XPS study of electrodes fromed from a mixture of carbon black and PTFE powder

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Introduction

Low temperature fuel cells are likely to become important for mobile energy systems. The Stuttgart DLR has developed gas diffusion electrodes for fuel cells for many years. The physical characterization of the electrodes and different treatment steps of the electrodes is a useful tool for this development.

The electrode consists of the electrocatalyst and an organic binder. In the gas diffusion electrode liquid and gaseous media must be transported. Noble metal catalysts supported by carbon black as carrier are used in the electrodes. Due to its high chemical stability polytetrafluorethylene (PTFE) is used as organic binder. The carbon black has a hydrophilic character whereas the PTFE is hydrophobic. In the preparation process the carbon black supported catalyst powder and PTFE powder were mixed in a knife mill and sprayed in a flux of nitrogen gas onto a carbon cloth used as backing or onto the polymer electrolyte membrane and fixed together with other components in a rolling process or by hot pressing.

Experimental

The surface composition of the electrodes were investigated by XPS, recording the F1s and the C1s levels. The carbon in the different components can be distinguished by the binding energy which is 284.5 eV for carbon black and 292.2 eV for the carbon in the PTFE. The concentration of PTFE and carbon black could be determined by the C1s spectra only or by the intensities of the C1s and the F1s signals.

Results

A spectrum of such a dry-coated electrode is shown in the bottom curve in Fig. 1. In XP spectra of the wet-prepared electrodes, shown in the upper curve in Fig. 1, the C1s signal from the carbon in the PTFE is split into two peaks, while the C1s signal from the carbon black is not. The same splitting of the C1s signal from the carbon in the PTFE is recorded for the F1s signal of the wet-prepared electrodes.

The hydrophilic character of electrodes can be changed by tempering. Fig. 2 shows the depth profiles of two identical electrodes, whereby one of them was annealed for 1 h at 650 K. At 650 K during annealing the PTFE becomes mobile and wets the carbon black surface, which leads to the enrichment of the PTFE on the surface of the carbon black particles. This explains the observed higher concentration of the PTFE on the surface and in the electrode. An annealing step leads to an enrichment of PTFE on the outer surface of the electrodes as well as on their inner surface in contrast to the enrichment of carbon black during the rolling step, which is restricted to the outer electrode surface.

The solid line in Fig. 3 shows the concentration of the PTFE on the electrode surface determined by XPS as function of the PTFE concentration in the initial powder mixture after dry preparation of the electrodes. On the surface of the dry-prepared electrodes the carbon black is more concentrated than in the initial powder mixtures. The significantly enriched concentration of the carbon black is observed for all different powder mixtures with exception of the electrode prepared from pure carbon black powder.

Due to mechanical stressing the surface composition changes. The contact with a lint-free cloth reduces the carbon black concentration and so the PTFE concentration increases as shown by the red line in Fig. 3. The surface composition of mechanically stressed electrodes with a high PTFE content is approximately the concentration of the initial powder mixture. On the electrode with low PTFE concentration the carbon black is still enriched after mechanical stressing.

For both kinds of electrodes not mechanically stressed and mechanically stressed a PTFE concentration on the surface determined by XPS of approx. 20 wt% is the limit for a change to hydrophilic.

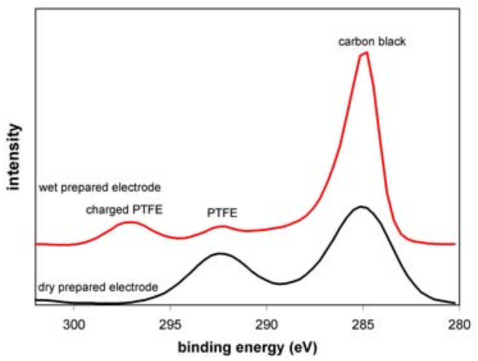

Fig. 1: XP spectra of a dry prepared electrode (bottom curve) and an electrode wet prepared from a suspension (upper curve)

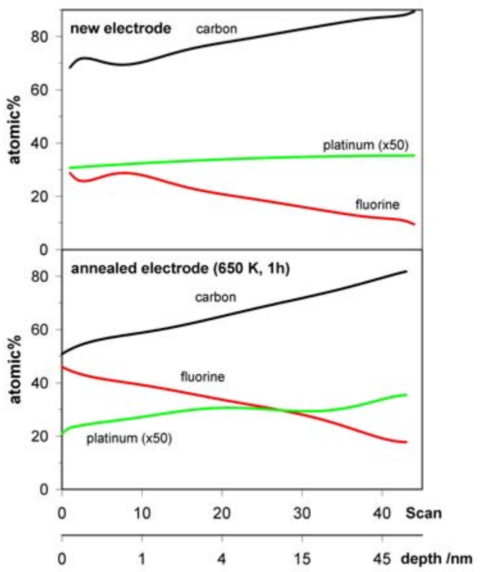

Fig. 2: Depth profile of an electrode before (upper part) and after tempering at 650 K for 1 h (bottom part)

Carbon black content [wt%]	Wetting behavior of non-stressed surface	Wetting behavior of mechanically stressed surface
30	Hydrophobic	Hydrophobic
40	Wetted by liquid water, not by water vapor	Hydrophobic
50	Wetted by liquid water, not by water vapor	Hydrophobic
60	Wetted by liquid water, not by water vapor	Hydrophobic
70	Hydrophilic	Hydrophilic
80	Hydrophilic	Hydrophilic
90	Hydrophilic	Hydrophilic
100	Hydrophilic	Hydrophilic

Table1: Hydrophilic and hydrophobic behavior of electrodes with different composition

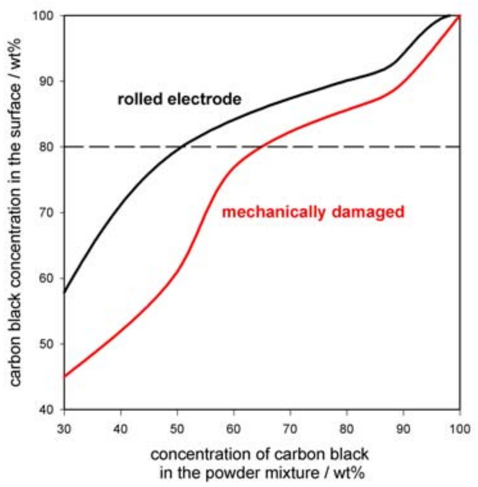

Fig. 3: Carbon black concentration in dry prepared electrodes before and after mechanical stressing of the surface

Conclusions

The hydrophilic and hydrophobic character is important for the transport of the media in technical gas diffusion electrodes for electrochemical applications.

The surface concentration of the components depends not only on the powder composition but also on the preparation technique, mechanical stressing and thermal process steps.

Mechanical stressing of the surface of the dry-prepared electrodes can change the surface composition, the carbon enrichment decreases but is not completely eliminated.

Thermal modification leads to an enrichment of the PTFE on the surface, whereby the inner surface in the electrode becomes more hydrophobic, too, whereas mechanical stressing influenced only the outer surface.

The critical concentration is approx. 20 wt% PTFE. An electrode with a high PTFE concentration on the surface is hydrophobic, with a lower PTFE concentration than 20 % it is hydrophilic.