



The effect of platinum electrode surfaces on precise primary pH measurements

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Abstract

For primary pH measurements, a platinum hydrogen electrode and a silver chloride electrode are immersed in the same solution in a cell without transference (Harned cell). The platinum electrode is covered with dispersed platinum (platinum black) to increase the surface area. To determine the influence of specific deposition conditions (current density, duration, and composition of the electrolyte) on the properties of platinum black, the surface area, and the electrode performance, platinized platinum electrodes were investigated systematically using scanning electron microscopy and optical microscopy. Confocal laser scanning microscopy was applied to obtain quantitative information about roughness parameters. After assessment of the surface structures, improved conditions for the fabrication of platinized platinum electrodes were derived. It was found that all investigated electrochemically coated platinum electrodes obtained comparable values of standard potential of Ag/AgCl-electrodes within the measurement uncertainty. The platinum layer obtained by sputtering was significantly less distinct and less homogenous than the layer of platinum obtained by electrochemical deposition. The examination of shiny (uncoated) platinum electrodes evidenced a significant difference between multiple-used and freshly prepared platinum electrodes. Thus, uncoated platinum electrodes are not suitable for the Harned cell measurement either. Thus, to obtain reliable and reproducible results in pH measurements using the primary method, an electrochemical coating of the platinum electrodes under defined conditions is required.

Keywords Primary pH measurement · Harned cell · Platinum hydrogen electrode · Electrode surface · Metrology

Introduction

The pH value is one of the basic properties of aqueous solutions and biological systems, making its measurement one of the most commonly used electrochemical methods.

There are different types of pH electrodes, based on different fields of application. Glass electrodes, for example, are being used for about 100 years because of its good performance and a wide range of practical application [1].

Furthermore, various types of solid-state electrodes whose surfaces are modified to suit particular applications are described in the literature, e.g., carbon electrodes [2–4].

Among the different types of solid-state pH electrodes, the platinum hydrogen electrode (PHE) has a special significance.

Due to its positive material properties, it has proven itself as appropriate measuring electrode for primary pH measurements [5, 6].

Platinum has a high affinity to hydrogen and can absorb molecular hydrogen. In literature, even the occlusion of hydrogen in electrodeposited platinum layers is described [7].

Another advantage of this electrode material is the particularly low overvoltage of noble metals [8].

The PHE is considered as a reversible gas electrode of the first kind, where an equilibrium between gaseous hydrogen and hydrogen ions is built on the surface [9, 10]. The surface

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of the bare platinum wire or plate is covered with a dispersed platinum layer applied by galvanization, thus, increasing the surface and favoring the adsorption of hydrogen. Due to the saturation of the platinized platinum surface, a platinum electrode out of “metallic hydrogen” [11, 12] is obtained.

In literature [13–15], the dispersed platinum obtained electrochemically is also referred to as “platinum black.” The electrochemical deposition is applied under defined conditions (deposition duration, current density, and composition of the electrolyte).

The specific parameters for the electrochemical deposition were determined empirically and are not standardized, so, it is realized worldwide using different methods [16–22].

Primary pH measurements by Harned cells are the basis for the hierarchical approach of metrological traceability of all pH measurements. In order to assure a reliable traceability chain and to obtain secondary standards with sufficient measuring uncertainties, primary pH measurements have to be as accurate as possible.

The aim of this work is to systematically determine the influence of different selected parameters on the geometric structure of the electrochemically coated Pt-electrodes. The further aim was to test the influence of different parameters (duration, current density, composition of the electrolyte) on the electrochemical deposition of the Pt-electrodes, their quality and surface area increase, and the resulting effects on the electrode performance.

With these experiments, the influence of the parameters' deposition duration and current density as well as the composition of the electrolyte on the properties of the deposition layer and finally on the electrode performance was tested.

Based on the investigation results, an optimal range of the parameters, influencing the development of a homogenous and reproducible surface structure, was determined. This results in a more reproducible response time of the platinum hydrogen electrode.

