

Short communication

Influence of the morphology on the platinum electrode surface activity

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Abstract

Polycrystalline Pt electrodes with different surface characteristics were investigated by cyclic voltammetry (CV) in 0.5 M H₂SO₄. Plane electrodes showed a decrease in electrochemically active surface area while cycling in the hydrogen underpotential region (H_{upd}), in contrast, electrodes roughened by intensive pre-cycling exhibited a stable value for the electrochemically active surface.

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1. Introduction

The reduction of the noble metal content in the catalyst layers of polymer electrolyte fuel cells (PEFCs) is one of the challenges for this fuel cell technology on the way to become cost competitive. The catalyst utilization has to be increased to compensate for the required decrease in total Pt content without performance penalty. Certainly, one way will be to optimize the three phase boundary. This is the region where the gas phase, the ionically as well as the electronically conducting phase merge together, hence called active layer. This active layer of gas diffusion electrodes (gdes) used in today's PEFCs consists in most cases of Pt nanoparticles supported on high surface area carbon. The low Pt loading (<1 mg cm⁻²) requires an impregnation of the active layer with solubilized proton-conducting ionomer material (Nafion® or others). The impregnation yields a thin film of solid electrolyte, which forms a proton-conducting pathway between the bulk membrane and those Pt particles not being in direct contact to the membrane. However, due to the properties of the ionomer film (low gas permeability, poor electronic conductivity), there is a limit to the amount, which can be added before adversely affecting the performance of the active layer. As a result, Pt particles exist, which are not part of the three phase boundary and therefore do not participate in the electrochemical process.

Comparable to the function of an ionomer layer, an extended Pt surface, which features continuous Pt–Pt contacts to the mem-

brane, enables Pt particles remote from the membrane to be electrochemically active [1,2].

It was shown that the cyclic voltammogram (CV) of Pt in contact with a Nafion® membrane is quite similar to the CV of a Pt electrode in 0.5 M H₂SO₄ [3]. The examination of polycrystalline Pt disc electrodes in 0.5 M H₂SO₄ can be very helpful to serve as a basis for the better understanding of the H_{upd} process at Pt based gdes. The behaviour of a polycrystalline Pt electrode in 0.5 M H₂SO₄, as observed during the recording of a CV, shows deposition of atomic hydrogen in the form of two well-resolved peaks, before the onset of hydrogen gas evolution. Due to the 1:1 relationship between a Pt-surface atom and an adsorbed H-atom, one can calculate from the measured charge the electrochemically active Pt surface (polycrystalline Pt: 210 μC cm⁻² [4]). AC electrochemical impedance spectroscopy (EIS) may reveal time dependent reaction steps of this H_{upd}-process. However, to carry out EIS over a certain frequency range, the electrode itself has to show stable performance. The aim of the described work is to prepare Pt electrodes, which do not show a decay of H_{upd}-adsorption/desorption in the range of several minutes.

2. Experimental

Three different types of electrodes (listed in Table 1) were used for linear potential sweep chronoamperometry experiments. Pt disc electrodes (denoted hereafter as E-1 electrodes) were fabricated by heat sealing a Pt wire (Alfa Aesar, 250 μm diameter, Premion®, 99.997%) in a glass capillary followed by polishing successively with 600 grit SiC paper, 5, 0.3 and

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Table 1
Electrode specification

Electrode type	Label	Electrochemically active surface (cm ²)	Roughness factor (R_f)
Flat Pt disc	E-1	8.3×10^{-4}	1.7
Roughened Pt disc	E-2	107.8×10^{-4}	22
Pt mesh	E-3	16.6	2.4

0.05 μm Al_2O_3 , and sonicating in water for 10 min prior to use. Pt disc electrodes (denoted hereafter as E-2 electrodes) were obtained from E-1 electrodes by cycling the electrode between -0.64 and 0.80 V versus an $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode (Radiometer Analytical S.A., 0.5 M H_2SO_4) at 200 V s⁻¹ for about 2×10^7 cycles. The Pt mesh electrode (denoted hereafter as E-3) was cleaned with a mixture from sulphuric acid and hydrogen peroxide prior to use.

