

Activity and long-term stability of PEDOT as Pt catalyst support in the DMFC anode

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Introduction

The direct methanol fuel cell (DMFC) as electrochemical power source has attracted considerable attention due to 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.

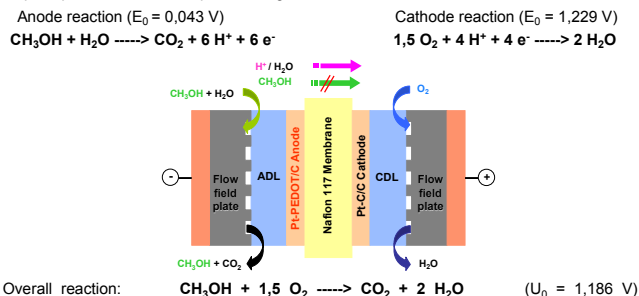


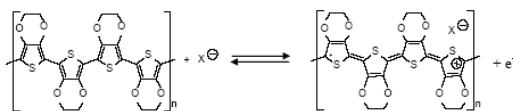
Figure 1: Scheme of the DMFC

Objectives

This project aimed at the development of a new type of membrane anode assembly in cooperation with Tianjin University (China) within the framework of the Joint Sino-German Project of DFG and NSFC. The new type of DMFC anode structure *PEM/PEDOT/CAT* was based on the conducting polymer Poly (3,4-ethylene-dioxythiophene) (PEDOT) as catalyst support, whereas the catalyst (CAT) was Pt.

Fundamentals

In the oxidized state, π -electron delocalization along sp^2 carbon leads to high electronic conductivity of conducting polymers. The polarity change has to be compensated by a counter-ion (X^-) transfer into the polymer matrix, whereas during reduction the process is reversed. In the case of PEDOT, the redox reaction for a single electron transfer (polaron state) is described as follows:



The ion exchange properties of the polymer film depend on the counter-ion embedded during the polymerisation process and on the available ions in the bulk solution. SO_4^{2-} -doped PEDOT conducting polymer membranes are anion exchangers in sulphuric acid. Cation exchange properties can be achieved by doping PEDOT with counter-ions with low mobility such as PSS⁻. Since PEDOT is an ionic and electronic conductor, only a two-phase boundary is a priori needed for the electron and proton transfer, compared to the three-phase boundary when carbon is used as catalyst support. For this reason, better utilization of the noble metal catalyst is expected for the methanol oxidation reaction (MOR).

Experimental

The development of the composite anode included the preparation of the conducting polymer powders, the catalyst deposition, the ink formulation and deposition on Toray carbon paper with the brush painting or spray method and finally its characterization in a half cell and a DMFC with a commercial Nafion 117 membrane and Pt-vulcan/C cathode.

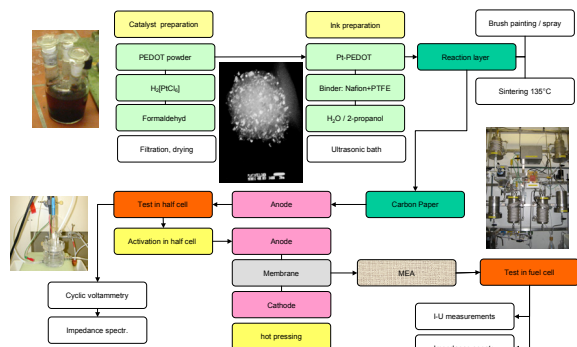


Figure 2: GDE and MEA preparation

Results

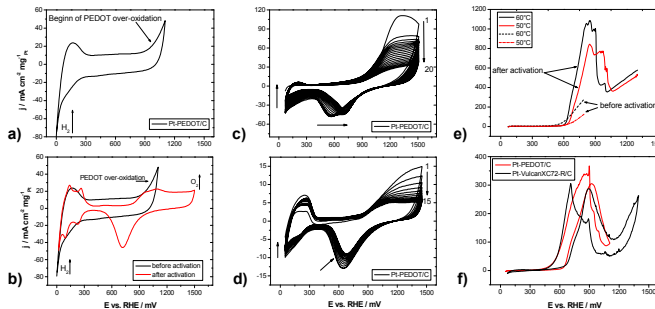
 Half-cell measurements: $1 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ Pt-PEDOT/C, Pt:PEDOT 60:100, 1M HSO_4 , 25°C


