INVESTIGATION OF GAS DIFFUSION ELECTRODES FOR ELECTROCHEMICAL OXYGEN REDUCTION

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Introduction

Electrochemical oxygen reduction reactions using silver as catalyst are highly important, e.g., in fields of alkaline fuel cells (AFC), industrial chlorine-alkali electrolysis or metal air batteries. In this regard, in AFC silver can be used as cathode catalyst. In order to enhance its catalytic activity in AFC, porous gas diffusion electrodes with a high surface area made of silver and polytetrafluorethylene (PTFE) (cf. Figure 1) can be prepared via a reactive powder-polymer mixing and rolling (RMR) technology [1,2]. In these electrodes PTFE acts as an organic binder providing both a higher mechanical stability and a hydrophobic pore system that both avoids flooding of the electrode by the electrolyte and improves the transport of oxygen to the reaction zone.

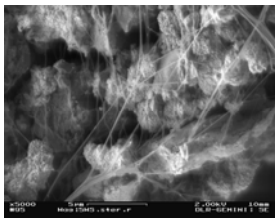

Figure 1: SEM micrograph of a porous PTFE-bonded silver GDE.

Since reaction steps of heterogeneous electrocatalytic processes take place at the solid-liquid interface, the surface structure of the electrodes and their composition can significantly influence their electrochemical performance. Therefore the investigation of degradation (ageing) effects and the long-term stability of the GDE are very important aspects.

In order to investigate the degradation of the GDE and the interaction of the silver electrode with the liquid medium, a combined analysis of electrochemical in-situ and ex-situ experiments were carried out. In this context electrochemical reactions on the surfaces of the silver GDE were investigated in-situ by electrochemical impedance spectroscopy (EIS) and cyclic voltammetry measurements, whereas the surface composition of the electrode and its structure were investigated by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).

XPS and SEM measurements

Since XPS is a highly surface-sensitive technique, the degree of degradation of the silver GDE surface after operation (i.e., oxygen reduction) has been investigated at several positions. The investigated lateral positions on the GDE are labelled as position “A”, “B”, and “C” corresponding in this order to positions having experienced increased electrochemical stress.

From the XPS overview spectrum of a GDE recorded at the position A (corresponding to an unused electrode, cf. Figure 2) can be clearly seen, that this surface, i.e. electrochemically unstressed surface, consists of PTFE and silver, whereas the PTFE concentration on the surface is significantly higher than the one of silver. This finding is in contrast to the ratio of silver and PTFE in the powder-polymer mixture, which was used for the preparation of the electrodes. Consequently, this observation reveals that due to the preparation processes, the concentration of the PTFE on the surface is higher than in the bulk indicating a partial coverage of the silver catalyst by a PTFE film.

Due to electrochemical operation the chemical composition of the GDE surface is changed. The PTFE in the electrode is partially decomposed, which can be seen from the C1s spectra recorded at the differently electrochemically stressed positions (A, B, and C):

With increasing electrochemical stress the XPS peak at around 295 eV, being assigned to C-F species in PTFE, broadens and decreases significantly. Furthermore, different degrees of local decompositions of PTFE are indicated by F1s detail peaks exhibiting full width at half maxima (FWHM) that increase from 2.8 eV to 3.9 eV when measuring at the position A, B, and C, respectively. These findings indicate a changed chemical composition of PTFE to some extend depending on the lateral position on the GDE.

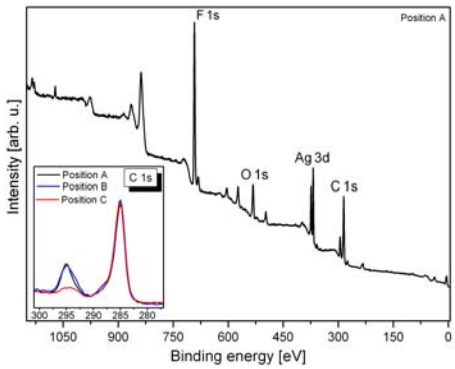

Figure 2: XPS overview spectrum (position A) and detail spectra (C1s) recorded at different positions (A, B, and C) of a silver GDE.

SEM-micrographs of an unused and used GDE (Figure 3) show that due to the electrochemical stressing of thte GDE the surface roughness of the catalyst surface area has decreased.