The electrolyte was 0.5 M H_2SO_4 prepared from sulphuric acid (Aldrich, 99.999%) and ultra-pure water [Christ Septron 1500, >18 M Ω , 5 ppb total organic carbon (TOC)]. The solution was initially deaerated with prepurified argon (Labclear[®] and Oxiclear[®] gas purifiers). During the experiments argon was continuously passed over the electrolyte surface.

The experiments were carried out at room temperature (21 °C) with a Pt wire counter electrode in a 25 ml one compartment glass cell. Cyclic voltammograms were recorded at a scan rate of 0.1 V s⁻¹ with an Autolab PGSTAT 20. The potential variation experiments with a scan rate of 200 V s⁻¹ were performed with an EG & G PAR Model 173 potentiostat, combined with a Model 175 programmer.

Before each experiment the working electrode was cycled between -0.64 and 0.80 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$ (denoted hereafter as extended potential region) until the typical polycrystalline Pt CV in diluted sulphuric acid (see CV (a) in Fig. 1) was obtained (up to about 20–50 cycles). This potential window includes the hydrogen region (between about -0.67 and -0.27 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$), the double layer region (between about -0.27 and 0.10 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$) and the oxygen region (between about 0.10 and 0.80 V versus $\text{Hg}/\text{Hg}_2\text{SO}_4$). In the next step, the potential region was scanned at 0.1 V s⁻¹ between the hydrogen and the double layer region (together denoted hereafter as limited potential region) for the periods of

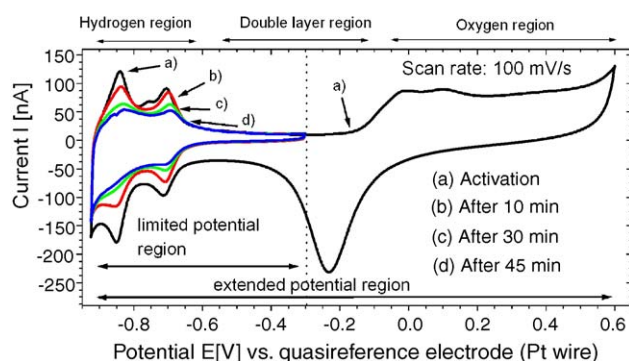


Fig. 1. Cyclic voltammograms of an E-1 electrode in the extended and limited potential region.

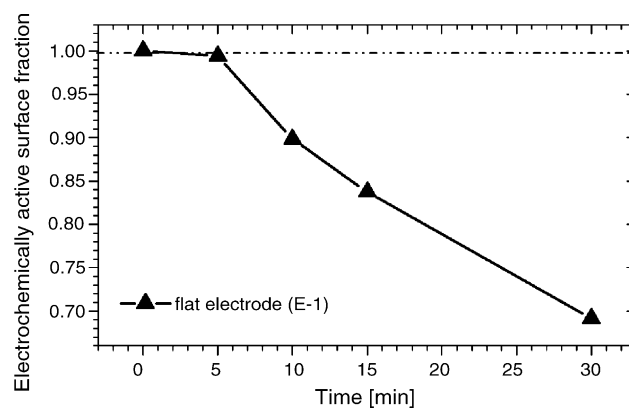


Fig. 2. Electrochemically active surface fraction (calculated from the CV data) at 0, 5, 10, 15 and 30 min after the activation of a flat E-1 electrode.

time given in Figs. 2 and 5. The electrochemical active surface of the different electrode types was determined, as described above. The calculated value for the electrochemically active surface, divided by the geometrical electrode surface, yields the surface roughness factor (R_f).

3. Results and discussion

3.1. Stability of H_{upd} coverage

Curve (a) in Fig. 1 shows the CV recorded over the hydrogen, double layer, and oxygen region (extended potential region) after cycling an E-1 electrode, until the typical polycrystalline Pt CV in diluted sulphuric acid was obtained. Curves (b)–(d) in Fig. 1 show CVs recorded in the limited range of hydrogen and double layer region after cycling for 10 min (b), 30 min (c) and 45 min (d) at 0.1 V s⁻¹.

