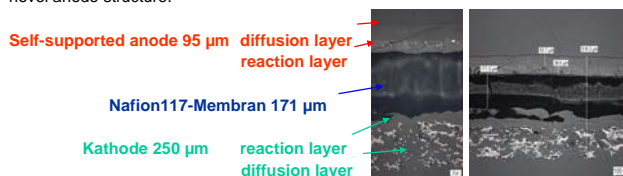
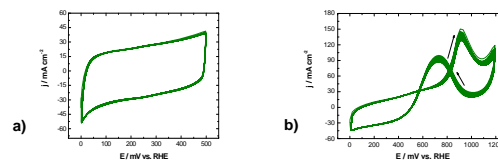


Figure 5: SEM pictures of a MEA cross section with a self-supported SWCNT-anode

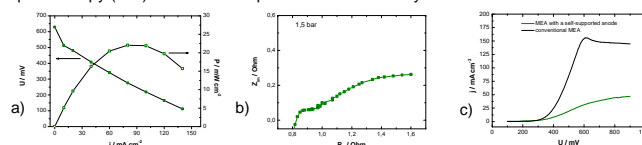
Half-Cell & DMFC measurements

The activity of the as-prepared PtRu-SWCNT/SWCNT electrode was investigated in the half-cell in 1 M H₂SO₄ and 2 M CH₃OH + 1 M H₂SO₄ solutions.


 Figure 6: CVs in half-cell of different of 1 mg cm⁻² PtRu-SWCNT/SWCNT GDEs in a) 1 M H₂SO₄ and b) 1 M H₂SO₄ + 2 M CH₃OH at 40 mV s⁻¹ and 25 ° C

- Comparable CVs of PtRu-SWCNT and PtRu-Vulcan in pure sulfuric acid solution.
- High activity of PtRu-SWCNT for methanol oxidation.

The performance of the 5 cm² MEA was evaluated by U-I, electrochemical impedance spectroscopy (EIS) and methanol permeation in electrolysis mode.


 Figure 5: a) U-I and P-I Curves b) EIS and c) methanol permeation of MEA with PtRu-SWCNT based anodes. Measurements were carried out at 1.2 bar methanol and pure oxygen back pressure and 80 ° C. Catalyst loading was 1 mg cm⁻² Pt for anode and cathode. Pt:Ru ratio was 1:1at.

- a 22 mW cm⁻² power density was measured with oxygen
- high ohmic impedance of the MEA due probably to residual Ni/Y catalyst
- low limiting current value that is an indication for a reduced methanol crossover

Conclusions

The feasibility of a MEA with a 100 μm self-supported anode was demonstrated in the DMFC for the first time. However, the performance in the DMFC was obviously still limited by poor methanol diffusion and high ohmic impedance in the anode chamber.

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