For the treatment of Pt-electrodes by electrochemical deposition, mostly a small amount of lead (II) acetate trihydrate, $\text{Pb}(\text{CH}_3\text{COO})_2 \times 3\text{H}_2\text{O}$, is added to the electrolyte to get a uniform dispersed adhered platinum black [13, 23, 24]. This addition of lead acetate is also described very differently in the literature [16, 25]. For this reason, the effect of the amount of lead acetate added to the electrolyte was also tested experimentally. Furthermore, during the tests, platinized Pt-electrodes were exposed to heat to investigate the effect of this thermic stress on the electrode surface as well. This experiment was done to determine if, at temperatures of above 50 °C, the properties of the electrode surface change during pH measurements in pH reference buffer solutions.

Besides the electrochemical treatment of Pt-electrodes, a sputter process was scrutinized and assessed. To do so, selected platinum plates were covered with platinum using magnetron sputtering. The examinations of the electrode surfaces

were carried out using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and a digital optical microscope (LM). Furthermore, at PTB, further examinations of selected electrode surfaces were carried out with a confocal laser scanning microscope (CLSM) to obtain quantitative information about the platinum layer.

The standard potentials of Ag/AgCl-electrodes were determined in Harned cells in a 0.01-mol/kg hydrochloric acid HCl at 25 °C to identify the effect of the surface structure of platinum electrodes on primary pH measurements.

Experimental/material and methods

The platinum electrodes investigated in this work consisted of a platinum wire with a platinum plate attached. Before the platinum electrodes were platinized, they were cleaned in hot aqua regia ($\text{HNO}_3 + 3 \text{HCl}$). Then they were cleaned electrochemically in 0.1 M nitric acid HNO_3 . The electrodes were platinized using a 3.5% solution of hexachloro-platinum (IV) acid hexahydrate, $\text{H}_2[\text{PtCl}_6] \times 6\text{H}_2\text{O}$, with 0.01% lead (II) acetate trihydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \times 3\text{H}_2\text{O}$. The method of constant current electrochemical deposition was applied.

The effect of the amount of lead acetate was investigated by also platinizing several electrodes with an electrolyte without this compound. In case phthalate buffers are used [5], the catalytic properties of platinum cause a reduction of the hydrogen phthalate ions. So, for this special type of application, an amorphous palladium layer was built on the electrode. Palladium also has a high affinity to hydrogen but a significantly lower catalytic effect than platinum [26, 27]. In this case, an amorphous palladium layer was built on the electrodes by electrochemical deposition using a 3% palladium chloride solution, PdCl_2 , with 0.01% $\text{Pb}(\text{CH}_3\text{COO})_2 \times 3\text{H}_2\text{O}$. Hydrochloric acid (4 mol/kg) was used as supporting electrolyte.

The amount of lead acetate was varied for some of the investigated Pd-coated electrodes so as to also identify its effect.

Pt-electrodes chosen for the experiments and the technical equipment used for the different techniques of coating the electrodes as well as the instrumentation used to examine the surface structure of the platinum electrodes are listed in the supplementary information Tables 2 to 4.

Table 1 shows the instrumentation used to determine the standard potential of Ag/AgCl-electrodes using differently coated platinum electrodes.

Results and discussions

The differently pre-treated platinum electrodes were investigated using SEM and LM to qualitatively assess the surface

Table 1 Technical equipment used to determine the standard potential of Ag/AgCl-electrodes using differently coated platinum electrodes

