New composite DMFC anode with PEDOT as mixed conductor and catalyst support

Report

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Outline of the project
The direct methanol fuel cell (DMFC) is an attractive energy supplier for mobile, portable and stationary applications because of its simple system design, low operating temperature, and convenient fuel storage, compared to other fuel cell systems. However, a wide introduction of this technology on the market is still hindered by high cost and poor efficiency. The latter is a consequence of the low kinetics of the anode reaction due to catalyst (CAT) poisoning by reaction intermediates and of the methanol crossover from the anode to the cathode through the polymer exchange membrane (PEM).

This project focuses on the development of a new type of membrane anode assembly $\text{PEM}/\text{PEDOT}/\text{CAT}$ based on conducting polymer Poly(3,4-ethylenedioxythiophene) (PEDOT) as catalyst support and methanol barrier, as well. The first part is devoted to the development and characterisation of PEDOT as Pt catalyst support for anodic methanol oxidation. Since PEDOT is a mixed electronic and ionic conductor, charge transfer kinetics and transport of protons and electrons within the anode structure were supposed to be enhanced. For these reasons, a better utilisation of the noble metal catalyst is expected. In this work, two strategies have been investigated for preparation of the membrane electrode assembly (MEA). One consists on the deposition of the catalyst ink on the gas diffusion electrode (backing) followed by hot pressing with membrane and commercial cathode, while the second one is based on membrane coating followed with hot pressing with two gas diffusion electrodes (GDE).

The second topic aims to develop a modified Nafion117 membrane with reduced methanol permeability compared to that of pure Nafion117. Conducting polymer films, such as polyanilin, polypyrrrol or PEDOT have a lower methanol permeability than Nafion that is, however, depending on counter-ions, temperature and oxidation grade and often accompanied by a decreasing of the ionic conductivity. In this work, the influence of counter-ion specie and
polymerisation time on methanol permeability and ionic conductivity of PEDOT modified nafion117 membranes has been studied.

Project overview
The work plan of the Karl-Winnacker-Institute is structured into six tasks. The first two tasks deal with the preparation and characterisation of the composite PEM/PEDOT/CAT system in a two-compartment cell with respect to methanol permeation and ionic conductivity. PEDOT coatings on Nafion membranes were obtained by a chemical diffusion-controlled process with monomer polymerisation and catalyst deposition, as well. The activity of the system for methanol oxidation was determined by electrochemical half-cell experiments. Task 3 is focused on the preparation and characterization of methanol tolerant membranes on PEDOT basis in a two-compartment cell and in the DMFC test cell. The aim here is to reduce the rate of the methanol crossover by coating the Nafion membrane with a thin conducting polymer film. Design and construction of a test bench for fuel cells are stipulated in task 4. The activity of GDL/PEDOT/CAT was investigated in task 5, whereas task 6 is devoted to the modelling of the anode reaction. Most important results obtained in this project have been already published or submitted for publication [1-4].

Task 1: Preparation of the composite system PEM/PEDOT/CAT

T 1.1. PEM/PEDOT subsystem
Experimental work has been focused initially on the sub-system PEM/PEDOT without catalyst. Chemical deposition of the conducting polymer poly(3,4-ethylenedioxythiophene) PEDOT on Nafion®117 polymer membranes was performed and the composite system was characterized with respect to its ionic conductivity and methanol permeability [1-2].

PEDOT-modified Nafion membranes were prepared by a chemical polymerization process with different counter-ions, oxidizing agents and polymerization time. In order to enhance the solubility of the monomer in water, the monomer EDOT was dissolved in a 0.1M NaPSS solution. The polymerization time was thus reduced from 1-2 days to few hours. Different oxidizing agents, such as FeCl₃, H₂O₂, and Na₂S₂O₈ were used for the chemical polymerization. Ionic conductivity of the membranes was measured by DC polarization and AC impedance measurements. Methanol permeability of the membranes was determined using a diaphragm diffusion cell.

