Calibration method for carbon dioxide sensors to investigate direct methanol fuel cell efficiency

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HIGHLIGHTS

- A calibration technique for carbon dioxide sensors is presented.
- A detailed error analysis demonstrates the sources of the remaining uncertainties.
- The accuracy is improved by a factor of 2–30 – depending on the metering range.

ARTICLE INFO

ABSTRACT

Methanol crossover is a process in direct methanol fuel cells which causes significant reduction of cell efficiency. Methanol permeates through the membrane electrode assembly and reacts at the cathode with oxygen to form carbon dioxide. This process is undesirable because it does not generate electric energy, but rather only increases heat production.

Different procedures have been used for the investigation of this crossover. One method uses the detection of carbon dioxide in the exhaust gas of the cathode by means of a carbon dioxide sensor. This technique is inexpensive and enables real-time measurements but its disadvantage is the low accuracy.

This paper demonstrates a simple method to generate gas mixtures for the calibration of the sensor in order to increase the accuracy. The advantages of this technique consist in the fact that only the existing devices of a direct methanol fuel cell test rig are needed and that the operator can adjust the carbon dioxide concentration for the calibration process. This is important for dealing with nonlinearities of the sensor. A detailed error analysis accompanies the experiments. At the end it is shown that the accuracy of the determined Faraday efficiency can be improved by using the presented calibration technique.

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1. Introduction

Direct methanol fuel cells (DMFC) are interesting for supplying electrical energy in applications with power requirements of up to a few kilowatts. One advantage of a DMFC system in comparison to other fuel cell systems is the high energy density of the methanol which enables a long operating time. A disadvantage of the DMFC is the methanol permeation from the anode of a membrane electrode assembly (MEA) to the cathode. On the cathode side, the methanol reacts with oxygen to form carbon dioxide. This crossover reduces the fuel utilization and therefore the efficiency of the system.

Researchers employ different techniques to investigate the correlations between operating conditions, materials used for the manufacturing of the MEA, and methanol permeation. Some of them analyze the cell voltage [1,2], whereas others investigate the exhaust gas composition of the DMFC [3–7] to determine the strength of the crossover. While precise techniques for investigations of the gas composition, such as mass spectroscopy and gas chromatography, are expensive and time-consuming, a cheaper infrared carbon dioxide sensor also enables real-time measurements. Unfortunately, the accuracy of this type of sensor depends strongly on the metering range. As a result, the relative uncertainty of the measurement can vary between 2% and more than 20% within the measuring range.

For DMFC investigations, operating conditions must be varied in order to analyze the correlations. During these variations, the carbon dioxide concentration in the exhaust gas can differ very

strongly, depending on the operation mode. Several approaches can be employed to avoid strong differences in the uncertainties of these measurements. First of all, it is possible to use several sensors with different metering ranges simultaneously. This circuitous method reduces the advantage of a cost-efficient measurement device. One further option is to use commercial calibration gases for a precise calibration of a sensor within a wide metering range. The problem with this method is that a nonlinearity in the metering range of the sensor requires many calibration gases with different concentrations to achieve high calibration accuracy. However, before calibration, the nonlinear metering ranges of a sensor are unknown so that the right choice of the necessary calibration gases is difficult.

The work presented here focuses on the development of an easily performable technique to calibrate a carbon dioxide sensor in a DMFC test rig within a wide metering range. The relation to the experimental station means that all relevant components for the calibration process can be taken from a DMFC test rig. In this study, the desired relative accuracy for a metering range of 0.2% v/v to 20.0% v/v is less than 3%. The idea of the method is to generate carbon dioxide by an electrochemical reaction. If the reaction is free of side reactions, the strength of the generation can be determined accurately by measuring the electric current between the electrodes. The continuously produced carbon dioxide is mixed with a nitrogen flow, whereat the flow rate of the nitrogen can be measured precisely by a laminar flow element. This method allows the production of calibration gas with an adjustable carbon dioxide concentration. In this way, the nonlinear metering ranges of the sensor can be analyzed very accurately and a wide range sensor calibration is possible.

By means of the improved sensor calibration, the accuracy of the Faraday efficiency from direct methanol fuel cell investigations can be determined more precisely. A reduction of the uncertainty of the calculated Faraday efficiency by a factor of up to 4 is demonstrated.