Equipment	Type	Manufacturer	Application range	Technical data/remarks
Measurement system consisting of 12 Harned cells	Model 3	Gebr. Rettberg	pH 1 to pH 10 at 5 to 90 °C	- Special glass construction - Special holding device for cells to be inserted in thermostatic bath
Gas supply system for hydrogen and argon	–	Linde AG	–	- Stainless steel needle valves for precise fine regulation of gas flow - Separate grounding
Flow meter	ADM 1000	Agilent Technologies	0 to 50 mL/min	- Resolution: 0.01 mL/min
Precision thermostatic bath with chillier	Proline PV 36 with DLK 25	Lauda	5 to 90 °C	- Glass window - Homogeneity: 10 mK - Stability: 5 mK (at 25 °C)
Platinum resistance thermometer	Pt 100, 4-wire	Electrotherm	5 to 90 °C	- 4 platinum resistance thermometers are located between the Harned cells
Precision multimeter for record of cell potential and temperature	Type 2700	Keithley Instruments, Inc.	0 to 1 V	- 40 measuring inputs for connection of 24 electrodes and 4 platinum resistance thermometers - Separate grounding - Shielded cables to minimize parasitic voltage
Precision pressure gauge	Model 370	Setra Systems, Inc.	800 to 1100 mbar	–
Software	Self-developed	ZMK	–	–

structure. In addition, the roughness of the surfaces of selected platinum electrodes was determined. First, with all methods, survey images were taken, which confirmed the overall picture to be almost homogenous. Then, a representative detail was chosen from the center of the surface and scrutinized and assessed with higher magnification.

Tests on electrochemically platinized and palladinized Pt-electrodes using scanning electron microscopy

The parameters duration and current density in electrochemical deposition were investigated by platinum-coating and palladium-coating of electrodes at different current densities (between 50 mA and 110 mA) and at different durations (between 2 min and 6 min). Moreover, the effect of the amount of lead acetate added to the electrolyte was investigated.

The different parameters of the electrochemical deposition were selected based on literature references and the previous or current methods applied by the institutes involved in this work.

In addition, two electrochemically coated Pt-electrodes were exposed to heat to allow for an assessment of the influence of the temperature on the electrode surface.

The detail views of the different microscopic methods confirm the thickness of the platinum layer or palladium layer, respectively, to increase with increasing coating duration.

After a large series of experiments, the deposition conditions (the parameters duration and current density) which yielded an almost homogenous surface structure were chosen for further investigations. This is constituted at a current density of 80 mA and a duration of 4 min as well as at a mass fraction of 0.01% of lead acetate in the electrolyte. As Fig. 1a clearly shows, the electrochemical deposition led to a significant surface increase.

The experiments without lead acetate evidenced the typical building of the amorphous platinum layer on the electrode surface (visible in Fig. 1a) not to take place. Figure 1b shows platinum to be precipitated, but only in a very low and irregularly spread amount.

In comparison, Fig. 10a, b show the electrode surfaces of a new and a multiple-used electrode before deposition of platinum.

At a mass fraction of lead (II) acetate trihydrate of 1.6%, large non-typical structures appeared between the structures of the deposited platinum.

For identification, an EDX analysis was made at a location on the electrode surface that does not have the typical structure of amorphous platinum. In comparison, an EDX analysis was made at a site representing the known structure (Fig. 2) confirming the significant difference between both deposition products.

Based on these results, it is most likely that the atypical structures identified between the amorphous platinum products are Pb compounds deposited simultaneously.

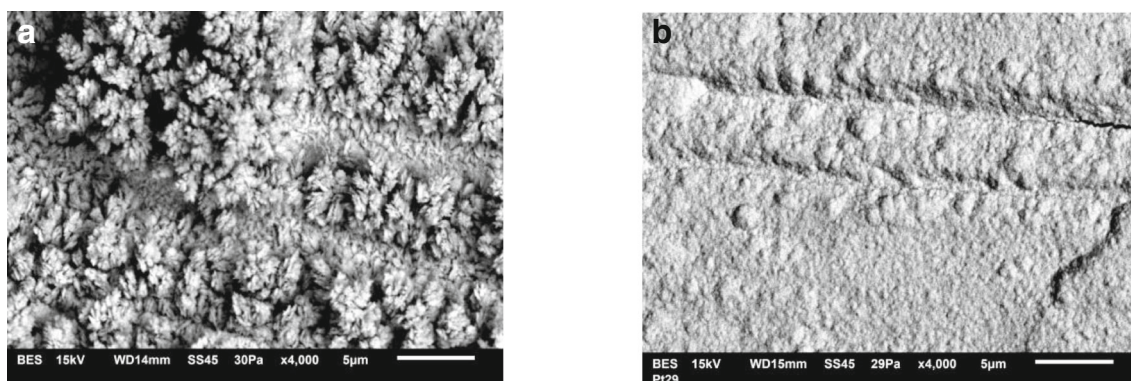


Fig. 1 **a** SEM picture of a platinum-coated platinum electrode (current density, 80 mA; duration, 4 min; mass fraction of lead acetate, 0.01%; $\times 4000$ magnification). **b** SEM picture of a platinum-coated platinum