SEM cross-sectional images of unmodified and PEDOT modified Nafion membranes are shown in Figure 1A-D. The cross-sectional morphology of the PEDOT modified Nafion membranes differs significantly depending on the oxidant used in the polymerization process. In the case of FeCl₃ as oxidizing agent, a thin PEDOT film is formed on the surface of the Nafion membrane (Fig. 1C and 1D), whereas in the case of H₂O₂, the SEM image in figure 1B is
similar to that of the unmodified Nafion membrane (Fig. 1A) although the color of the modified membrane was black and PEDOT was identified by EDAX. Therefore, PEDOT must have been deposited inside the pores in the near-surface region of the Nafion membrane.

Figure 1: SEM micrograph of the cross-section of (A) a Nafion® 117 membrane, (B) the PEDOT modified Nafion membrane prepared by polymerization of EDOT dissolved in water for 24h with H₂O₂ as oxidant, (C) and (D) a PEDOT modified Nafion membrane prepared by polymerization of EDOT dissolved in water for 24h with FeCl₃ as oxidant.

T 1.2. PEM/PEDOT/CAT system

In order to increase the catalytic activity and to decrease the internal resistance of the fuel cell, catalysts are usually deposited directly on the PEM surface by chemical or mechanical methods. In this project, mainly diffusion-based chemical deposition methods were investigated. The carbon catalyst support was completely substituted by the conducting polymer PEDOT. Additional experiments were carried out with polypyrrole (PPy). Pt was used as catalyst and unmodified Nafion® 117, PPy-modified Nafion117 and PEDOT-modified
Nafion117 membranes were used as PEM. The following methods for chemical deposition of the catalyst were investigated:

1) Chemical diffusion in the system (I): H2PtCl6 | PEM | reducing agent
   NaBH4 and formaldehyde were used as reducing agents. Membranes used: Nafion®117, PPy-modified Nafion with FeCl3 as oxidizing agent, PEDOT-modified Nafion with FeCl3 or H2O2 as oxidizing agent.

2) Chemical diffusion in the system (II): [Pt(NH3)4]Cl2 | PEM | reducing agent
   The reducing agent was NaBH4. Membranes used: Nafion®117, and PEDOT-modified Nafion with FeCl3 or H2O2 as oxidizing agent.

3) Chemical diffusion in the system (III): EDOT-NaPSS | Nafion | H2PtCl6
   H2PtCl6 was used as oxidizing agent for EDOT polymerization. In this case EDOT polymerization and Pt deposition took place simultaneously on the PEM surface in contact with H2PtCl6.

4) Chemical diffusion in the system (IV): EDOT-NaPSS | Nafion | FeCl3 + PtRu
   Unsupported PtRu catalyst particles were mixed with the oxidizing agent and incorporated into the growing PEDOT layer.

5) Impregnation-reduction method in the system (V): PEM + (precursor) | NaBH4
   The membrane was first impregnated and soaked with [Pt(NH3)4]Cl2 solution for several hours and immersed in the reducing NaBH4 solution (one side only). PEM Membranes used were Nafion®117 and PEDOT-modified Nafion.

6) Impregnation-reduction method in the system (VI):
   a) Nafion + (monomer) | oxidizing agent
   b) Pt precursor | polymer + Nafion | reducing agent
   By this method the Nafion®117 membrane was first impregnated in solution of the monomer (Py or EDOT-NaPSS) for 5 - 40 min for pyrrole and several hours for EDOT. The monomer was then polymerized using the diffusion method. Finally, Pt was deposited on the membranes according to method 1.

7) Impregnation-reduction method in the system (VII): PEM + [Ru(NH3)4]Cl2 | reducing agent
   Membranes were first impregnated in [Ru(NH3)4]Cl2 solution for several hours and then immersed in reducing NaBH4 solution for Ru deposition. Finally, Pt was deposited on the membrane according to method 1. PEM membranes used were Nafion®117 and PEDOT-modified Nafion.