Comparing the CVs (a)–(d), it is apparent that the area under the H_{upd} peaks decreases with time. In other words, the H_{upd} process seems not to be reversible. This decrease could be interpreted as a decrease in electrochemically active electrode surface, as shown in Fig. 2.

One possible explanation for this phenomenon is that traces of organic impurities gradually contaminate the Pt surface [5].

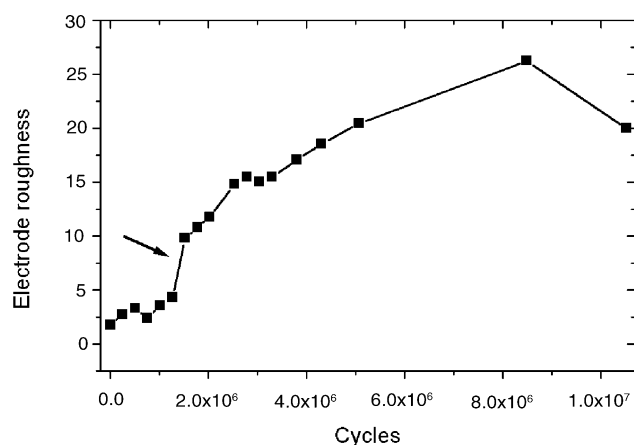


Fig. 3. Electrode surface roughness changes as a function of the number of cycles.

This fact has also to be considered when working with polymer membranes as solid electrolyte, due to the fact that these technical products can be a continuous source of impurities being leached-out. For these measurements, the H_{upd} behaviour of polycrystalline Pt electrodes in 0.5 M H_2SO_4 will be a baseline.

Hence, the application of EIS to characterize processes in this potential region requires a “constant H_{upd} -behaviour” during the time of the EIS measurement. Similar comments with respect to the impurity argument can be found in [6] for AC measurements with single crystal electrodes.

3.2. Roughening process

By cycling an E-1 electrode between the onset potentials for H_2 and O_2 evolution at very high scan rates, it is possible to influence the surface roughness of this electrode. In Fig. 3 is displayed, how the surface roughness of an initially flat disc electrode (E-1) changes with the number of cycles.

The values for the electrode roughness show that, until a certain steady state is observed, the roughness increases with the number of cycles. In the example shown in Fig. 3, a tem-

