Test of non-fluorinated polymer membranes for the middle temperature DMFC

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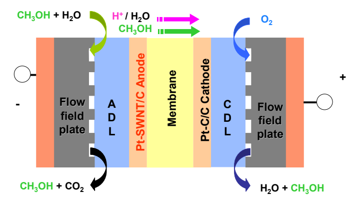
Introduction

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.

Anode reaction (E_0 = 0,043 V)
$$CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^-$$

Cathode reaction (E_0 = 1,229 V)
$$1{,}5\,O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$$



Overall reaction: $CH_3OH + 1{,}5\,O_2 \rightarrow CO_2 + 2\,H_2O$ (U_0 = 1,186 V)

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 topic focuses on the test of non-fluorinated middle temperature membranes (100-130°C), which were prepared in the Institute of Chemical Process Engineering at Stuttgart University and especially on the improvement of the membrane-electrode boundary.

Characterisation of the non-fluorinated polymer membranes

Three different membrane types were studied:
1) Ionically cross-linked blend membrane (Typ 504) made of a mixture of sulfonated acid polymer Polyetherketone (sPEK) and base polymer Polybenzimidazole (PBI)
2) Ionically cross-linked blend membrane with zirconium phosphate (Typ 504ZrP)
3) Covalently cross-linked blend membrane with PEK, Polyethersulfone (PSU) and zirconium phosphate nanoparticles (Typ A1418ZrP)
Some relevant properties are listed in following table:

	504 (sPEK-PBI)	504 (sPEK-PBI+ZrP)	A1418 (sPEK-PSU+ZrP)
Resistance [Ω cm]	32,5	19,4	10,03
Thickness δ [µm]	95	62	76
Ionic exchange capacity [meq g^{-1}]	1,24	1,23	1,59
Water content at 25°C [%]	30	34,9	31,64
Water content at 40°C [%]	37	41,9	35,00
Water content at 60°C [%]	37	43,4	48,33
Water content at 90°C [%]	60	74,4	53,87

Table 1: *Data sheet of the membranes used in this work (Stuttgart University)*

The ionic conductivity of the membranes was measured in a special PTFE cell with two gold electrodes by means of electrochemical impedance spectroscopy at room temperature. The membranes were previously immersed in a 1M H_2SO_4 solution. The Nafion117 membrane was used as reference. Following formula was used for the calculation of the specific ionic conductivity where A is the membrane area:

$$\sigma = \frac{\partial}{A \cdot R_E}$$

	Nafion117	504	504ZrP	A1418ZrP
Electrolyte resistance R_E [Ω]	0,514	1,151	0,917	0,558
Spez. Ionic conductivity σ [mS cm^{-1}]	42,1	10,5	8,6	17,4

Table 2: *Ionic conductivity of the different membranes used in this work*

➢ The specific ionic conductivity of the membrane 504 is still 4 times lower than that of the commercial Nafion117. For practical use in the fuel cell, however, the overall resistance value is more relevant. Here, similar values were found for A1418 and Nafion.

One of the more crucial issue of the non-fluorinated membranes (NFM) is their poor compatibility with the electrode materials. In order to extend the ionic conducting zone and the quality of the membrane-electrodes adhesion, the press parameters and Nafion content were varied. The best results were obtained with 10% Nafion, 6 bar and 130°C. However, the adhesion degree of the reaction layers on the NFMs (2b-e) is far below than that obtained with the Nafion membrane (2a).

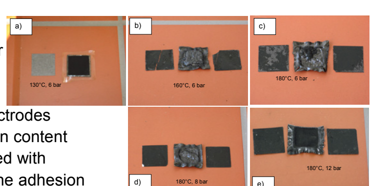


Figure 2: *MEAs with a) Nafion & b-d) non-fluorinated membranes*

Measurements in the fuel cell

The influence of some parameters, such as working temperature and pressure, on the MEA performance in the DMFC can be seen in Figures 3 & 4. A MEA with a Nafion117 membrane was used as reference.

