Gas analytical investigation of PEMFC based on photoacoustic spectroscopy

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Motivation

The main objective of the IGF project „CO2-Detektor“ (17851 N (09555/11) is the development of a high precision, low cost CO_2 detector based on a photoacoustic spectroscopy for better understanding and quantification of the carbon support corrosion in PEMFC cathodes during normal and start-stop operating conditions.

Although PEMFCs have achieved a significant progress in recent years, their limited lifetimes belong to one of the primary problems. One process which shortens the lifetime is the oxidative breakdown of the catalyst´s carrier. In the presence of water carbon is unstable towwards corrosion if the potential is higher than 0.207 V vs. NHE. Since the degradation of carbon causes the generation of CO_2, the reaction can be pursued spectroscopically. In this project the emitted CO_2 was detected by photoacoustic spectroscopy (PAS). For this purpose, a part of the cathodic flow exhaust was inserted into the photoacoustic cell while the PEMFC cell voltages were changed starting from 0.3V to 1.6 V. The cathode gas was artificial air at a constant gas flow of 90 $l.h^{-1}$. 50 cm^2 ZBT standard PEMFC was tested at 80°C, 90% relative humidity, lambda air of 2.5 and ambient pressure. The membrane was Nafion 117 (thickness of 180 µm). This type of membrane ensures stable PEMFC operation and prevents mixing of the anode and cathode gases during the electrochemical aging.

Electrochemical testing and aging protocol

1. **Activation:** 1h at U = 0.4 V
2. **Performance of the activated PEMFC:**
   - 2.1. Polarization curve: 0.3 V – OCV
   - 2.2. Cyclic voltammetry
     (Electrochemically active surface area)
3. **CO_2 detection during potentiostatic measurements at:**
   - 3.1. Normal PEMFC operation:
     U [V] = 0.3 / 0.4 / 0.5 / 0.6 / 0.7 / 0.8 / 0.9 / 1
   - 3.2. Simulated start-stop aging:
     U [V] = 1.2 / 1.4 / 1.6
4. **PEMFC state of health after the aging:**
   - 4.1. Polarization curve: 0.3 V – OCV
   - 4.2. Cyclic voltammetry
     (Electrochemically active surface area)

Photoacoustic spectroscopy

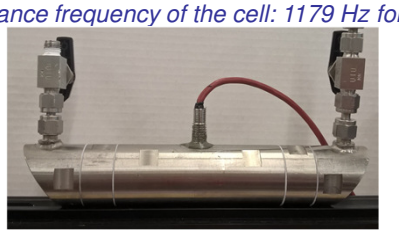
The photoacoustic spectroscopy originates from the conversion of absorbed energy into sound waves. PAS roughly combines the advantages of absorption spectroscopy with those of emission spectroscopy. Because of its high sensitivity PAS enables trace analysis. Trace analysis of gas mixtures is carried out by exciting a single isolated rotational-vibrational overtone-combination of the chosen molecule.

In this experiment, a rotational state of an overtone-combination mode of CO_2 (2723 nm) was selected. The design of the acoustic resonance cell considered the high operation temperature and the high amount of gaseous and liquid water.

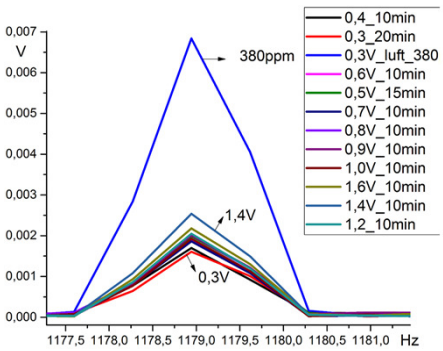
Gas analysis

Acoustic resonance cell with Brewster windows and central MEMS-Microphon

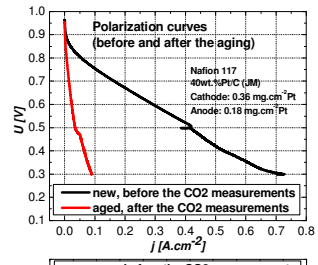
(resonance frequency of the cell: 1179 Hz for 99°C)

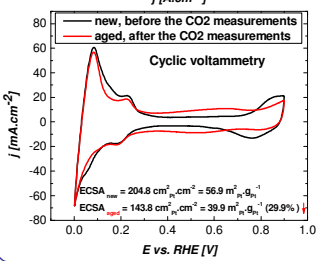


Evolution of CO_2 as a function of selected parameters of the fuel cell



Electrochemical results





After the aging during which CO_2 was measured the cathode lost ca. **30 %** of its electrochemically active surface area (estimated via Had region of the cyclovoltammogram) while the **PEMFC was almost dead.**

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