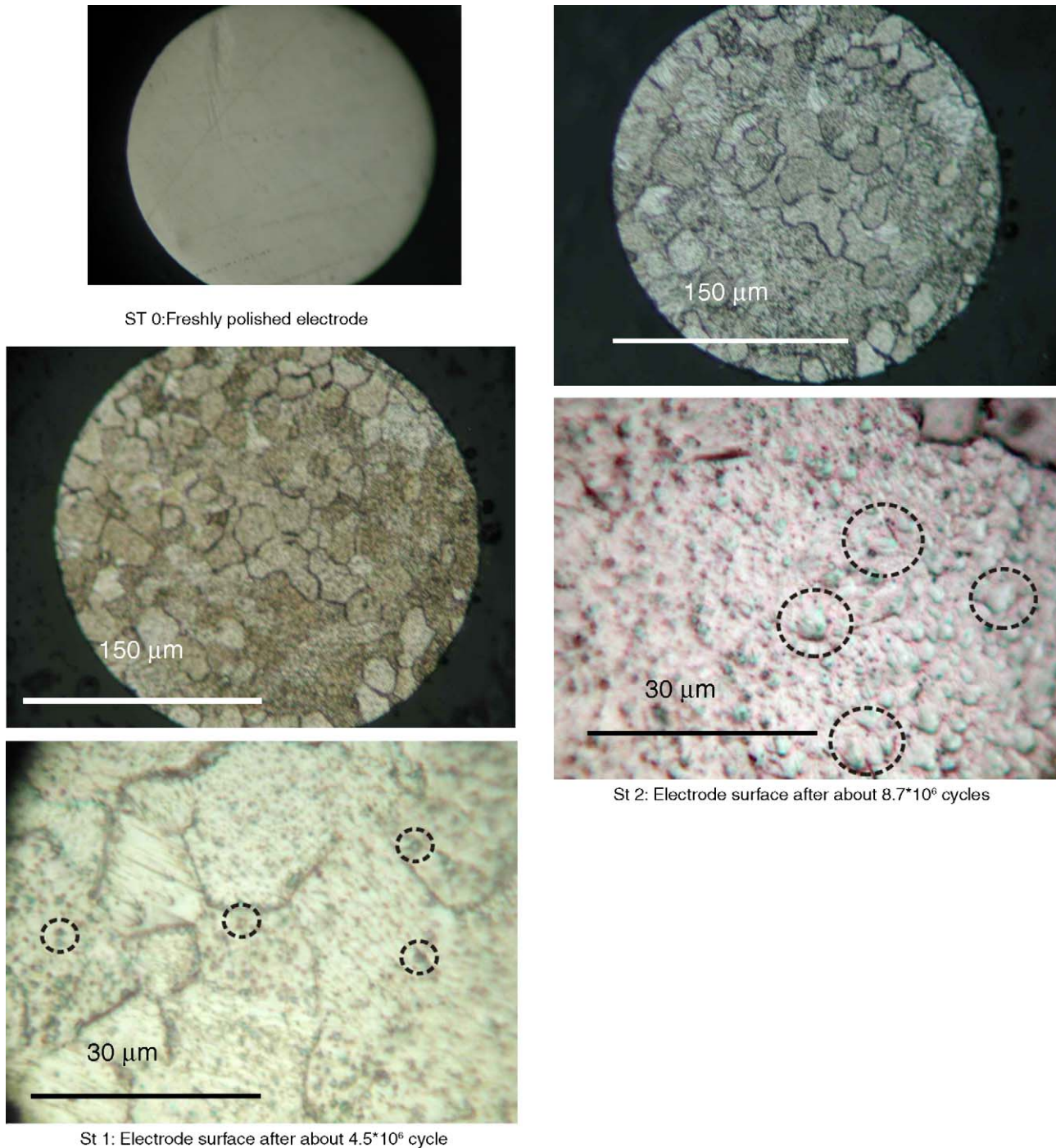


Fig. 4. Different stages of the electrode surface roughening process.

porary decrease in roughness was observed. This may be due to a loss of already roughened electrode material. The steep increase between 1.27×10^6 and 1.52×10^6 cycles (see arrow in Fig. 3) is likely due to an unintended current pulse, which led to a strong gas evolution. Possibly, it was an oxidizing current pulse with oxygen evolution that led to the unusually high roughness increase.

In the following section, optical microscope images are shown, which demonstrate how the intensive potential cycling affects the surface morphology of a freshly polished Pt disc electrode.

A freshly polished electrode surface (St 0) showing a metallic shine is displayed in Fig. 4. The pictures of the electrode surfaces, which have been taken after 4.5×10^6 (St 1 in Fig. 4) and 8.7×10^6 cycles (St 2 in Fig. 4), respectively, look like as if they were composed of several small crystalline islands. Within each of these islands, the surface seems to be quite uniform. Presumably, these self-contained regions contact each other by grain boundaries. Proceeding from St 1 to St 2 the surface roughness increases and it appears that the surfaces of the islands are covered by growing holes.

The growing holes, which cover the electrode surface (see the different hole sizes indicated by the circles in St 1 and St 2 in Fig. 4), can be explained by a mechanism for surface-oxide growth on Pt electrodes in aqueous sulphuric acid, as suggested in the literature [7]. The penetration of oxygen ions into the topmost layer is one of the steps of this mechanism. During the reduction process, the oxide ions have to leave the metal lattice again so that the roughening of the surface becomes understandable. Probably, the restructuring of the reduced Pt surface atoms is not ideal, i.e. in the outermost layer of the surface dislocations and holes remain. The extensive repetition of the activating cycle can then result in the surface roughening.