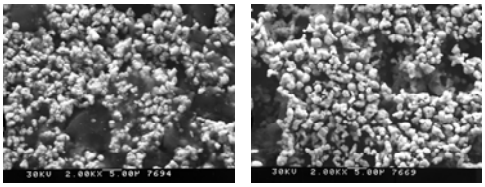

Figure 3: SEM micrograph of unused (left) and used (right) silver GDE.

Electrochemical measurements

In order to analyze the long-term behaviour, i.e., the degradation (ageing) process of silver electrodes during oxygen reduction, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) have been performed.

As shown in Figure 4, the EIS spectrum changes with operating time. For the evaluation of the EIS spectra an equivalent circuit with various impedance elements is used; these elements are generally represented as ohmic, capacitive and inductive components.

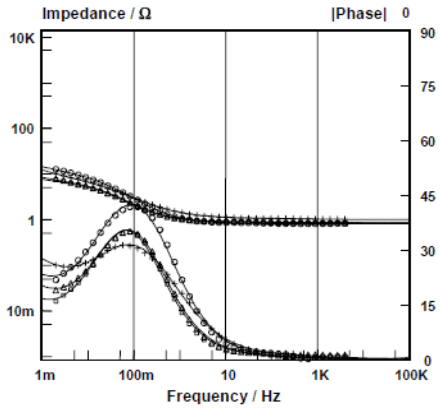

Figure 4: Bode diagram (log |Z| vs. log f) of the impedance spectra of the silver GDE measured at OCP (70 °C, 30wt% KOH) during oxygen reduction at different times of operation at 100 mA cm^{-2}.

“O”: unused electrode (0 h), “□”: after 24 h, “Δ”: after 160 h, and “+”: after 1185 h.

The observed fast change of the impedance elements in the beginning can be interpreted as cleaning of the surface. Due to the transfer through the air, the electrode surfaces can be easily oxidized or polluted. Impurities can be quickly removed by the electrochemical operation, also the oxidation state of the catalyst can quickly change in the electrochemical environment. Therefore, the surface area increases while the impurities are removed; consequently the double layer capacity increases. In addition to the active surface, the charge transfer resistance decreases, because the reaction is not hindered after removing of the impurities. Besides this, the slow change of the impedance elements at high frequencies can be related to the degradation of the electrodes.

The anodic potential range in the CV diagram (Figure 5) from 210 mV to 450 mV vs. Hg/HgO is characterized by the oxidation of silver, whereas in the cathodic potential range from 210 mV to -700 mV the oxygen reduction reaction overplayed in the potential range from 210 mV to 90 mV by the silver oxide reduction reaction can be observed.

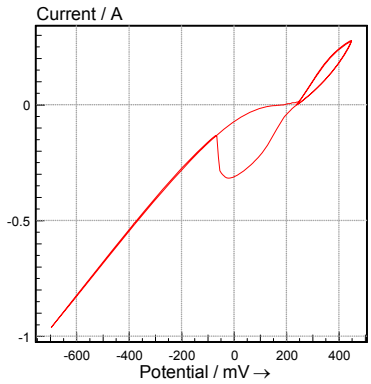

Figure 5: CV diagram of an Ag-GDE, scan rate 1 mV/s, 10 N NaOH at 80°C recorded in the potential range from 450 mV to -700 mV vs. Hg/HgO.

The decomposition of the PTFE in the silver gas diffusion electrode reduces the hydrophobic behavior of the electrode and, accordingly this process affects the three phase zone between catalyst, electrolyte, and gas phase being relevant for the oxygen reduction reaction. This means that the electrode will be more flooded by the liquid electrolyte and as a result the gas transport in the electrode will be more hindered.

Conclusion

The combined analysis of the silver GDE using in-situ electrochemical measurements (EIS, CV) and ex-situ surface sensitive techniques (XPS, SEM) show that the performance of the silver GDE is significantly influenced by the degree of degradation of the electrodes, e. g., the reduction of the active surface due to the decomposition of the PTFE. These findings indicate a different degree of decomposition of the PTFE depending on the position on the silver GDE.

Acknowledgement

The authors gratefully acknowledge the BMBF (SVK project) for financial support and I. Plock for performing SEM measurements.

References

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[2] N. Wagner, M. Schulze, E. Gülzow; J. Power Sources,
127 (2004), 264.