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Quantitative study of ruthenium cross-over in direct methanol fuel cells during early operation hours



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HIGHLIGHTS

• Ru dissolution and deposition on the cathode already occurs during MEA fabrication.

• Cell potential seems to have only a negligible effect on Ru cross-over.

• The amount of Ru on the cathode correlates mainly with DMFC runtime.

• There is evidence of two Ru dissolution processes, a fast and a slow process.

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In direct methanol fuel cells (DMFC), ruthenium cross-over is an important degradation phenomenon. The loss of ruthenium from the anode, its transport through the membrane and its deposition onto the cathode are detrimental to the fuel cell performance and limit the fuel cell's lifetime. Here we present a quantitative study on the fraction of ruthenium being transferred from the anode to the cathode during early operation hours (0–100 h) of a DMFC. Already during fabrication of the MEA ruthenium is transferred to the cathode. In our pristine MEAs about 0.024 wt% Ru could be found in the cathode catalyst. The cell potential during operation seems to have only a minor influence on the dissolution process. In contrast, the operation time appears to be much more important. Our data hint at two dissolution processes: a fast process dominating the first hours of operation and a slower process, which is responsible for the ongoing ruthenium transfer during the fuel cell lifetime. After 2 h held at open circuit conditions the Ru content of the cathode side was 10 times higher than in the pristine MEA. In contrast, the slower process increased that amount only by a factor of two over the course of another 100 h.

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1. Introduction

In the field of portable, automotive and off-grid systems fuel cell technologies are a promising candidate. However, to date the market share of fuel cells is still very low. This is mainly due to their high costs, which are driven by the noble metal catalysts, the membrane and the low overall lifetime of the polymer electrolyte fuel cell (PEMFC) system. The periodically updated reports of the U.S. Department of Energy's (DOE's) Office of Energy Efficiency and

Renewable Energy (EERE) [1] list a set of goals addressing these shortcomings. One of these refers to the long term stability of direct methanol fuel cells (DMFC). In the majority of cases the end of life of a DMFC is not defined by a complete failure of the cell. Rather it is defined by the slow, but constant degradation of fuel cell performance reaching a level where the power, that can be delivered, is not sufficient for the intended application anymore. Usually different degradation mechanisms contribute to this degradation [2], amongst others Ru dissolution from the anode and cross-over to the cathode [3–12].

In the state-of-the-art binary Pt-Ru catalyst ruthenium adatoms provide oxygen-containing species on their surface, which are required for the complete oxidation of methanol. Due to this so



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called bifunctional mechanism [13,14] and others, Pt–Ru catalysts show the highest activities for the methanol oxidation reaction (MOR), although the optimum Pt:Ru ratio is still under debate [15,18]. Dissolution of ruthenium from the anode catalyst reduces its catalytic activity for the MOR [19]. Furthermore, the transferred ruthenium deposits onto the cathode catalyst and impedes the oxygen reduction reaction (ORR) [20,21]. It has been observed that significant amounts of Ru get dissolved from the state-of-the-art Pt–Ru anode catalyst during DMFC stack testing and can be found on the Pt cathode catalyst, but also on the gas diffusion layers and in the flow fields post mortem [6,8,22–24].

Since certain operation modes of fuel cell stacks can lead to fuel depletion and other harsh conditions, the stress on the catalysts can be very high compared to the normal operation protocol of single cell DMFCs. It was observed by accelerated stress tests using either high anodic potentials [4] or methanol starvation [5] in DMFC single cells, that these harsh conditions significantly increase the dissolution of Ru.

By performing electrochemical stripping experiments on welldefined platinum–ruthenium electrodes Gasteiger et al. [15] have shown, that high anodic potentials above 750 mV vs. NHE will lead to ruthenium dissolution. However, under normal DMFC operation conditions the anode potential remains well below 750 mV vs. NHE as it was demonstrated by reference electrode measurements [25,26].

Zelenay et al. [8] observed for MEAs prepared from unsupported Pt–Ru catalysts that ruthenium dissolution and transfer onto the cathode catalyst already occurs during humidification of the DMFC at open circuit potential (OCP). Their analyses also demonstrated that further Ru dissolution takes place under all DMFC operation conditions. Wang [9] et al. performed a series of single cell DMFC tests using commercial Pt black and Pt–Ru black catalysts. They found a performance loss, measured by voltage decay of the cell after 117 h, 210 h and 312 h of operation, which is especially pronounced during early operation hours. This is in good agreement with results obtained by Liu et al. [27] using a model fuel cell set-up, which allowed for the measurement of cross-over ruthenium. These authors observed the highest fraction of dissolved Ru over a period of 28 h.