2. Experimental

The following sections present the experimental setup used for the investigation of DMFC MEAs. After a short description of the devices four different operating modes are explained. One mode is used to calibrate the carbon dioxide sensors, the other modes are

important for DMFC operation. The accuracies of the devices are mentioned and form the basis for the following error analysis. Finally, the fault effect analysis is complemented by some necessary basic inspections.

2.1. Experimental setup

In the middle of Fig. 1, which is divided in side A and side B, an MEA is located between two flow fields and two end plates. On the left a peristaltic pump (Reglo digital, Ismatec) is used to pump aqueous solution of methanol or formic acid from a tank to a pre-heater which tempers the solution to operating temperature. Afterward, a gas separator removes the dissolved gas and the solution flows into the test cell. During DMFC operation methanol is oxidized at the anode (side A) forming carbon dioxide which is mixed with the aqueous methanol solution.

At the anode output a gas separator is used to remove carbon dioxide from the outlet solution. The carbon dioxide is separated from the liquid phase by injecting nitrogen gas bubbles into the liquid phase via a porous glass plate. The nitrogen volume flow is controlled by a mass flow controller (5850S, BROOKS, adjustment range: 0—1 slpm (standard liter per minute), accuracy: 0.4%· metering range + 0.2%·reading, all flow rates in this study are related to standard conditions: $p_s = 101{,}325$ Pa, $T_s = 273.15$ K). At the end, the liquid phase flows through a valve back to the tank or to the waste water system, depending on the operation mode.

After the separator the water vapor of the gas output is condensed out at room temperature. The gas temperature is recorded by a digital voltmeter (Hexagon 720, BEHA, temperature accuracy: 0.4 °C) and the absolute pressure is determined by a pressure transmitter (PTU30T, Vaisala, pressure accuracy: 45 Pa). The carbon dioxide volume concentration σ_A in the gas mixture is quantified by a carbon dioxide sensor (GMT221 — transmitter, GMP221 — sensor, Vaisala, metering range: 20% v/v).

At side B of Fig. 1 a nitrogen or air gas flow, controlled by a mass flow controller (5850S, BROOKS, adjustment ranges: 0—1 slpm or 0—0.12 slpm, accuracy: 0.4%·metering range + 0.2%·reading) can be humidified and preheated before entering the test cell. To measure the relative humidity, the output gas at side B can be preheated up to 130 °C. This temperature is chosen because the relative humidity of the gas is smaller and therefore the sensitivity
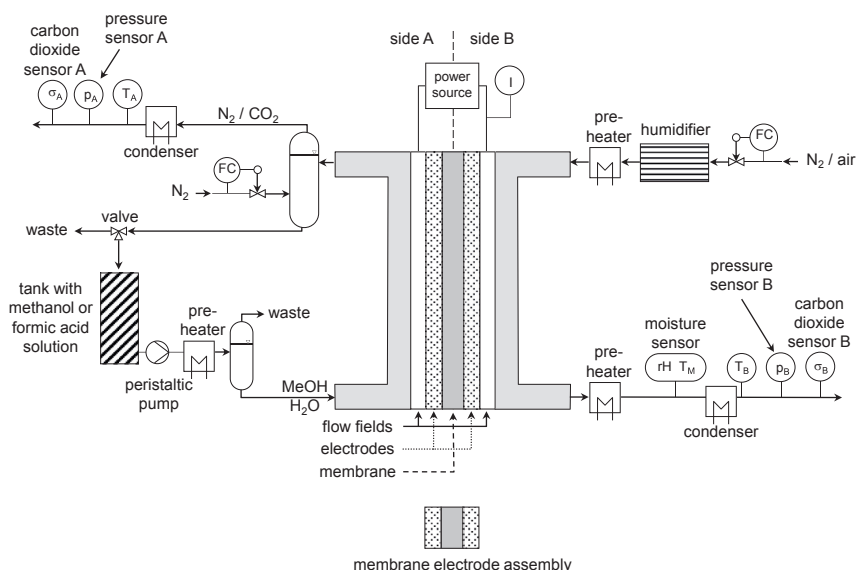

Fig. 1. Illustration of the experimental setup used for the investigations.