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In situ electrochemical STM study of platinum nanodot arrays on highly oriented pyrolythic graphite prepared by electron beam lithography

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ABSTRACT

Model electrodes consisting of platinum dots with a mean diameter of (30±5) nm and heights of 3–5 nm upon highly oriented pyrolytic graphite (HOPG) were prepared by electron beam lithography and subsequent sputtering. The Pt nanodot arrays were stable during scanning tunnelling microscopy (STM) measurements in air and in sulphuric acid electrolyte, indicating the presence of "anchors", immobilising the dots on the HOPG surface.

Electrochemical STM was used to visualise potential induced Pt, carbon and Pt-influenced carbon corrosion *in situ* in 0.5 M sulphuric acid under ambient conditions. Potentiostatic hold experiments show that the Pt dots start to disappear at electrode potentials of $E > 1.4$ V vs. SHE. With increasing time and potential a hole pattern congruent to the original dot pattern appears on the HOPG basal planes. Corrosion and peeling of the HOPG substrate could also be followed *in situ*.

Dissolution of Pt dots appears to be accelerated for potential cycling experiments compared to the potential hold statistics.

1. Introduction

Carbon-supported platinum is an electrocatalyst widely used in polymer electrolyte fuel cells (PEFC). Despite high corrosion resistance of Pt as well as carbon, numerous studies have confirmed that lifetime and stability of PEFC is greatly limited by corrosion and degradation processes occurring on the surface of the catalyst resulting for example in a reduction of catalytically active surface area (see for instance [1–8]). There is general agreement that the loss of Pt active area can be assigned to three fundamental degradation processes such as (i) Pt dissolution and redeposition (Ostwald ripening), (ii) migration and sintering of Pt atoms on the carbon support and (iii) Pt detachment triggered by corrosion of the carbon support [1,8]. Most of this knowledge is based on *post mortem* analysis of different catalysts degraded under different working conditions in different PEFC setups. As a consequence, a detailed assignment of the degradation mechanisms to defined reaction conditions, such as time, potential or temperature is missing.

Fundamental research on well defined model electrodes consisting of carbon supported Pt is rarely portrayed. Such model systems could be investigated via e.g. *in situ* scanning probe methods, thus enabling records of changes in morphology of the electrode materials during degradation. Some of the requirements for an "ideal" model catalyst were listed by Zoval et al. in 1998 [9]: (i) the particles should be of monodisperse size and shape, (ii) should have an electrical connection to a (catalytically inert) support, which facilitates the characterisation of the particles, (iii) should be well-separated from each other, (iv) their structure and the structure of the support should be accessible to certain measurement techniques before, during and after the involved catalytic process and, finally, (v) the particles should be stable for a long time.

A method to prepare monodisperse, well-separated Pt particles on a flat carbon substrate was described e.g. by Lindström et al. [10], who studied oxidation of carbon monoxide and formaldehyde on nanostructured Pt/glassy carbon (GC) electrodes, prepared by hole mask colloidal lithography [10]. Pt nanoparticles with a well-defined diameter and a controlled arrangement on GC can also be prepared by extreme ultraviolet inference lithography (EUV-IL) or electron beam lithography (EBL), followed by Pt deposition via sputtering, as reported recently [11,12]. In case of EBL, an area of one square centimetre on GC could be homogeneously patterned by the Pt dots after modifying several parameters relevant for the EBL process (for details refer to [12]). Recently, we communicated that platinum nanodot arrays on HOPG can likewise be prepared by EBL and subsequent platinum deposition via sputtering [13]. It was shown that the Pt dot pattern was stable during scanning tunneling microscopy (STM) measurements in air and *in situ* in 0.5 M sulphuric acid electrolyte at a potential of 0.7 V vs. SHE, indicating immobilisation of the Pt dots, which are otherwise reported to be mobile on the untreated HOPG surface [14,15]. Stepwise increase of the electrode potential led to a Pt loss, which was indicated by a hole pattern appearing on the HOPG surface congruent with the formerly existing dot pattern. The exact origin of the holes observed after oxidation, however,

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required clarification. They may be either defects created on the HOPG surface during the e-beam exposure or the subsequent sputter process. Pt induced carbon corrosion could also explain the formation of holes on the HOPG surface [13].

In this paper, the possible reasons for the strong Pt adhesion to HOPG and the origin of holes are discussed in more detail. Further, *in situ* STM investigations of Pt-nanodot arrays on HOPG in 0.5 M sulphuric acid providing more statistics are presented. The oxidation of Pt/HOPG model electrodes is performed by means of stepwise potential increase and for comparison by potential cycling with increasing upper vertex potential. In good agreement with literature, if cycled accelerated dissolution of the Pt dots occurs. Besides Pt loss and subsequent appearance of the hole pattern, carbon corrosion starting on the step edges of the HOPG terraces is observed.

2. Experimental

2.1. E-beam lithography

The EBL preparation procedure was performed according to [12,13]. Pieces of HOPG (Tectra GmbH, ZYH-grade) with the dimensions $15\times15\times1$ mm^3 were freshly cleaved with a scotch-tape. Two-layers of a poly(methyl-methacrylic acid) (PMMA)/ethyl lactate solution, a 2% solution of PMMA with the molecular weight (MW) of 50 k and a 1% solution of PMMA with the molecular weight of 950 k, were used as photoresist. The HOPG samples were first spin-coated with a 35 nm PMMA layer of the lower molecular weight. Afterwards, the samples were soft-baked on a hot plate at 175 °C for 5 min. Then, a second PMMA layer (MW 950 k) of approximately 30 nm was spincoated upon the first layer. After this step the sample was soft-baked again on a heated plate at 175 °C for 5 min to remove the solvent. Therefore, it was possible to obtain an undercut profile during the lithography process promoting the lift-off process after metal deposition.