Figure 3: CV of a freshly prepared Pt-PEDOT electrode a) before and b) after activation. Electrochemical activation of a c) freshly prepared and d) 1-month-old Pt-PEDOT/C GDE. e) Influence of activation on Pt activity for methanol oxidation. f) Comparison of the MOR at electrochemically activated Pt-PEDOT/C and commercial Pt-vulcan/C GDEs.

- electrochemical PEDOT over-oxidation led to strengthening of Pt characteristics
- Long-time storage induced decrease in activity of PEDOT redox charge
- Both processes led to an increase of Pt-PEDOT/C activity for methanol oxidation

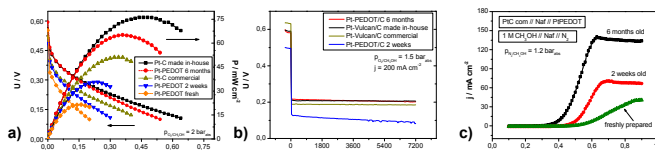
 Fuel cell measurements: Anode & Cathode: 1 mg cm^{-2} Pt, Nafion 117, 2M MeOH/O_2


Figure 4: influence of Pt-PEDOT storage time in air on the performance in a) & b) DMFC and c) electrolysis configuration.

- Increase of DMFC performance with higher storage time of the anode in air
- Comparable high stability of well-activated Pt-PEDOT/C and Pt-Vulcan/C for MOR
- Strong ohmic and diffusion controlled MOR at the fresh Pt-PEDOT/C electrode

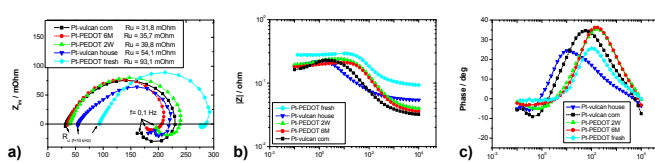
 Fuel Cell measurements: EIS mode in 2M $\text{CH}_3\text{OH} / \text{O}_2$ at 100 mA cm^{-2} , 1.5 bar and 80°C


Figure 5: a) Nyquist and b) & c) Bode plots of different Pt-PEDOT/C and Pt-Vulcan/C GDEs

- Impedance of MEA decreased with increasing storage time of Pt-PEDOT/C anode in air

REM / EDAX measurements

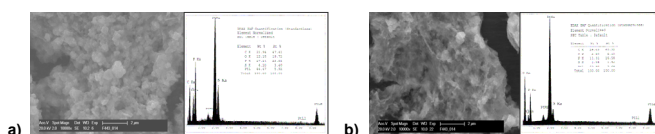


Figure 6: REM/EDX images of a) freshly prepared and b) 3-month-old Pt-PEDOT/C GDE

- Degradation of PEDOT particles was observed after electrode exposition in air
- High S and O depletion in PEDOT matrix after 3 months' storage time compared to that measured at the fresh material

Conclusion

Freshly prepared Pt-PEDOT/C GDEs showed poor activity for methanol oxidation. A clear improvement was observed after electrochemical over-oxidation or long-time storage of the Pt-PEDOT/C electrode in air. This can be explained by the fact that both procedures led to a substantial depletion of S and O in the polymer matrix and furthermore to an increase in porosity of the reaction layer that improved methanol accessibility to the catalyst active centres. For the first time, the feasibility of PEDOT supported Pt catalyst as a DMFC anode material was demonstrated. However, after storage in air for several weeks, an impressive change in morphology was observed in the reaction layer, whereas PEDOT behaved more or less as a carbon precursor. PEDOT degradation was obviously accelerated by the high Pt ratio of 60 wt%.