8) Brush painting method on GDL for comparison with corresponding half cell experiments (see task 5); system: C | Pt-PEDOT+ 10% Nafion + 20% PTFE.
Task 2: Characterization of the composite system PEM/PEDOT/CAT

T 2.1 PEM/PEDOT subsystem
Ionic conductivity was determined by four-electrode DC and AC (impedance) measurements in a two-compartment cell. Methanol permeability was tested in a diaphragm diffusion cell. Methanol concentration was measured by gas chromatography.

Ionic conductivity and methanol permeability of the PEDOT-modified membrane were measured as a function of the temperature. An Arrhenius-type temperature dependence of methanol permeability and ionic conductivity was found for all membranes prepared. Activation energies were determined and compared. Methanol crossover was found to be substantially decreased by deposition of PEDOT, but the ionic conductivity was also reduced to a certain extent. Ionic conductivity of PEDOT/Nafion membranes prepared with FeCl₃ was found to be higher compared to that of the membranes prepared with H₂O₂ at comparable polymerization time. PEDOT/Nafion membranes prepared with FeCl₃ showed lower methanol permeability than those prepared with H₂O₂.

EDOT-NaPSS | Nafion membranes prepared with H₂O₂ exhibited higher ionic conductivity compared to those with FeCl₃ (Figure 2a). However, methanol permeability with FeCl₃ was lower than that with H₂O₂ for identical polymerization times (Figure 2b). PEDOT-modified Nafion membranes exhibit lower methanol permeability while maintaining adequate ionic conductivity in comparison to unmodified Nafion®117 membranes.

![Figure 2a: Dependence of the ionic conductivity $\sigma$ on the polymerisation time $t_p$ at 25°C](image)

![Figure 2b: Dependence of the methanol permeability $P$ on the polymerisation time $t_p$ at 25°C](image)
Impedance spectra of PEDOT and PEDOT-PSS modified free standing Nafion membranes were measured in a two compartment cell using the four-electrode technique at different DC-currents. By this method, it is possible to separate the conductivity contribution of the Nafion membrane from that of the conducting polymer film. The heterogeneous pore model for mixed electron and ion conductors (transmission line) was found to fit the impedance data sufficiently well [1-2].

**T 2.2. PEM/ PEDOT/ CAT system**

Electrochemical activity of PEDOT and Pt-PEDOT modified Nafion membranes was evaluated in 1 M H$_2$SO$_4$ and 2 M CH$_3$OH + 1 M H$_2$SO$_4$ solution by cyclic voltammetry in half cell experiments. Electrode/membrane assemblies prepared with method 2, 5, 6 and 7 showed a significant methanol oxidation activity. Particle size was in the range of 100-250 nm. Pt loading was controlled by the reduction time. Nevertheless, the activity of these systems for methanol oxidation was lower than that of Pt-PEDOT coated on carbon Toray paper (GDL). Best results were obtained with PEDOT as catalyst support prepared with method 6. Figures 3a and 3b show cyclic voltammetry results of the Pt/PEDOT/Nafion membrane electrode in pure sulphuric acid and methanol containing electrolyte, respectively. They were prepared by Pt deposition on PEDOT modified Nafion membrane for 30min (..), 60min (---) and 90min (——) with [Pt(NH$_3$)$_4$]Cl$_2$ as Pt precursor. PEDOT modified Nafion membranes were prepared by polymerization of EDOT dissolved in NaPSS for 3h with FeCl$_3$ as oxidant, according to method 6.

![Figure 3a](#) CVs of Pt/PEDOT/Nafion membranes in 1 M H$_2$SO$_4$ at 40 mV/s and 25°C

![Figure 3b](#) CVs of Pt/PEDOT/Nafion membranes in 1 M H$_2$SO$_4$ + 2 M CH$_3$OH at 40 mV/s and 25°C
The catalyst loading was determined gravimetrically yielding 0.76, 1.32 and 2.06 mg cm\(^{-2}\) after 30, 60 and 90 min Pt deposition time. The maximum specific current density for methanol oxidation was 64.5 mA cm\(^{-2}\) mg\(^{-1}\) Pt at 40 mVs\(^{-1}\), 25°C and 30 min Pt deposition time.

