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SHORT COMMUNICATION

On the microstructure of teflon-bonded platinum–carbon electrodes

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1. Introduction

In recent years the interest in electrochemical energy conversion and electrochemical analysis/synthesis has increased substantially. In many electrochemical cells, in fuel cells and batteries as well as in electrochemical reactors, porous electrodes are used to increase current density and space-time-yield. For some applications air-oxygen consuming gas-diffusion electrodes are fundamental. Two working principles and essentially different types of porous gas-diffusion electrodes have been developed: hydrophilic electrodes with pressure gas feeding and semi-hydrophobic electrodes containing hydrophobic agents like teflon (PTFE) or polyethylene. In the first case the gas-electrolyte boundary is established in the porous structure by an overpressure of the feed gas, in the second case the hydrophobic agents cause a wetting gradient from a nearly totally wetted surface on the electrolyte side to a dry surface on the gas side. Much work had been devoted to mathematical models describing the performance of these electrodes [1, 2], less has been published about their microstructure [3]. In our investigations on porous air–oxygen electrodes for reactive metal–air batteries we have made micrographs in a scanning electron microscope (SEM) besides a number of different electrochemical measurements. As a result we propose a microstructure model for teflon-bonded platinum–carbon gas-diffusion electrodes.

2. Experiments and results

Teflon-bonded platinum–carbon electrodes were prepared according to well known methods described by many authors, e.g. [4, 5, 6]. Platinum–carbon was suspended in water and mixed with teflon dispersion (TF 5032, Hoechst AG). The slurry was rolled to layers of about 0.8 mm thickness. The layers were dried at various temperatures between 20 and 300° C and pressed between a porous teflon foil and a silver wire mesh current collector. Samples prepared as described were used as air oxygen electrodes in a plexiglass cell, filled with 3 mol dm^{-3} NaCl electrolyte and air or oxygen was reduced at 20 mA cm^{-2} for 48 and 96 h. From each used and each unused electrode small pieces were taken. To avoid surface charging in the SEM, from each pair one sample was coated with gold in a sputter apparatus. (Polaron Equipment Ltd. SEM coating unit E 5000.) The average gold layer thickness was increased successively to 75.0 nm.

A Leitz microscope and SEM Stereoscan S4 (Cambridge Scientific Instruments), combined with a multi-channel energy analyser (Ortec 6200 with Ortec Si (Li)-Detector) for EBMA [7] were used. A large number of SEM-photographs were taken (Figs. 1 and 2). Additionally the samples were inspected in the light-microscope.

On uncoated probes small numbers of fibrils were visible in the light microscope. With increasing thickness of the gold coating up to 75.0 nm

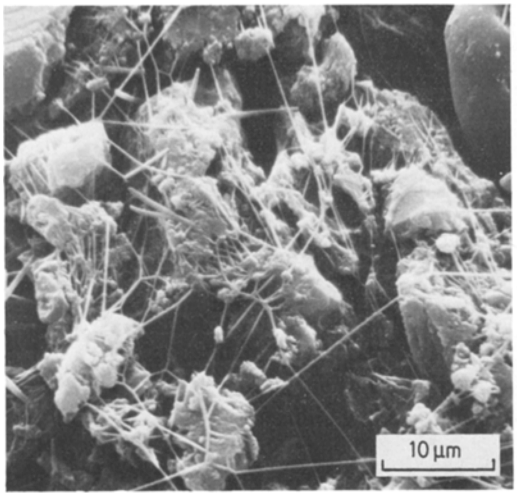

Fig. 1. Teflon-bonded platinum–carbon electrode, fabrication pressure 200 bar, SEM 25 kV, gold sputtered.

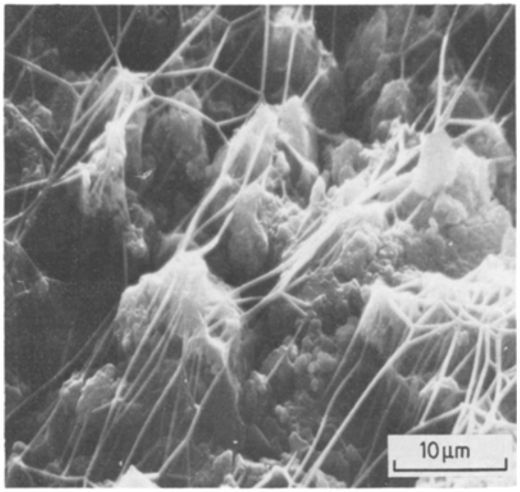

Fig. 2. Teflon-bonded platinum–carbon electrode, fabrication pressure 100 bar, SEM 25 kV, gold sputtered.

the number of fibrils, especially small fibrils, visible in the light microscope increased, due to the reflectivity of the gold layer. In the SEM all fibrils were visible when the layer thickness was greater than about 20.0 nm. According to these observations the fibrils were no artefacts produced during electrolysis, gold-sputtering or in the SEM vacuum. No dependence on electrolysis time and electrolyte composition was found. The influence of the drying temperature (ranging from 20 to 300° C, always kept below the melting temperature of teflon (330 to 350° C)) is not significant, different fabrication pressures of 200 bar (Fig. 1) and 100 bar (Fig. 2) showed no different results. Both micrographs show catalyst agglomerates, sticking together and three-dimensionally interconnected by fibrils. The fibrils were stable against water and 6 mol dm^{-3} KOH. The composition of the fibrils was analyzed by EBMA [7]. Carbon could not be identified with the used X-ray detector, and fluorine was just at the lower end of its working range.

To keep the influence of the matrix low and to be sure that no platinum of the catalyst was analysed, a point on a fibril with no platinum in the surrounding matrix was searched. The analysis showed gold (of the sample coating) chlorine (from the electrolyte), but no platinum or another element heavier than fluorine could be identified as constituent of the fibrils.

3. Discussion

Taking into account the results of the EBMA, SEM and light microscopy, the structural features of the fibrils and their electron–optical transparency we concluded, that the fibrils must be composed of teflon. In a previous published paper Haldeman and co-workers [3] showed a transmission electron micrograph of a silicon replica taken from a teflon-bonded platinum-black electrode. It was claimed, that some visible fibrils were composed of teflon, but no analysis was published. The authors believed with respect to their micrographs, taken by a complicated method via replicas, that the teflon aggregates and fibrils bind the platinum together and provide water repellancy. We showed fibrils *in situ* on electrodes without any intermediate processing or electrode treatment and analysed the fibril composition.

Until today the microstructure of teflon-bonded, porous electrodes is described as "flooded agglomerates". During the preparation of the active-layer mixture carbon (or other catalysts) and teflon-particles agglomerate to form large particles. After pressing and drying (sometimes sintering) these agglomerates stick together, forming channels accessible for gas and electrolyte, thus creating large electrochemically active surfaces [8, 9]. Besides this structural element, which can be found in the structure of sintered metal electrodes too (in both cases sintering processes between very small particles take place [10, 11]), another structure-forming, particle-connecting process has to be assumed. Probably during the stirring of the platinum–carbon suspension mixed with the teflon dispersion, small surface active particles (with partially strong, hydrophobic properties) are coming into contact; in many cases agglomerates are formed, but sometimes the particles are separated again. (Similar processes and structures are observed in emulsifying salves [12]). Probably the fibrils are formed during this separation process, finally leading to the interlocked structure of the electrodes after rolling, drying and pressing.

As a result we confirm, that the microstructure of teflon-bonded carbon electrodes, prepared after the described methods is determined both by direct adherence of agglomerates and teflon-fibrils, interconnecting these agglomerates.

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