



# Development of a novel experimental DEMS set-up for electrocatalyst characterization under working conditions of high temperature polymer electrolyte fuel cells



C. Niether<sup>a,\*</sup>, M.S. Rau<sup>a</sup>, C. Cremers<sup>a</sup>, D.J. Jones<sup>b</sup>, K. Pinkwart<sup>a</sup>, J. Tübke<sup>a</sup>

<sup>a</sup>Fraunhofer-Institut für Chemische Technologie ICT, Joseph-von-Fraunhofer-Straße 7, 76327 Pfinztal, Germany

<sup>b</sup>JCGM – UMR5253 – Agrégats, Interfaces et Matériaux pour l'Energie, Université Montpellier 2, 2 Place Eugène Bataillon – CC 1502, 34095 Montpellier cedex 5, France

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## ABSTRACT

A new set-up for conducting differential electrochemical mass spectroscopy (DEMS) analysis at temperatures between 120 and 180 °C is presented. It enables the characterization and testing of model electrodes in a three electrode assembly under experimental conditions close to those in a high temperature proton exchange membrane fuel cell (HT-PEMFC). This is of special interest for the study of the degradation of fuel cell materials as well as the electro-oxidation reactions of small organic molecules used in direct alcohol fuel cells (DAFCs). While other DEMS set-ups only allow for studying reactions occurring in a liquid electrolyte, the HT-DEMS set-up makes it possible to study reactions in the gas phase. The design of the set-up is presented. Cyclic voltammetry (CV) measurements at 150 °C were carried out on Pt/C and Pt black catalysts under nitrogen atmosphere. Oxidation of adsorbed CO and bulk oxidation of ethanol were performed on Pt/C.

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## 1. Introduction

The evolution of electrochemical power systems depends on the optimization of the electrodes and the electrolyte. Electrochemical devices transforming chemical energy into electric energy, such as fuel cells (FCs), can contribute to solving the present sustainable energy dilemma; because they are an efficient and clean alternative to combustion engines for supplying electrical power for mobile applications [1]. An interesting type of fuel cell is the high-temperature proton exchange membrane fuel cell (HT-PEMFC) running at temperatures in the range of 120–200 °C [2–6]. In comparison to fuel cells working at lower temperature their CO tolerance is improved dramatically [4] in particular above 160 °C, and the high temperature enhances the activity for the oxidation of small organic molecules such as methanol and ethanol [6–11]. Thus, HT-PEMFC technology is well suited for the development of direct alcohol fuel cells (DAFCs).

In order to enable the improvement of the electrode materials, and therefore the performances of HT-PEMFCs, tools are required to allow the characterization and evaluation of the electrocatalytic activity of the electrodes under working conditions.

The performance of the electrodes in a fuel cell depends on a combination of factors such as surface reactivity, electronic and

ionic conductivity or facile mass transport of molecules [12,13], the latter being based on the architectural design of both electrodes in the cell [14]. In the case of DAFCs the selectivity of their anode electrocatalyst regarding different possible oxidation products is a relevant factor concerning their performance and efficiency [15,16].

The coupling of electrochemical measurements with mass spectrometry (MS) has been recognized as a powerful tool for the qualitative and quantitative identification of products and intermediates involved in the mechanisms of diverse electrochemical reactions. A key challenge is the coupling interface between the electrochemical cell and the mass spectrometer. The concept of the membrane introduction to conduct MS measurements (MIMS) was introduced by Hoch and Kok in the early 1960s [17]. Because of their rapid response time and low selectivity [18] porous PTFE membranes are widely used for DEMS applications. Using the flexibility of these membranes, the use of MS was adapted to different electrochemical applications [19–22].

Bruckenstein and Gadde [20], who collected gaseous electrochemical reaction products in a vacuum system before detecting them by MS, were the first to implement this technique for the evaluation of electrochemical reactions. They placed a Teflon® (polytetrafluoroethylene, PTFE) membrane between the porous electrode and the mass spectrometer chamber so that volatile reaction products permeating through the membrane and could be ionized by electron impact (EI) without the interference of the solvent.

\* Corresponding author.

E-mail address: [christiane.niether@ict.fraunhofer.de](mailto:christiane.niether@ict.fraunhofer.de) (C. Niether).

Some years later Wolter and Heitbaum [22] established differential electrochemical mass spectrometry (DEMS) as an analytical tool, developing a set-up with a significantly reduced delay time. As a matter of fact, the term “differential” was established in order to distinguish between the time- and potential-resolved correlation of the mass ion and electrode current technique [22] from unresolved methods [21].

To study the product distribution in DAFC anode reactions, a pressurized high temperature DEMS set-up was developed by Behm et al. to conduct liquid phase measurements at temperatures up to 100 °C [8,23–27]. On-line mass spectrometric investigations of the product distribution in the exhaust of HT-PEM single cells could be conducted under HT-PEM temperature conditions [15,16]. However, no DEMS measurement has been conducted in the gas phase using a half cell set-up yet.

In view of implementing mass spectrometry to detect the species involved in DAFC reactions, in this work a set-up is presented to carry out DEMS measurements on model electrodes under HT-PEMFC conditions.