3.3. Influence of the morphology on the H_{upd} stability

The stability of the electrochemically active surface area for different Pt electrode morphologies, while cycling in the H_{upd} region, is shown in Fig. 5 [8].

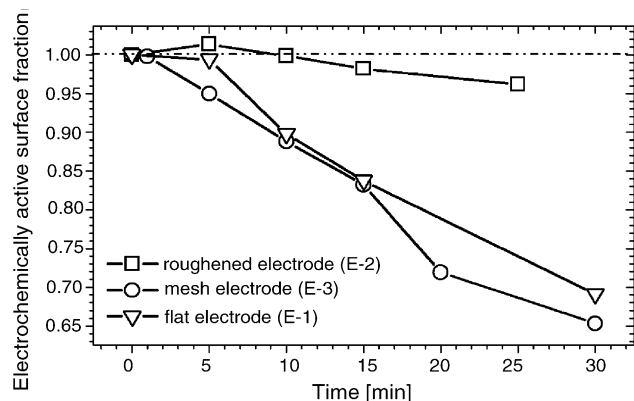


Fig. 5. Changes in the electrochemically active surface fraction concerning the H_{upd} process as a function of time for electrodes with different morphologies.

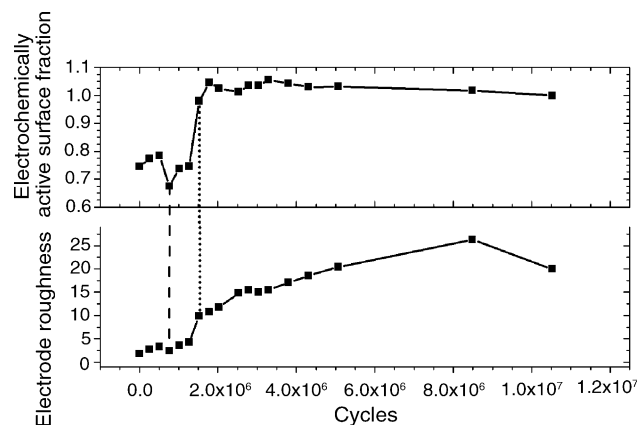


Fig. 6. Correlation between the electrode roughness and the electrochemically active surface fraction.

Contrary to the behaviour of the E-1 electrode, the roughened Pt disc electrode (E-2) shows a stable active surface. To clarify whether or not the increased absolute surface area (because of roughening) or the morphology is the reason for this stability, the measurement was repeated using a mesh electrode (E-3). Like the E-1 electrode, the E-3 electrode shows a significant decrease in active surface area over a similar cycling time [9,10]. The E-3 electrode has a much larger electrochemically active surface than the E-2 electrode; therefore, we believe that the roughness is the main responsible factor for the properties of the E-2 electrode.

3.4. Correlation between surface roughness and H_{upd} stability

After each roughening step, in addition to the R_f value, a CV, after cycling in the limited potential region for 5 min, was recorded. In this way, it is possible to get a first impression, how the H_{upd} stability, of surfaces, differing in their roughness, changes with the number of activation cycles.

Fig. 6 indicates that until a surface roughness of about a factor of 12 is reached, there is a direct correlation with the electrochemically active surface fraction. When the surface roughness increases, the active surface fraction also increases (see, for example, the dotted line). If the surface roughness decreases temporarily (for an explanation see Section 3.2) the active surface fraction also decreases (see, for example, dashed line). Furthermore, it is apparent that after reaching a roughness value of about 12, relatively stable surface conditions exist.

4. Conclusion

By the intensive cycling of the Pt disc electrodes it was possible to influence the morphology of the Pt surfaces.

The roughened electrodes show stable H_{upd} adsorption/desorption properties concerning the H_{upd} signal during at least 25 min.

Utilizing these electrodes, it should in principle be possible to carry out AC impedance measurements and gain more information about the H_{upd} process.

Acknowledgment

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