XPS characterization of silver electrodes and catalysts for oxygen reduction

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Introduction

Electrochemical oxygen reduction reactions using silver as a catalyst are highly important, e.g., in fields of alkaline fuel cells (AFCs), industrial brute electrolysis or metal air batteries. For AFCs silver is a superior cathode catalyst. In order to enhance its catalytic activity, porous gas diffusion electrodes are used which are used for 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.

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 (4% in the XPS 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 C1s 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 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 the silver GDE and the interaction of the silver electrode with the liquid medium, a combined analysis of electrochemical measurements (EIS, CV) have been performed. Furthermore, different degrees of decomposition of PTFE are indicated by C1s peaks (cf. Figure 3) exhibiting full width at half maxima 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 extend.

Figure 2: XPS overview spectrum of an unused GDE (sample A) and detail spectra (C1s) recorded at OCP after electrochemical operation.

XPS measurements

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique that is unique in providing information about chemical state bonding. Since this technique is highly surface-sensitive the degree of degradation of the GDE surface (cf. Figure 2) 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 3: XPS overview spectrum of an used GDE (sample C) and detail spectra (C1s) recorded at OCP after electrochemical operation.

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) measurements, whereas the surface composition of the electrode was investigated by X-ray photoelectron spectroscopy (XPS).

Figure 4: Bode diagram (log |Z| vs. log f) of the impedance spectra of the silver GDE measured at 70 °C, 30 wt% KOH during oxygen reduction at different times of operation at 100 mAcm-2. “O” unused electrode (0h), “-” after 24 h, “•” after 160 h, and “□” after 1150 h.

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.

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 overlayed in the potential range from 210 mV to 90 mV by the silver oxide reduction reaction can be observed.

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

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References