

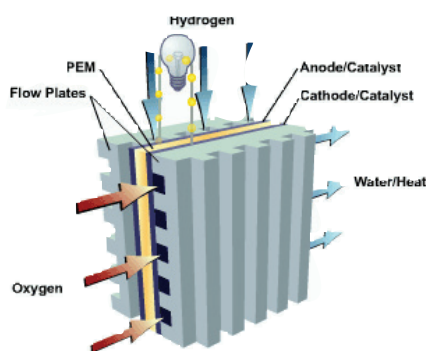
Analyzing fuel cell electrode corrosion by electrochemical QCM-D

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are promising for use in applications such as cars, laptops and stationary applications. However, corrosion of the electrodes shortens their lifetime, and better understanding of these processes is necessary to improve PEMFCs and make them a realistic alternative as a source of electricity. Here, QCM-D combined with electrochemistry was used to investigate corrosion of PEMFC electrodes.

Introduction

PEMFCs use electrochemical reactions of oxygen and hydrogen gas to convert chemical energy into electrical energy. Polymer electrolytes have some obvious advantages in comparison to other fuel cell technologies. The low operating temperature enables a fast start-up, a requirement for most applications. However, the low temperature also implies that a catalyst is needed for the electrochemical reactions, normally platinum (Pt). In contrast to other possible electrolytes, a polymer membrane decreases the volume necessary to provide the same amount of energy.

The overall oxidation of hydrogen is divided into electrochemical half-cell reactions that occur on the anode and cathode (Figure 1). A typical PEMFC electrode consists of Pt nanoparticles finely distributed onto a porous surface of carbon particles. Critical parameters for the lifetime of these electrodes are corrosion of carbon support and Pt dissolution, leading to a loss of electrode surface area. Consequently, the short lifetime of PEMFC has so far limited their use as a competitive source for electrical energy.



[Figure 1]: Schematic illustration of a typical Polymer Electrolyte Membrane Fuel Cell (PEMFC). The anode and cathode are physically separated by a membrane structure (PEM).

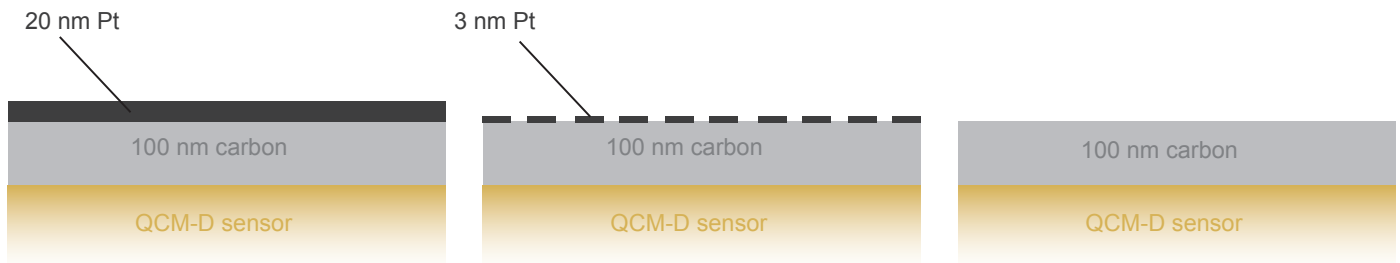
The analysis of corrosion-induced degradation of Pt/carbon electrodes is normally monitored by indirect methods, greatly limiting the information acquired. In this study, Quartz Crystal Microbalance with Dissipation (QCM-D) monitoring combined with electrochemistry (EQCM-D) was used as a more direct way of probing electrode degradation. The EQCM-D unveiled the total mass loss upon corrosion and also probed the temperature dependence of these reactions in real time, demonstrating that QCM-D can be used to further develop more stable fuel cells.