electrode (current density, 80 mA; duration, 4 min; mass fraction of lead acetate, 0%; $\times 4000$ magnification)

Furthermore, a relatively high proportion of oxygen was determined (8.4%). It is obvious that this is due to the property of platinum to absorb higher amounts of oxygen [28].

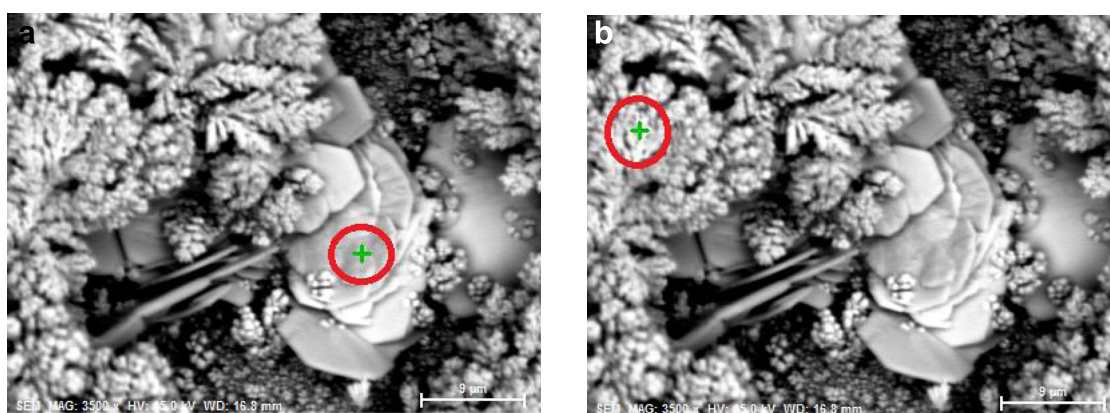
In the case of the simultaneous presence of lead in solution, also lead oxides could be formed and deposited on the electrode surface. The second EDX measurement in Fig. 2 shows that even in the amorphous Pt deposit lead was detected with a mass fraction of 30%. Therefore, the addition of 1.6% lead (II) acetate trihydrate to the electrolyte is too high and limits the formation of the known amorphous platinum layer on the electrode surface by deposition of lead or lead compounds. Consequently, a smaller active surface area of the platinum-plated platinum electrode is available for the adsorption of hydrogen.

Investigations on Pd-coating of Pt-electrodes by electrochemical deposition showed the thickness of the structure built on the platinum surface to increase with increasing current density and deposition duration. In contrast to Pt-coating,

Pd-coating provides a regularly granular surface structure even without the addition of lead acetate. The thickness of the Pd-layer is increased with increasing mass fraction of Pb(II) in the electrolyte. Figure 3a shows that under the conditions given, an almost homogenous Pd-layer is built.

At a current density of 150 mA, the platinum electrode is not completely covered by palladium. The Pd-layer shows gaps (see Fig. 3b).

To investigate the effect of the temperature on the surface structure, Pt-electrodes were exposed to heat. This was done by leaving them in hot ultrapure water at 80 °C for over 4 h and then drying them in the drying cabinet at 80 °C before they were investigated using an SEM. The images did not show the surface structure of the electrochemically coated Pt-electrodes to be significantly affected by the heat exposure. From this test result, it was concluded the surface structure of the electrodes not to be significantly affected by the



w(Pb) = 63.3% w(Pt) = 10.5%
w(Cl) = 11.4% w(O) = 8.4% w(C) = 6.4%

w(Pt) = 60% w(Pb) = 30%
w(C) = 6% w(O) = 2.5% w(Cl) = 1.5%

Fig. 2 EDX analysis on the surface of a platinized platinum electrode.

