



A novel differential electrochemical mass spectrometry method to determine the product distribution from parasitic Methanol oxidation reaction on oxygen reduction reaction catalysts



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HIGHLIGHTS

- Novel DEMS setup which allows to investigate catalysts under gas-phase conditions.
- Investigation of Pt/C and Pt₃Co/C catalysts in the novel setup.
- Successful evaluation of methanol tolerance for the two catalysts.
- Determination of parasitic methanol oxidation reaction's product distribution.
- Observation of CO₂ evolution due to carbon corrosion.

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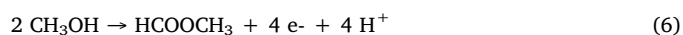
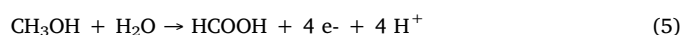
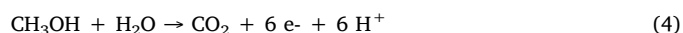
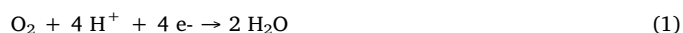
ABSTRACT

The oxygen reduction reaction is in research focus since several decades due to its importance for the overall fuel cell performance. In direct methanol fuel cells, the crossover of methanol and its subsequent parasitic oxidation are main issues when it comes to preventing fuel cell performance losses. In this work, we present a novel differential electrochemical mass spectrometry method to evaluate oxygen reduction reaction catalysts on their tolerance to methanol being present at the cathode. Besides this, the setup allows to measure under more realistic fuel cell conditions than typical rotating disc electrode measurements, because the oxygen reduction reaction is evaluated in gaseous phase and a gas diffusion electrode is used as working electrode. Due to the new method, it was possible to investigate the oxygen reduction reaction on two commonly used catalysts (Pt/C and Pt₃Co/C) in absence and presence of methanol. It was found, that Pt₃Co/C is less prone to parasitic current losses due to methanol oxidation reaction. By connecting a mass spectrometer to the electrochemical cell, the new method allows to determine the products formed on the catalysts due to parasitic methanol electrooxidation.

1. Introduction

Fuel cells convert chemical energy of fuels to electric power. In general, a fuel like hydrogen or methanol is oxidized at the anode while oxygen is reduced at the cathode. In most commercial fuel cell systems, anode and cathode are separated by a proton-exchange membrane (PEM). In direct methanol fuel cells (DMFCs), methanol is used as fuel. A main issue of these fuel cells is the permeation of methanol from the anode to the cathode through the PEM [1,2]. Due to the methanol permeation, two reactions compete at the cathodic catalytic surface: oxygen reduction reaction (ORR, Eqs. (1)–(3)) and methanol oxidation reaction (MOR, Eqs. (4)–(7)). This leads to a mixed potential at the cathode and a reduced availability of catalytic sites for the oxygen

reduction reaction; both effects result in an overall lowered fuel cell performance.



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In recent years, materials science in fuel cell technology focussed on two different approaches to mitigate the problem of the so called methanol crossover. The first approach deals with the membrane itself. A well-known and commonly used PEM material for DMFCs is Nafion[®], which shows high ionic conductivity and stability [3]. Even though Nafion[®] has superior proton-exchange properties, it lacks the ability to block methanol from permeation to the cathode of the DMFC (methanol diffusion coefficient = $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) [4,5]. Therefore, several research groups work on polymers which are likewise proton-conductive but are able to hinder methanol to diffuse to the cathode [6,7]. For example, Li et al. could recently show higher ionic conductivities for their hyperbranched sulfonated macromolecules based PEM in comparison to Nafion[®] but a lower methanol crossover [8]. The second approach to overcome problematic methanol crossover is to design oxygen reduction reaction catalysts, which are highly active for ORR but almost inactive for the parasitic methanol oxidation reaction in the presence of oxygen [9–14]. Therefore, these catalysts are less prone to the deactivation of ORR catalysis by simultaneously engaged MOR. In the early 2000s, it was reported by several research groups that Ru- or Co-based catalysts inherit high electrocatalytic activity for ORR in presence of high concentrations of methanol [15–18]. However, stability of these catalysts under fuel cell conditions is rather low due to their non-precious characteristics. Additionally, in DMFC tests, single cells with Pt-based cathode catalysts showed significantly higher power outputs [18]. In the following years, it was repeatedly reported that alloying or mixing Pt with Co results in a more stable ORR catalyst with higher methanol tolerance [12,19–23]. Even though several studies could also show that PtCo catalysts are also excellent catalysts for methanol electrooxidation in oxygen-free electrolytes [24–26], the said catalysts tend to predominantly reduce oxygen instead of oxidizing methanol as soon as oxygen is present in the electrolyte. Today, carbon supported Pt and PtCo catalysts are commercially available and are often used as reference material for further development of methanol tolerant ORR catalysts. Recent research on methanol tolerant ORR catalysts focuses on developing trimetallic catalysts. Jeon et al. showed that it is possible to increase the active surface area of Pt-Co by adding Cr and annealing. The resulting PtCoCr catalyst showed a higher ORR mass activity [27]. By varying the amount of added Cr, the trimetallic catalyst was even further enhanced [28]. Recently, Asteazaran et al. reported on PtCoRu catalysts and found that these trimetallic catalysts are more tolerant to the presence of methanol during ORR than Pt [29,30]. Still, Pt is the common point of reference.