## 2. Material and methods

### 2.1. Cell design

The goal of this work was to develop a three electrode DEMS cell to study model electrodes under working conditions close to those of a HT-PEMFC. Thus, the cell had to be able to withstand temperatures up to 200 °C and to keep the temperature stable for a long time during measurements.

A MS is connected to the three electrode cell by a heated capillary that is placed in the gas outlet coming from the cell. In this way, volatile products formed during a reaction at the working electrode can be pumped into the MS, which enables the qualification and quantification of the produced compounds by measuring their corresponding mass currents [28].

The cell was first designed to study the oxidation of alcohols at the anode side of a DAFC operating at high temperature and atmospheric pressure. The reactants under these temperature conditions are not dissolved in a liquid electrolyte but enter the cell as preheated vapor. For this reason condensation must be avoided to offer a homogenous distribution of the gases.

As the model electrode is supposed to be as close to an actual HT-PEMFC as possible, the working electrode (WE) used in this work is a gas diffusion electrode (GDE), consisting of a catalyst layer coated on a gas diffusion layer (GDL). In the set-up the GDL has the same function as in the fuel cell, *i.e.* providing stability to the electrocatalyst and allowing a continuous transport and even distribution of the gases [29].

The other two electrodes used in the set-up are a counter electrode (CE), and reference electrode (RE) connected *via* a Luggin-Haber capillary, which allows the accurate measurement of the WE potential. Ionic conduction between the electrodes is a required condition. To achieve this, the counter and reference electrode need to be immersed in a liquid electrolyte. In contrast, in order to function, the WE must not be soaked in electrolyte, because this would prevent the gaseous reactants from reaching the catalyst layer. Thus, a separator that allows ion exchange with the electrolyte at high temperature is needed. To this purpose a polybenzimidazole (PBI) membrane doped with phosphoric acid was employed. This type of proton exchange membrane is commonly used for the same task in HT-PEMFCs [30–33] and also allows for the impregnation of the WE with the required amount of phosphoric acid to form three phase boundaries. Consequently, concentrated phosphoric acid was the obvious choice as electrolyte.

The material chosen for the cell was polyether ether ketone (PEEK). This polymer is mechanically stable at the desired temperatures as well as chemically resistant to hot concentrated phosphoric acid [34]. In addition this material can be easily processed into the parts required for the set-up.

The cell design is depicted in Fig. 1. As can be observed, the cell is composed of three main PEEK parts: a top, a body and a bottom part.

The bottom of the cell plays the most relevant role. It contains a conical chamber with the gas inlet which provides reactants to the WE (1) *via* a nozzle (2) in the center. The WE is supported on a PEEK sieve (3) above the chamber with the catalyst layer side on top, facing the PBI membrane (4). Between the PEEK support and the WE a thin gold mesh (5) enables electron conduction to a contact outside the cell. From the conical chamber underneath, the gas outlet (6) leads outside and provides connection to the MS.

A 1/16" PEEK capillary with an inner diameter of 1 mm and a length of approximately 5 cm leads outside the cell. A heated 1/8" capillary is fitted over the 1/16" capillary. The former is connected to a 2 m heated capillary with an inner diameter of 0.25 mm which leads inside the MS. (8) This construction has been necessary because of the tendency of the 0.25 mm capillary to get blocked by phosphoric acid that can get inside the space underneath the working electrode. It also prevents pressure build-up in the cell.

The PBI membrane and the cell body are stacked on top of the GDE. The body of the cell contains concentrated H<sub>3</sub>PO<sub>4</sub>. On the underside it is closed by a borosilicate glass-filter (7), which allows the electrolytic contact of the solution with the membrane, while compressing the membrane and WE to reduce ohmic and contact resistance. The CE (8) and a Luggin capillary (9) connecting the RE (10) are suspended inside the cell body through holes in the top of the cell.

The three cell parts of the set-up are stacked on top of the copper heating plate and a mount that can be held by a clamp. A flat PTFE gasket is used to seal the connection between cell bottom and cell body. All parts are vertically connected by four threaded bars (diameter 4 mm) and screwed together.

The cell can be fed with diverse gaseous reactants as well as with liquid reactants, provided they can be vaporized at temperatures up to roughly 180 °C. Gaseous reactants are heated up to 120 °C before entering the cell, in order to prevent abrupt temperature changes in the cell, while the liquid fuel is evaporated using an electrically heated microstructured heater obtained from the Institute for Micro Process Engineering at Karlsruhe Institute of Technology (KIT) [35].

The cell is electrically heated by two independent control loops due to the different heat capacity of the body and bottom of the cell. The bottom part of the cell is heated from underneath by a home-made heating copper plate (11). The corresponding thermocouple (12) is encased in a closed off PEEK capillary and situated inside the chamber underneath the working electrode. The body of the cell can be heated either with a home-made glass encased heating finger inside the electrolyte or as pictured with a HORST-GmbH heating jacket (13) specifically designed for this application. In either case the corresponding thermocouple (14) is encased in a glass capillary and situated inside the electrolyte. In addition, the electrochemical cell is fully thermally isolated in order to avoid temperature variations.

### 2.2. Experimental parameters

In the following experiments, a large area platinum mesh electrode was used as counter electrode. The reference electrode was a home-made reversible hydrogen electrode (RHE) in the same

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