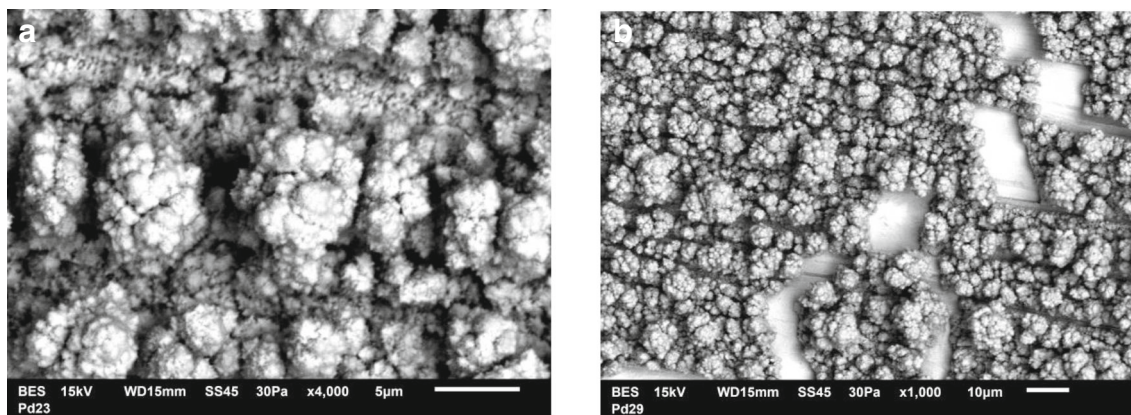


Fig. 3 **a** SEM picture of a palladium-coated Pt-electrode (current density, 110 mA; duration, 4 min; mass fraction of lead acetate, 0.01%; $\times 4000$ magnification). **b** SEM picture of a palladium-coated Pt-electrode

(current density, 150 mA; duration, 4 min; mass fraction of lead acetate, 0.01%; $\times 1000$ magnification)

temperature when Pt-plated or Pd-plated electrodes are used for the determination of pH reference buffer solutions in Harned cells at temperatures above 50 °C.

Investigations of sputtered platinum electrodes

Besides the electrochemical deposition, the sputtering [29] of platinum electrodes was also investigated. To do so, selected platinum plates were covered with platinum using magnetron sputtering. Afterwards, the sputtered platinum electrodes were investigated using SEM (Fig. 4).

The platinum layers obtained by sputtering are very thin (approx. 1 μm), so, the surface of the platinum plate is not significantly increased.

A visual comparison of a sputtered and an electrochemically platinized Pt-electrode reveals the black coloring of the platinized electrode surface, which is typical for amorphous structures (platinum black); the sputtered platinum surface, in contrast, is almost shiny.

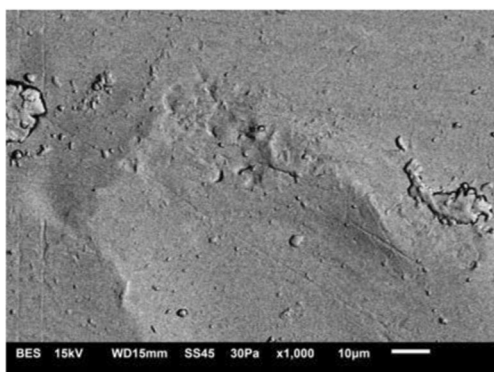


Fig. 4 SEM picture of a sputtered Pt-electrode (No. S1) ($\times 1000$ magnification)

Figure 5 shows a comparison between a sputtered Pt-electrode and an electrochemically platinized Pt-electrode.

