

Influence of the purification and functionalization of carbon nanotubes on PtRu activity for methanol oxidation in 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.

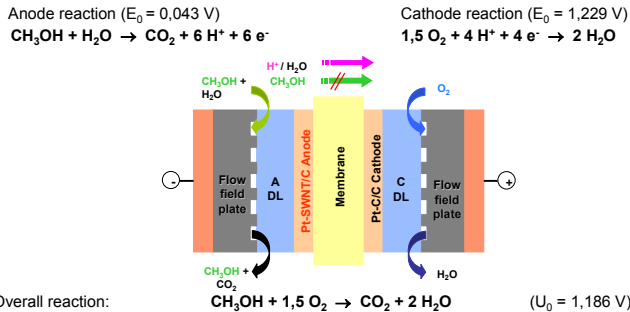


Figure 1: Scheme of the DMFC

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. The first step of this project focuses on the study of the influence of the chemical functionalization of single-walled nanotubes on their physical and electrochemical properties.

Preparation of 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:Y catalyst and a graphite cathode B. The reactor was pressurized 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.

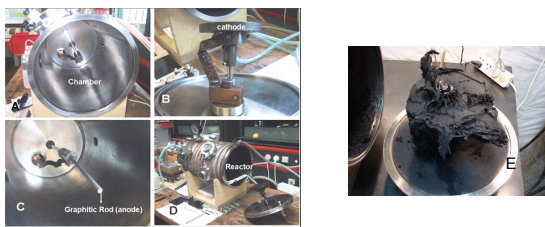


Figure 2: Reaction chamber with graphite electrodes (a, b, c, d) and reaction products (e)

Purification and functionalization of single-walled CNTs

The purification process of pristine SWCNT1 aims at removing residual catalyst (Ni/Y) and amorphous carbon. In this work, dry ($\text{O}_2/\text{SWCNT2}$) and wet ($\text{HNO}_3/\text{SWCNT3}$) chemical or both ($\text{O}_2+\text{HCl}/\text{SWCNT4}$) 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 specific area and promote further catalyst deposition, such as PtRu. The results of the near infrared (NIR) and inductively coupled plasma (ICP) spectroscopy are listed in table 1.

Methode	NIR	ICP	
		Ni Gew.-%	Y Gew.-%
Sample	CNTs %		
SWCNT 1 / raw material	36	6,5	1,1
SWCNT 2 / air oxidated at 300°C	47	8,6	1,7
SWCNT 3 / concentrated HNO ₃	-	4,4	0,7
SWCNT 4 / air oxydation 300°C + HCl	-	8,3	0,9

Table 1: Results obtained from NIR and ICP measurements at the different SWCNT samples

- CNTs purity was increased up to 47% by air oxidation treatment at 300 °C
- Nitric acid treatment of pristine CNTs led to a decrease of residual Ni and Y catalyst ratio down to 4,4% and 0,7%, respectively.

Scheme of the anode & MEA fabrication

The development of the composite anode includes the preparation of the carbon nanotube powders, the catalyst deposition, the ink formulation and deposition on Toray carbon paper with the spray method, and finally its characterization in a half-cell and in a DMFC with a commercial N117 membrane and Pt-Vulcan/C cathode.

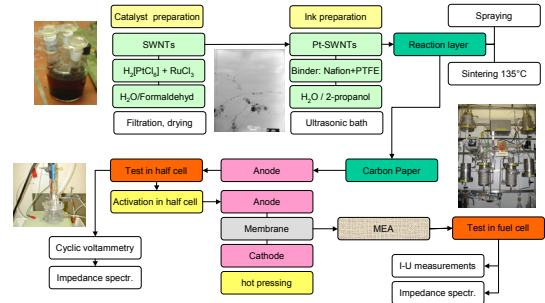


Figure 3: GDE and MEA preparation

Half-Cell & DMFC measurements

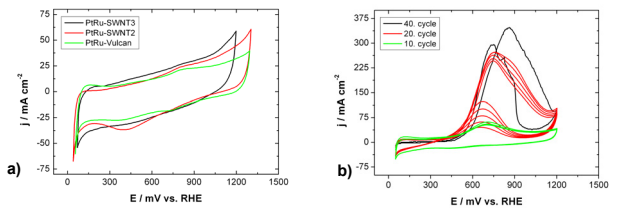


Figure 4: CVs in half-cell of different 1 mg cm^{-2} PtRu-GDEs in a) $1 \text{ M H}_2\text{SO}_4$ and b) $1 \text{ M H}_2\text{SO}_4 + 2 \text{ M CH}_3\text{OH}$ at 40 mV s^{-1} and $25 \text{ }^\circ\text{C}$

- Comparable CVs of PtRu-SWCNT and PtRu-Vulcan in pure sulfuric acid solution.
- Higher activity of PtRu-SWCNT for methanol oxidation.
- Methanol diffusion limitation is due to high Pt-catalyst:substrate weight ratio of 60:100 and the presence of Ru.

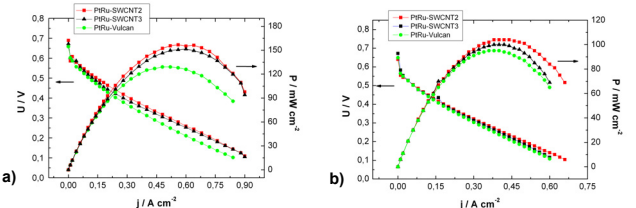


Figure 5: U-I and P-I Curves of MEAs with PtRu-SWCNT based anodes. Measurements were carried out at 2 bar a) methanol and b) oxygen/air back pressure and $80 \text{ }^\circ\text{C}$. Catalyst loading was 1 mg cm^{-2} Pt for anode and cathode. Pt:Ru ratio was 1:1at.

- 10-15% higher power density was measured in the DMFC with PtRu-SWCNT2 as anode material compared to that of the MEA with PtRu-Vulcan.

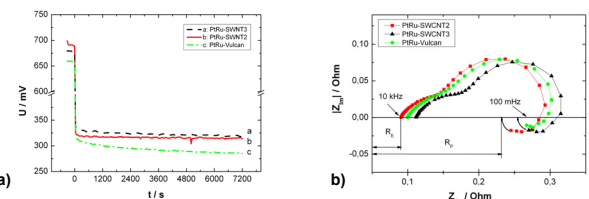


Figure 6: a) U-t curves recorded at 200 mA/cm^2 , $80 \text{ }^\circ\text{C}$ and 1,2 bar. b) Nyquist plots of MEAs with different anodes recorded at 100 mA cm^{-2} , $80 \text{ }^\circ\text{C}$ and 1,5 bar. Anode and cathode catalyst loading was 1 mg cm^{-2} Pt. Pt:Ru ratio was 1:1at.

- MEAs with SWCNT based anode show a stable cell voltage over the measuring time
- Higher activity of PtRu-SWCNT in DMFC can be explained by lower R_E and R_p values from impedance (EIS) measurements

Acknowledgments

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