**Task 3: Preparation of the MEA with PEM/PEDOT/CAT anode**

**T 3.1 PEM/PEDOT subsystem**

This work was focused on the development of new composite Nafion-based membranes with low methanol permeation and high proton conductivity. Details about the membrane preparation and characterization in a half cell are described in [29, 30]. In these experiments, FeCl\(_3\) was used as oxidant for the polymerization, while the reaction time was varied from 1 to 4 hours. Two identical commercial gas diffusion electrodes GDEs with 1 mg cm\(^{-2}\) Pt catalyst loading and a Pt/C weight ratio of 20% (ElectroChem, Inc.) were used as anode and cathode for MEA fabrication. Methanol permeation in DMFC was measured by feeding the cathode with \(\text{N}_2\) (electrolysis mode). Figure 4a shows potentiodynamic polarisation curves of MEAs with unmodified and PEDOT-modified Nafion membranes. Cell voltage is thereby determined by cathodic hydrogen evolution and anodic methanol oxidation, while the limiting current density at \(U > 600\) mV is determined by the permeation of methanol through the membrane.

![Figure 4a](image1.png)

**Figure 4a:** Methanol permeation measurements in 1M \(\text{CH}_3\text{OH} / \text{N}_2\) at 1.2bar and 80°C using LSV at 1mVs\(^{-1}\)

![Figure 4b](image2.png)

**Figure 4b:** DMFC performances of different MEAs in 2M \(\text{CH}_3\text{OH/O}_2\) at 1.2bar\(_{\text{abs}}\) and 80°C

As expected, methanol permeation decreased with increasing PEDOT loading. The methanol permeation rate through pure Nafion MEAs is in good agreement with literature data. After 1h polymerisation, methanol permeation was reduced by about 20% for the MEA based on PEDOT modified Nafion compared to that with pure Nafion.
Figure 4b shows current-voltage and current-power characteristics of the MEAs with the PEDOT modified membrane in DMFC mode. Similar to Nafion®117, the PEDOT modified Nafion membrane of 1h polymerisation time exhibits good proton exchange properties, even in absence of PSS as counter-ion. However, the performance in the fuel cell decreased dramatically with higher PEDOT loading. This can be explained by the decrease in ionic conductivity of the composite membrane. Some recent experiments after longer activation time showed increasing performances for the 2h PEDOT modified membrane exceeding that of the system with commercial components.

T 3.2. PEM/PEDOT/CAT system
PEDOT modified Nafion membranes prepared as described in task 2, method 6 showed the best performance with a maximum specific current density of about 95 mA cm² mgPt⁻¹ at room temperature; EDOT polymerisation time was 3 hours.

Task 4: Design and construction of a single cell test unit for MEAs

The test unit for fuel cells was designed and constructed. A picture of this unit is shown in figure 5. The fuel cell can be fed either with methanol or hydrogen. If methanol is used, the fuel cell can be run in batch or continuous operation mode. Temperature and pressure of the reactants can be controlled up to 90°C and 4 bar, respectively. One commercial 25 cm² single fuel cell with PIN flow pattern was purchased by ElectroChem, Inc. and two 5 cm² single fuel cells with serpentine flow pattern have been designed and constructed in-house. Up to now, most of measurements have been carried out with the 5 cm² cells in order to limit material expenses.

Figure 5: Fuel cell test unit
Task 5: Preparation of the GDL/PEDOT/CAT system

Research activities of this task can be summarised as follows:

- Preparation of conducting polymer powder PEDOT by chemical polymerization of EDOT
- Pt catalyst deposition on PEDOT by chemical reduction with formaldehyde
- Preparation of anodes with Pt-PEDOT ink using the painting or spraying method
- Characterization of the GDEs in half cell and DMFC with a commercial cathode by cyclic voltammetry, impedance spectroscopy and current-voltage characteristics.
- Characterization of GDL/PEDOT/CAT by SEM, EDAX, TEM, BET