Comparison between electrochemically coated and sputtered platinum electrodes using confocal laser scanning microscopy

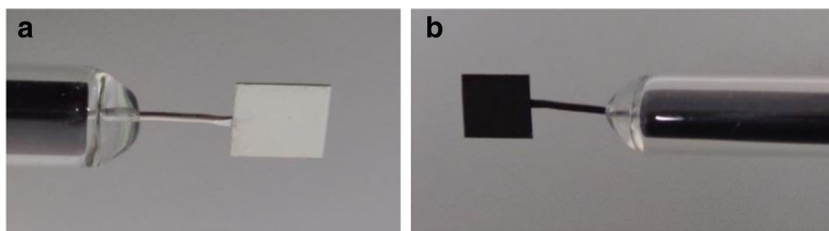
With SEM and optical microscopy, qualitative information about the surface of platinum electrodes have been obtained. To allow quantitative statements about the amount of platinum or palladium applied, respectively, selected platinum plates with platinum and palladium layer obtained by electrochemical deposition and two sputtered electrodes were compared using confocal laser scanning microscopy (CLSM) (Fig. 6).

The CLSM topography measurements reveal a grainy appearance of the electrode with palladium layer and consequently a much higher roughness compared to the rather smooth features on the electrode with platinum layer. The structures measured on the second one (b) are twice as thick as on the first (a).

Figure 7a shows a survey image of a sputtered electrode, which was assembled from several individual images (image stitching). Figure 7b shows a topographic image of the sputtered platinum electrode.

The images clearly show the difference between a sputtered and an electrochemically coated surface, thus, evidencing the sputtering method not to significantly increase the surface. It has to be taken into consideration that CLSM resolves the electrode surface with its texture, i.e., it shows a $2\frac{1}{2}$ -dimensional view of the surface. This allows for changes of the thickness to be captured, so, roughness parameters can be determined. As this method cannot see into or through the layer, it is not possible to draw conclusions concerning its exact thickness.

Fig. 5 **a, b** Comparison of a sputtered and a Pt-coated platinum electrode (80 mA/4 min)



However, for an assessment of the metrological use of Pt-electrodes in the primary pH measuring method, it is not necessary to know the exact thickness of the layer, anyway. On the other hand, this method is well-suited for a comparison between the roughness parameters of the electrochemically coated and the sputtered electrode.

Roughness parameters of electrochemically coated and sputtered platinum electrodes

With CLSM, quantitative information about the structure of the Pt- or Pd-coatings can be obtained, as it yields a topography image (height measurement). It thus allows, within certain limits set, e.g., by the steepness of slopes, to determine the surface area increase due to the grainy structures and roughness compared to the flat 2D-projection of the measured field. In this way, the effective active surface decisive for the efficiency of the electrodes can be determined in a good approximation. Different roughness parameters can be determined, which allows for a comparison between differently coated electrodes. For these experiments, the surface roughness average S_a as well as the surface area of the uncoated electrodes and the effective surface were determined. The surface increase was derived from the relation between the effective surface and the uncoated surface. The roughness average and the surface increase for each electrode investigated are shown in Fig. 8.

The test results show significantly higher roughness values, thus, a very much increased active surface for the electrodes treated by electrochemical deposition. The largest active surface determined was found on the Pt-electrode with palladium layer.

For the sputtered electrodes, a surface increase of about 1.1 was determined, i.e., only a 10% increase. Obviously, the surface increase obtained by electrochemical deposition is significantly higher. As in this method, the investigated object is scanned only vertically by the CLSM; the calculated surfaces do not exactly equal the actual surfaces.

The CLSM method only allows for a view on the surface of the object, i.e., undercut surface components are hidden for the measurement beam and therefore cannot be detected. Consequently, even larger active surfaces than measured by CLSM can be expected, particularly at the grainy electrochemically coated electrodes. Extreme outliers, a common measurement artifact in CLSM, could largely be avoided during the measurements by careful adjustment of the measurement parameters, and the remaining spikes were eliminated in the data sets before calculation of surface parameters so that an artificial increase of the effective areas by such spikes can largely be excluded. The clear main finding of these CLSM investigations is that the sputter process, compared to electrochemical deposition, is not able to increase the surface of platinum electrodes significantly; thus, they cannot be used as platinum hydrogen