Experimental

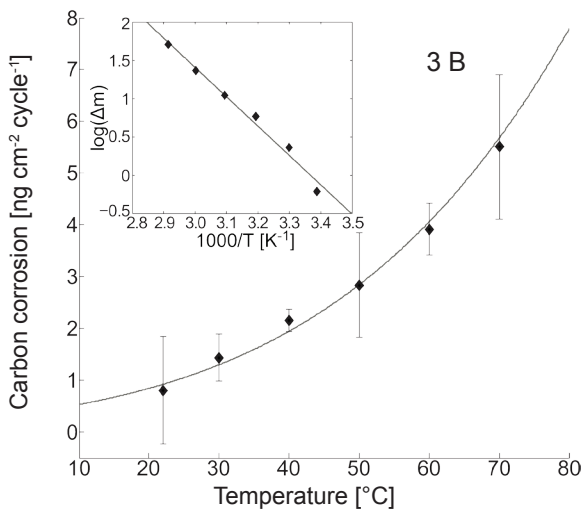
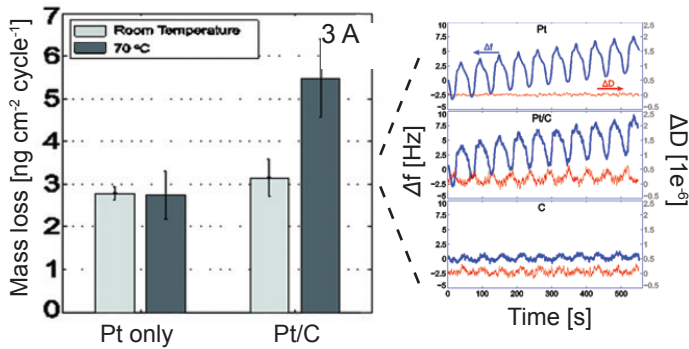
Three differently coated QCM-D sensors were used to mimic the electrodes used in PEMFCs (Figure 2). The coated sensors were Pt-only, carbon-only and Pt/carbon on which Pt partially covers the carbon nanoparticle surface. These sensors were subjected to cyclic corrosion EQCM-D measurements with synchronized time scales in a three-electrode flow-cell setup. Measurements were made at room temperature and up to 70 °C, to probe mass loss as an indicator of electrode corrosion (Δf and ΔD responses to the cyclic corrosion at 70°C are shown in the inset in Fig. 3 A). The lack of change in dissipation (ΔD) justified calculating the mass loss with the Sauerbrey equation, using the change in frequency (Δf) from the third and fifth overtones in the QCM-D measurements.

Results and discussion

The three sensor surfaces responded differently to the cyclic corrosion experiments, as revealed by QCM-D measurements. It was noted that the carbon-only sensor displayed very marginal mass losses (Figure 3A inset) and the higher mass loss during the Pt-only experiment is due to Pt dissolution. The values obtained correspond well with previous studies. For the Pt/carbon sample,



[Figure 2]: Illustration of analyzed model samples; Pt-only (left) and carbon-only (right) samples consist of planar smooth films. The Pt/C (middle) sample consists of Pt nanoparticles on top of the carbon substrate.



[Figure 3]: (A) Mass loss normalized to electrochemical surface area of Pt, determined from cyclic corrosion QCM-D data, which is shown in the inset. (B) Mass loss as a function of temperature during Pt-induced carbon corrosion (Pt/carbon sample). The inset shows the Arrhenius plot in which the temperature dependence of the mass loss is fitted to a linear regression.

an approximately two-fold larger loss of mass was observed compared to Pt alone (Figure 3A). This difference could not be explained solely by Pt-only dissolution, but is due to Pt-catalyzed carbon corrosion. The loss of mass during carbon corrosion is attributed to carbon oxidation to CO₂. In addition, Pt/carbon was the only sample that displayed temperature dependence (Figure 3A). To further probe details of the temperature dependence of Pt-catalyzed carbon corrosion, several temperatures between 22°C and 70°C were applied. The temperature experiment resulted in a so-called Arrhenius temperature dependence (Figure 3B). The authors conclude that Pt causes a temperature-dependent acceleration of carbon corrosion with an apparent activation energy of 0.33 eV.

Conclusions

This application note highlights the possibility of using QCM-D in combination with electrochemistry as a tool to probe electrode degradation relevant for PEMFCs. As a real-time technique, QCM-D studies can be synchronized in time with electrochemistry measurements and used to elucidate detailed mechanisms, possible intermediate formation and rates during electrode corrosion and related degradation processes in fuel cell research. In addition, this study highlights the use of QCM-D to study dissolution of metals. By increasing our understanding of these processes, fuel cells in general and PEMFCs in particular might be considered a competitive alternative for energy conversion into useful electric energy.

Acknowledgements

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References & further reading:

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