5.1 Preparation of the conducting polymer powder
Conducting polymer powders were synthesized by chemical polymerisation of the monomer EDOT (Bayer) with Na₂S₂O₈, FeCl₃ or H₂O₂ as oxidizing agent in presence or absence of NaPSS. However, polymerisation with H₂O₂ could not be achieved. The following powders were prepared:

- PEDOT (Na₂S₂O₈)
- PEDOT-PSS (Na₂S₂O₈)
- PEDOT-PSS (FeCl₃)
- PEDOT-PSS from Baytron P (H.C. Starck GmbH)

Reaction time was about 2-3 days with Na₂S₂O₈ and several hours with FeCl₃. The suspension was filtrated and washed several times with de-ionized water in order to remove monomer and oxidizing agent residuals. The slurry was dried at 60°C for two days.

5.2 Pt deposition on conducting polymer powder
Pt deposition on PEDOT powder was carried out by chemical reduction in formaldehyde at 80°C for 1 hour. Catalyst/substrate ratios were fixed at 20, 40 and 60:100. In the second step, the catalyst/substrate suspension was filtered through a polycarbonate membrane, washed with de-ionized water and dried at 60°C for 6 hours.

5.3 Preparation of the GDE anode
Analogous to common fuel cell electrodes, new composite electrodes are composed of a backing, gas diffusion and reaction layer. We have opted for the following components:

- Backing layer: Toray Paper TGP-H -60 (30%wt PTFE)
- Gas diffusion layer: conducting polymer (PEDOT or PEDOT-PSS) + binder (PTFE or/and Nafion)
- Reaction layer: catalyst loading was fixed to 1 mg/cm² for comparison with commercial MEA (ElectroChem, Inc.).
Preliminary experiments were focused on the GDL/PEDOT system. Different inks have been tested regarding homogeneity, adherence on carbon paper, substrate and electrochemical activity [3]. The most delicate steps were the preparation of a homogeneous ink and the sintering process, since the critical temperature of conducting polymers is around 140-150°C. After coating the backing layer by brush painting (or spraying), electrodes were tested in an electrochemical half cell by cyclic voltammetry and electrochemical impedance spectroscopy. Good adherence was observed at sintering temperatures below 120°C.

T 5.4 GDE characterization
Conducting polymer/C subsystem

Half cell measurements showed good reproducibility and stability of PEDOT/C and PEDOT-PSS/C. About 10% charge loss of the conducting polymer was observed after 130 cycles in 1M H₂SO₄ at 40mV/s scan rate and room temperature. For fuel cell applications a low onset potential for oxidation of the conducting polymer is required. Figure 6a exhibits cyclic voltammograms of different PEDOT systems. The onset potential of PEDOT without PSS is at about −200 mV vs. RHE.

Impedance measurements reveal that the PEDOT-PSS system exhibits high electron transfer resistance at the methanol oxidation onset potential, whereas PEDOT without PSS shows purely capacitive behaviour similar to carbon (cf. Figure 6b). Therefore, PEDOT-PSS seemed to be inadequate as electrode material and was not further investigated in this work.
**Pt-PEDOT/C**

Preliminary half-cell results showed low activity of Pt-PEDOT/C for methanol oxidation compared to that of conventional Pt-C/C system. Two main reasons have been suggested: Poor access of the reactant to the active sites in the reaction layer and/or difficult evacuation of reaction products because of low porosity of the reaction layer and/or catalyst poisoning caused by S from PEDOT.

An activation process was developed based on anodic polarisation of Pt-PEDOT/C at potentials where partial over-oxidation of the conducting polymer can take place. This procedure leads to reorganisation of the Pt-PEDOT structure as indicate by REM. After partial PEDOT over-oxidation, the potential window of the CV is limited by hydrogen and oxygen evolution at about 0 V and 1.5 V vs. RHE, respectively, which is typical for polycrystalline platinum (figure 7a). For comparison, a Pt-VulcanXC72/C GDE was prepared. Figure 7b shows cyclic voltammograms of both systems in 1M H$_2$SO$_4$. The influence of carbon on the CV is obvious. The double layer region is more pronounced at Pt-C/C, whereas the hydrogen peaks are less distinct compared to Pt-PEDOT/C.