Most research groups test their cathode catalysts by carrying out ORR experiments in rotating disc electrode (RDE) measurements in presence of methanol. Even though these kind of measurements give a prediction on the catalysts ability to deal with the presence of methanol during ORR, these tests are not able to evaluate the reaction products from MOR, which will be formed at the cathode and therefore will be found in the exhaust of DMFC cathodes. Also, these experiments are carried out in an oxygen-enriched liquid electrolyte (e.g. HClO₄ or H₂SO₄ solutions) and are therefore not a realistic scenario of a PEM-based gas diffusion cathode. Hence, results obtained by RDE experiments are not inevitably transferable to fuel cell conditions. In this study, we present a half-cell setup which enables the testing of ORR catalysts under gas-phase conditions. By switching the catalyst/liquid electrolyte interface (RDE conditions) to a catalyst/solid electrolyte (Nafion) interface, the novel setup enables to measure under more realistic fuel cell conditions. Furthermore, by coupling the half-cell with a mass spectrometer, it is possible to detect products from parasitic methanol electrooxidation competing with oxygen reduction reaction. In this sense, commercially available Pt/C and Pt₃Co/C were tested as cathode catalysts in this setup to evaluate feasibility of the setup. By varying test parameters like operation temperature or methanol concentration in the gas-phase, the parasitic methanol oxidation competing with ORR on Pt/C or Pt₃Co/C was further investigated in detail.

2. Experimental section

2.1. Materials

Commercially available catalysts were used in this study: Pt/C (40 wt% Pt on Vulcan, HiSPEC[™] 4000, Alfa Aesar) and Pt₃Co/C (Pt:Co = 3:1, 60 wt% metal on Vulcan, Johnson Matthey). Nafion[®] N117 (DuPont) was used as proton-exchange membrane. Catalyst inks were prepared from a 60.0 wt% PTFE dispersion (ElectroChem Inc.) as binder. Gas diffusion layers (GDLs, SIGRACET[®] 10AA, SGL Carbon) were used as electrode substrates for catalyst layers.

To conduct the electrochemical measurements 4 M H₂SO₄ solution (Carl Roth) was used as electrolyte. Experiments were carried out in either Nitrogen (N₂, 99.999%, Linde) or synthetic air (20% O₂, rest N₂, H₂O ≤ 2 ppm, CO ≤ 1 ppm, CO₂ ≤ 1 ppm, NO_x ≤ 0.1 ppm, Linde). To evaluate the influence of methanol on ORR on the catalyst, synthetic air was enriched with methanol by bubbling synthetic air through either a 2 wt%, 4 wt% or a 10 wt% methanol solution (CH₃OH, p.a., Merck Millipore) at room temperature. According to the literature, this leads to a proportion of approx. 0.2 vol%, 0.4 vol% or 1.0 vol% of methanol in the synthetic air flow [31], which roughly corresponds to concentrations of 0.05 mol L⁻¹, 0.10 mol L⁻¹ or 0.25 mol L⁻¹, respectively. Measurements in absence of methanol were done with humidified N₂ or synthetic air by bubbling through deionized water at room temperature.

2.2. DEMS setup

The DEMS setup combines an electrochemical half-cell with a mass spectrometer (MS). The design of the electrochemical cell is described in detail in a former study [32]. A scheme of the electrochemical cell is shown in Fig. 1. The electrochemical cell allows to measure under gaseous flow. The gases were supplied to the cell at a flow rate of 50 ml min⁻¹. A heated capillary was used to connect the electrochemical cell with the MS. In this way, volatile products formed during a reaction at the working electrode are transported to the MS, which enables the analysis of the produced compounds by measuring their corresponding ion currents [33]. During electrochemical tests the ion currents of MS signals $m/z = 22, 44, 46, 60$ were monitored to evaluate the reaction products of methanol oxidation (cf. Eqs. (2)–(5)): carbon dioxide (CO₂), formic acid (HCOOH) and methyl formate (HCOOCH₃). Note, that it is not possible to directly detect formaldehyde (H₂CO) as the MS signals of formaldehyde overlap with the ones of methanol itself.

As shown in Fig. 1, the electrochemical half-cell consists of a working electrode (WE), reference electrode (RE) and counter electrode (CE). A platinum wire and a reversible hydrogen electrode (RHE, HydroFlex[®], Gaskatel GmbH) were used as CE and RE, respectively. The working electrode is supposed to be as close to a cathode in DMFCs as

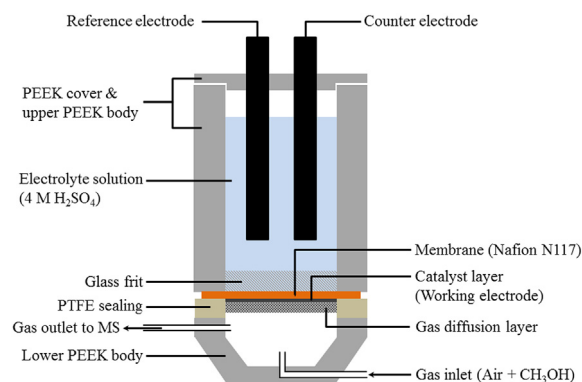


Fig. 1. Scheme of the used electrochemical half-cell.

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