

XPS characterization of silver electrodes and catalysts for 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 brine electrolysis or metal air batteries. For AFC silver is a superior cathode catalyst.

In order to enhance its catalytic activity, porous gas diffusion electrodes with a high surface area made of silver and polytetrafluoroethylene (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 avoids flooding of the electrode by the electrolyte and improves the transport of oxygen to the reaction zone.

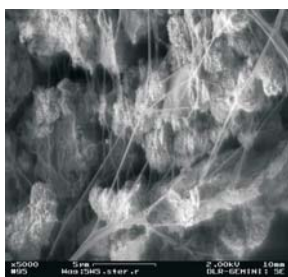


Figure 1: SEM micrograph of a porous PTFE-bonded silver GDE

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 ex-situ and electrochemical in-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 (CV) measurements, whereas the surface composition of the electrode was investigated by X-ray photoelectron spectroscopy (XPS).

XPS measurements

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique that is unique in providing information about chemical state bonding. Since this technique is highly surface-sensitive the degree of degradation of the silver GDE surface after electrochemical operation (i. e., used as oxygen reduction electrode) has been studied. Therefore, three samples, one unused electrode labelled "A" and two used electrodes after operation (i.e., after oxygen reduction) named "B" and "C" have been investigated.

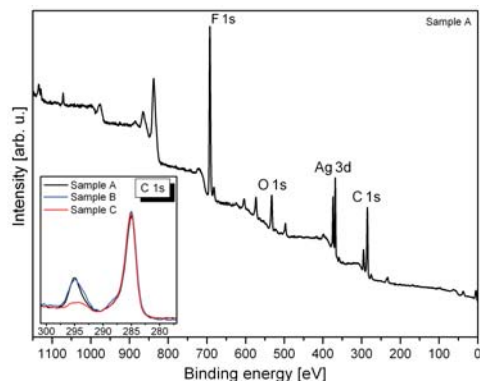


Figure 2: XPS overview spectrum of an unused GDE (sample A) and detail spectra (C 1s) recorded at GDE after electrochemical operation.

From the XPS overview spectrum of an unused GDE (sample A, Figure 2) it can be clearly seen that the fresh surface consists of PTFE and silver. Thereby, the PTFE concentration (At%) on the surface is significantly higher than the one of silver: the ratio of fluorine to silver (F:Ag) is ~9:1 (taking into account that the sensitivity of the F 1s signal in the XP spectra is approx. 20% of the one of Ag 3d signal). 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 process, 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 (i. e., oxygen reduction) the chemical composition of the GDE surface is changed (cf. Figure 3). The F:Ag ratio of sample C is approx. 2:1.

Further, the PTFE in the electrode is partially decomposed, which can be seen from the C 1s spectra (Figure 2) recorded at different samples (A, B, and C): After electrochemical operation of the silver GDE the XPS peak at ~295 eV being assigned to CF₂ species in PTFE broadens and decreases significantly.

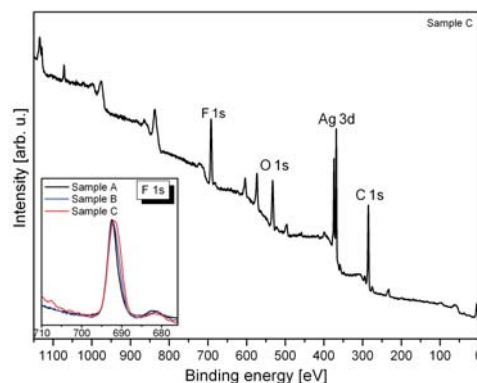


Figure 3: XPS overview spectrum of an used GDE (sample C) and detail spectra (F 1s) recorded at GDE after electrochemical operation.

Furthermore, different degrees of decomposition of PTFE are indicated by F 1s peaks (cf. Figure 3) exhibiting full width at half maxima (FWHM) that increase from 2.8 eV to 3.9 eV when measuring the used samples after operation. These findings indicate a changed chemical composition of PTFE on these GDE to some extent.

Electrochemical measurements

In order to analyze additionally the long-term behaviour including 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.

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 are quickly removed by the electrochemical operation and also the oxidation state of the catalyst may change immediately in the electrochemical environment. Therefore, the surface area increases while the impurities are removed; and 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.

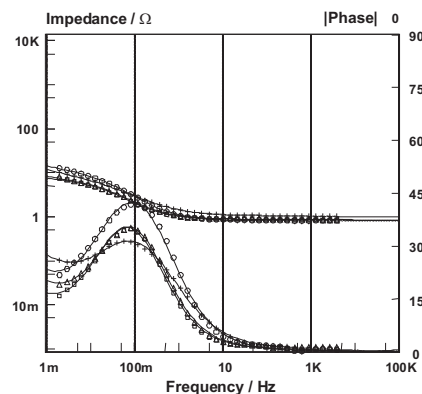


Figure 4: Bode diagram (log |Z| vs. log f) of the impedance spectra of the silver GDE measured at OCP (70 °C, 30wt% KOH) during oxygen reduction at different times of operation at 100 mA cm⁻². "O": unused electrode (0 h), "□": after 24 h, "□": after 160 h, and "+": after 1185 h.

The anodic potential range in the CV diagram (cf. 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 overlaid in the potential range from 210 mV to 90 mV by the silver oxide reduction reaction can be observed.

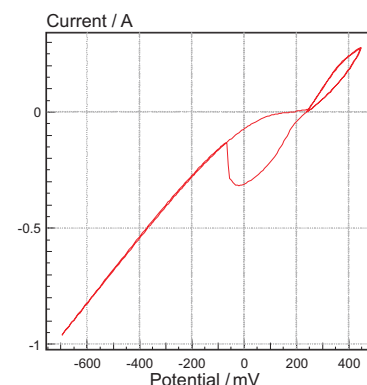


Figure 5: CV diagram of a silver GDE, scan rate 1 mV/s, 10 N NaOH at 80°C recorded in the potential range from 450 mV to -700 mV vs. Hg/HgO.

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 wetting by the liquid electrolyte is increased and as a result the gas transport in the electrode is hindered.

Conclusion

The combined analysis of the silver GDE using an ex-situ surface sensitive technique (XPS) and in-situ electrochemical measurements (EIS, CV) 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 on the on the GDE.

Acknowledgement

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References

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