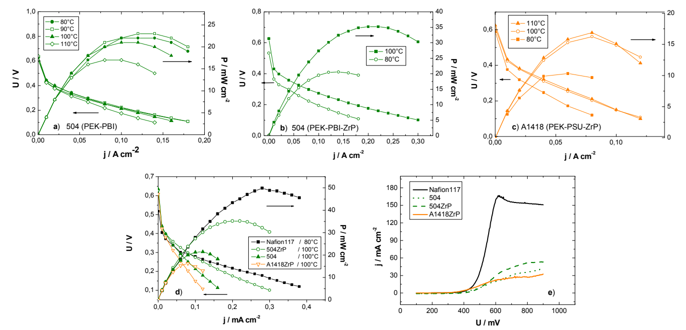


Figure 3: *a-d) U-I and P-j characteristics of different MEAs with commercial Pt electrodes at 2 bar methanol and oxygen pressure. The Pt loading was 1 mg cm^{-2} Pt for all the systems. e) Methanol permeation experiments in electrolysis mode at 5mV s^{-1} potential scanning rate with 1 M CH_3OH and nitrogen.*

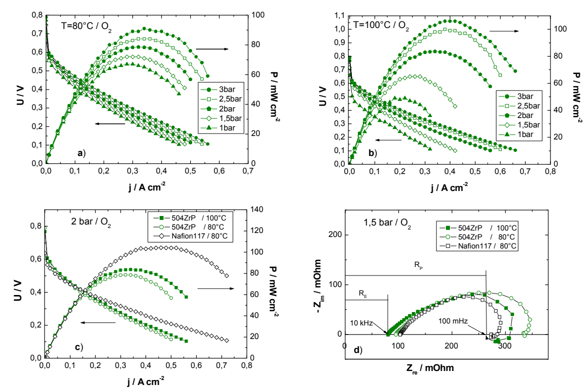


Figure 4: a-c) *U-I and P-I curves & d) EIS response of different MEAs with PtRu as anode catalyst. Catalyst loading was 1 mg cm^{-2} Pt for anode and cathode. Pt:Ru ratio was 1:1at.*

MEA	Anode	Cathode	Polymerelektrolyt	Power density / mW cm^{-2} at 2 bar: Oxygen 80°C	Oxygen 100°C	Air 80°C	Air 100°C
1	Pt-Vulcan	Pt-Vulcan	Nafion117	50	n. m.	33	n. v
2	Pt-Vulcan	-	sPEKs-PBI	22	21	5	5
3	Pt-Vulcan	-	sPEKs-PBI+ZrP	20	35	n. m.	16
4	Pt-Vulcan	-	sPEKs-PSU	12	17	8	9
5	PtRu-Vulcan	-	Nafion117	100	n. m.	64	n. m.
6	PtRu-Vulcan	-	sPEKs-PBI	n. m.	30	n. m.	n. m.
7	PtRu-Vulcan	-	sPEKs-PBI+ZrP	79	84	21*	22*
8	PtRu-Vulcan	-	sPEKs-PSU+ZrP	23	26	10***	n. m.
9	PtRu-SWCNT	-	sPEKs-PBI+ZrP	22**	n. m.	n. m.	n. m.

Table 3: *summary of different tests in the DMFC. (n.m= non measurable)*

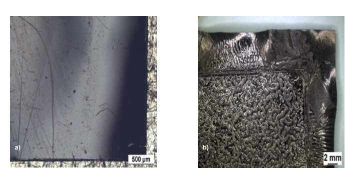


Figure 5: Pictures of a sPEK blend membran 504Zr a) before and b) after test procedure in the DMFC

➢ ZrP doped sPEK-PBI membrane showed the best performance in the DMFC
➢ no further increase of the performance was observed at temperatures higher than 100°C
➢ MEAs with non-fluoratinated membranes showed lower methanol permeation rate compared to that of the MEA with a Nafion117 membrane
➢ MEA with a Nafion membrane still exhibited the highest power density
➢ after the tests in the DMFC, channels were observed on the NFM that could lead to MEA degradation and performance loss

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