![Figure 6a: CVs of Pt-PEDOT/C in 1M H$_2$SO$_4$ at 40mV/s and 25°C](image)

![Figure 6b: CVs of Pt-PEDOT/C and Pt-C/C in 1M H$_2$SO$_4$ at 40 mV/s and 25°C](image)

Comparable activity was also found in methanol containing solution (Fig. 7a). Steady state current densities of up to 150 mA cm$^{-2}$ were obtained for methanol oxidation on Pt-PEDOT/C and Pt-C/C systems at room temperature. DMFC test experiments with Pt-PEDOT/C | Nafion$^{®}$117 | Pt-C/C are presented in Figure 7b. At 3 bar, the maximum power density of about 32 mW cm$^{-2}$ is lower by about 10-20% than that of the Pt-C/C anode.
Nonetheless, feasibility of Pt-PEDOT for electrochemical methanol oxidation under DMFC conditions was demonstrated in this work for the first time. Regarding porosity and specific surface area of the catalyst support, the reaction layer is still amenable to optimization (this will be part of the next proposal).

**T 5.5 SEM, TEM and FTIR investigations**

Pt particle size on PEDOT was in the range of 4 to 6 nm (TEM). SEM pictures showed a porosity increase after the activation of the reaction layer, whereas FTIR and EDAX investigations confirmed partial degradation of PEDOT.

**Task 6: Modelling of charge/mass transport and electrode reactions of the anode part of the cell assembly**

Most of our efforts have been focused on the experimental part of this project so that this task is still on the agenda.

**Cooperation work with our project partner, Prof. Y. Wang, China**

The results obtained so far have been discussed with Prof. Y. Wang during the 3rd Sino-German Workshop on Fuel Cells in Shanghai from 1-4 May 2005. It was stipulated to exchange the new materials prepared within the frame of this project between the two laboratories. In particular, anode structures of PEDOT-Pt/C developed in our laboratory have been sent to China for preparation and testing.
of new MEAs consisting of our GDL anode and the polymer-exchange membrane developed in China. Corresponding measurements will be performed in our laboratory using the membranes developed by Prof. Y. Wang (see next proposal).

Publication of the results in scientific journals

Formation and characterization of PEDOT-modified Nafion 117 membranes
*Journal of Solid State Electrochemistry*, available online.

PEDOT-modified Nafion membrane for DMFC applications

New composite DMFC anode with PEDOT as mixed conductor and catalyst support

Ion conductivity and methanol permeability of PEDOT-modified Nafion 117 membranes

Oral presentations on international conferences and symposia

J.-F. Drillet, R. Dittmeyer, R., K. Jüttner, L. Li
New composite DMFC anode with PEDOT as mixed conductor and catalyst support
3rd Sino-German Workshop on Fuel Cells, Shanghai / China, 1-4 May 2005.

J.-F. Drillet, L. Li, R. Dittmeyer, K. Jüttner
New composite DMFC anode with PEDOT as mixed conductor and catalyst support
Joint Workshop of the Karl-Winnacker-Institute and the Institute of Chemical Technology
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L. Li, J.-F. Drillet, R. Dittmeyer, K. Jüttner
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German-Italian Workshop of Electrochemistry, Berlin, 4-5 July 2005.

K. Jüttner, J.-F. Drillet, L. Li, R. Dittmeyer
New composite DMFC anode with PEDOT as mixed conductor and catalyst support
L. Li, J.-F. Drillet, R. Dittmeyer, K. Jüttner
Ion conductivity and methanol permeability of PEDOT modified Nafion-117 membranes
7th European Symposium on Electrochemical Engineering, Toulouse, France, 3-5 October 2005.

J.-F. Drillet, R. Dittmeyer, R., K. Jüttner, L. Li
New composite DMFC anode with PEDOT as mixed conductor and catalyst support
28th International Exhibition-Congress on Chemical Engineering, Environmental