The source of the cross-over ruthenium is still under discussion. Zelenay et al. [8] proposed the diffusion of one nanometer sized RuO₂ particles surrounded by structural water through the pores of the Nafion[®] membrane. In agreement, Corpuz et al. [21] observed that Pt-Ru anode catalysts containing a larger amount of ruthenium oxides, especially hydrous oxides, seem to be more prone to dissolution. Consequently, higher amounts of transferred Ru were found on the cathode catalysts for anode catalysts containing more oxidic Ru species. Park et al. [4] concluded from HR-TEM analysis that the Pt-Ru particles of their unsupported catalysts decomposed into small fragments, which could be easily oxidized. Wang et al. [28] observed that the content of metallic ruthenium decreases while the fraction of ruthenium oxides increases with time of operation. In contrast to previous works, they concluded from their findings that metallic Ru is more easily dissolved from the catalyst, while the oxide fraction is more stable. Moreover, the composition of the available platinum-ruthenium catalysts is complex [16,17,29,30] and changes during operation of the DMFC depending e.g. on the potential [5,29,31]. Hence, the anode catalyst composition and morphology are likely to influence the mechanism and extent of ruthenium dissolution.

The aim of this work is to elucidate the effect of cell potential and operation time on the amount of ruthenium transferred onto the cathode catalyst with the main focus on the early hours of DMFC operation. As the composition or the kind of ruthenium species in the anode catalyst is likely to influence the dissolution, initially the as-received and as MEA-prepared carbon supported Pt-Ru anode catalysts were characterized by X-ray powder diffraction (XRD) and X-ray absorption spectroscopy (XAS). Rietveld refinement of the XRD data was used to determine the crystalline phases and particle size whereas extended X-ray absorption fine structure (EXAFS) analysis was used to gain additional information about the amorphous ruthenium species in the anode sample. Afterwards, several identically produced MEAs were operated in a single cell DMFC under defined conditions avoiding fuel depletion and other harsh operation conditions. After the tests, the cells were disassembled and the catalyst materials analyzed ex-situ by XRD, XAS, X-ray fluorescence (XRF) spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS). Furthermore, the leaching of Ru from the Pt-Ru anode catalyst in media present in a DMFC (methanol, water and formic acid) without applying a potential was investigated by ICP-MS. Possible dissolution mechanisms are discussed in the light of the physicochemical findings.

2. Experimental

Membrane electrode assemblies with 2 mg/cm² catalyst loading were prepared by the Forschungszentrum Jülich using commercial Johnson Matthey HiSpec 12100 (50 wt% Pt, 25 wt% Ru) and HiSpec 13100 (72 wt% Pt) carbon supported catalysts and Nafion[®] 117 membranes. Details on the ink preparation can be found in Ref. [32]. In brief, 1-hexanol based inks of the aforementioned catalysts were screen-printed onto a decal transfer medium. The catalysts were dried at 170 °C for 6 h and a layer of Nafion[®] (1 mg/ cm²) was sprayed on top to enhance bonding with the membrane. After drying, these 5×5 cm² electrodes were hot-pressed onto the Nafion[®] membrane. Each MEA was individually packed and sealed in a plastic bag under air. The packed MEAs were stored no longer than 1 month under ambient conditions till being used in the experiments described below.

All fuel cell tests were done using a single cell Quintech[®] EFC-25-01 fuel cell setup with all graphite column flow pattern flow fields and gold-plated bipolar plates with heating pads. The anode fuel feed of 3 ml/min 1 M methanol (MilliQ[®] ultra-pure water, Merck[®] ICP grade MeOH) was supplied by a peristaltic pump and the cathode feed of 100 ml/min dry O₂ (Air Liquide[®] 99.95% purity) was controlled by a mass flow controller. The cell temperature was kept constant at 70 °C. After cell disassembly and removal of the MEA the flow fields and fittings were thoroughly cleaned, while the diffusion layers (Freudenberg[®] H2315 I3) were discarded and replaced with new ones. The detailed description of the test bench can be found elsewhere [33].

Two of the MEAs were never assembled in a DMFC, but used as as-prepared references. Three MEAs were subjected to open circuit potential (OCP) conditions in a DMFC for 0.5 h, 10.5 h and 100.5 h, respectively. These samples are further referred to as 'time series'. Another three MEAs were run at OCP conditions for 0.5 h each as a break-in protocol and thereafter subjected to constant potentials of 600 mV, 400 mV and 200 mV for 1 h, respectively ('potential series'). An illustration showing the sample histories is given in Fig. 1.

The cathode and anode catalyst samples were thoroughly scratched off the MEA with a scalpel, carefully avoiding contamination. The powdered samples were mixed with cellulose as matrix material and 13 mm diameter pellets were prepared using a hydraulic press. Each sample was embedded in Kapton[®] tape to avoid contamination and damaging. The cellulose itself was analyzed using ICP-MS, and the data showed no detectable amounts of either ruthenium or platinum. Also no changes to the diffraction pattern with cellulose as binder were observed.

To analyze the crystalline content of the catalysts with respect to structure and crystallite size X-ray diffraction patterns of the Download English Version:

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