A Vistec EBPG5000Plus electron beam lithography tool, operated at 100 keV, was used to pattern the photoresist. This e-beam writer is equipped with a pattern generator, which can be operated at beam stepping frequencies up to 50 MHz, and a deflection system, capable of deflecting the beam to large angles so that a writing field as large as 512×512 μm^2 can be exposed without any stage movements. The Gaussian shaped beam was focused to approximately 10 nm in diameter at a beam current of 10 nA. Rectangular dot arrays on an area of one square centimetre were generated by setting the beam step size equal to the dot pitch of 70, 100 or 200 nm, so that the exposure of each dot was performed within a single "beam shot" with a dose of 105, 75 and 14 μC cm^{-2}, respectively.

The exposed samples were developed in an isopropanol (IPA) : methyl-isobutylketone (MIBK) 3:1 mixture for 45 s, rinsed in IPA for 30 s and dried by centrifugation at 3000 rpm. Deposition of Pt on the developed samples was performed with a DC magnetron-sputtering device TIPSI with an Ar pressure of 10^{-3} mbar and a power of 30 W. Alternatively, vapour deposition of Pt was performed in a Balzers BAK 600 (Oerlikon Balzers, Liechtenstein) evaporator.

After Pt deposition the lift-off process was accomplished by soaking the samples overnight in acetone and rinsing them with acetone and isopropanol the following day.

2.2. Characterisation methods and instrumentation

The surface of the obtained samples was investigated by scanning electron microscopy (SEM) (ZEISS SUPRA 55 VP). The detection of back scattered electrons was carried out by an In-Lens detector in vacuum at acceleration voltages between 2 and 4 kV with a working distance between 2 and 7 mm.

STM measurements were conducted with a 10 μm STM scanner in constant current mode with the set point current of 1 nA using an Agilent PicoLe™ microscope equipped with a bipotentiostat (PicoStat, Molecular Instruments).

The *in situ* EC STM measurements were conducted in an electrochemical STM cell with a three electrode arrangement where the sample acted as working electrode (WE) and two annealed high purity Pt wires with a diameter of 0.5 mm (FG 999.5, Carl Schaefer AG) as quasi-reference (RE) and counter (CE) electrodes, respectively. An area of 0.8 cm^2 of the working electrode was exposed to the electrolyte (Silicon sealing, inner diameter 10 mm). The 0.5 M H_2SO_4 electrolyte was diluted from sulphuric acid 95–97% (pa, Merck) using UHQ (ultra high quality, Millipore) water (>18 MΩ cm).

For tip preparation a gold wire with a diameter of 0.25 mm (FG 999.9, Carl Schaefer AG) was etched in hydrochloric acid (30% HCl, Baker Analyzed™ Reagent) by applying a DC voltage of 1.7 V between the gold wire and the surrounding Pt ring. After etching, the tips were immersed into hot UHQ water (Millipore, >18 MΩ cm and partially coated with apiezon wax (B7276, Plano GmbH, Germany).

The STM images were processed using WSxM 5.0 Develop 3.1. software [16].

The mean diameters of Pt dots on the support were determined from SEM and STM images using image software Image J 1.43 (W. Rasband, NIH, USA).

2.3. Electrochemistry

The oxidation of Pt/HOPG model electrodes was performed in air saturated 0.5 M sulphuric acid by the means of stepwise potential increase (potentiostatic hold) or potential cycling at room temperature. All potentials in the paper have been converted to the standard hydrogen electrode (SHE) scale by adding 0.89 V to the values measured with the Pt quasi-reference electrode which was calibrated against an Hg/Hg_2SO_4 reference electrode. For the potential hold measurements, the STM tip was approached under potential control at $E_{start}=0.7$ V. An STM image was recorded within 8–10 minutes (scan rate: 0.8–1.0 lines/s). Then, the potential was increased by 0.1 V at a scanrate of 5 mV s^{-1} and an STM image acquired at 0.8 V, the time for the image acquisition was again 8–10 min. The procedure was repeated in 0.1 V steps up to the potential of 1.9 V. After reaching 1.9 V, the potential was scanned back to $E_{end}=0.7$ V with a scanrate of 5 mV s^{-1} and again images were recorded at $E_{end}=0.7$ V.

In case of potential cycling, the scan-rate was set to 20 mV s^{-1} and the sample cycled for 10 cycles between 0.6 V and the upper vertex potential, which was stepwise increased from 1.0 V to 1.9 V. All images were recorded at the lower vertex potential of 0.6 V, avoiding gas evolution on the electrode and bias-related artefacts possibly occurring during the potential hold experiments, as the STM tip was set to a constant potential of 0.4 V. The time for the image acquisition was again 8–10 minutes.

3. Results

3.1. Preparation and characterisation of Pt/HOPG model electrodes

Typical SEM images of model electrodes after the lift-off procedure are shown in Fig. 1a, b. Fig. 1a represents an image of an area with a complete pattern, while Fig. 1b displays an example of an only partially successful exposure/lift-off. Some areas on HOPG were "under" exposed, bearing no dots at all (a1 in Fig. 1b) while other areas were still covered by Pt covered photoresist after lift-off (a2 in Fig. 1b). Finally, on some areas both the exposure and the lift-off process went well exhibiting an intact pattern (a3 in Fig. 1b).

However, on most of the structured samples, areas of (50×50) μm^2 showing almost intact pattern of Pt dots could be observed with SEM.

Fig. 1c, d show the particle size distribution on two different samples by means of two histograms. The vertical lines indicate the respective mean diameter as obtained by this analysis. Table 1 lists