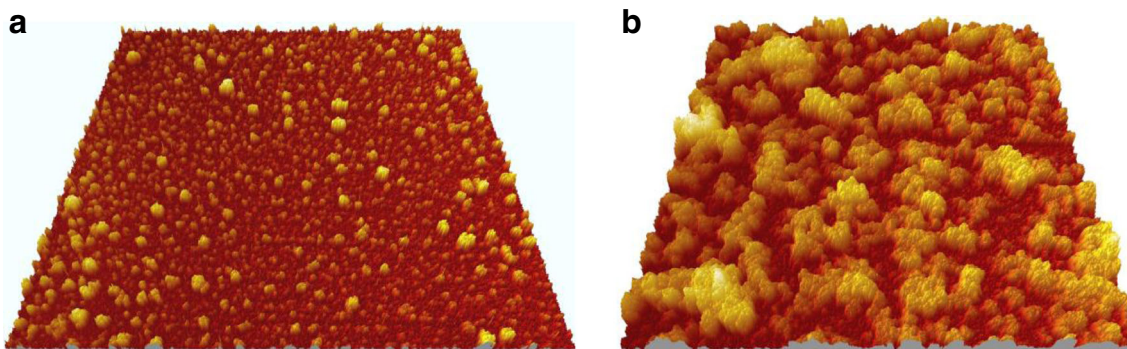


Fig. 6 **a** CLSM image of a platinized electrode. Deposition conditions: 80 mA/4 min/lead acetate: 0.01%; 3D view of topography; axes scaling ratio is 1:1:1; approx. 645 μm \times 645 μm \times 31 μm ; Olympus LEXT CLSM, $\times 20$ objective, zoom $\times 1.0$. **b** CLSM image of a palladinized

electrode. Deposition conditions: 110 mA/4 min/lead acetate: 0.01%; 3D view of topography; axes scaling ratio is 1:1:1; approx. 645 μm \times 647 μm \times 75 μm ; Olympus LEXT CLSM, $\times 20$ objective, zoom $\times 1.0$

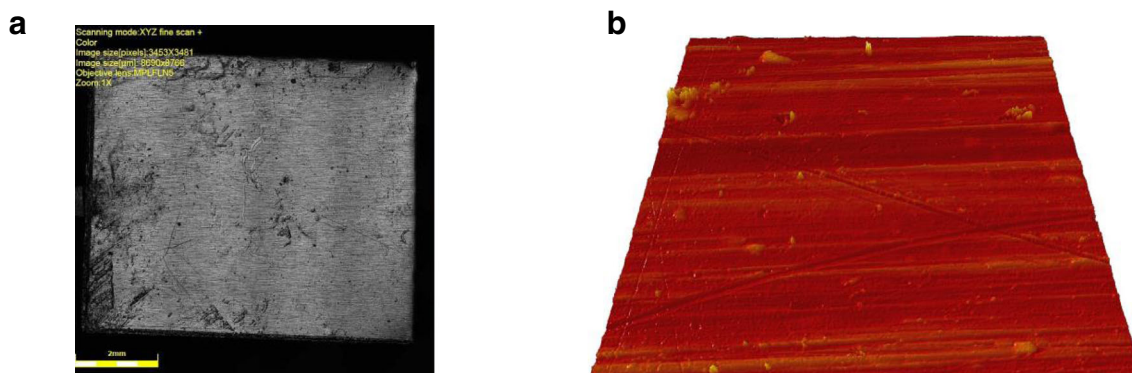


Fig. 7 **a** Survey image of a sputtered electrode with $\times 5$ objective, stitched from 9 individual pictures of $2577 \mu\text{m} \times 2579 \mu\text{m}$ each (intensity image Olympus LEXT). **b** Sputtered electrode; 3D image of

topography; axes scaling ratio is 1:1:1; approx. $130 \mu\text{m} \times 130 \mu\text{m} \times 1.4 \mu\text{m}$; Olympus LEXT CLSM, $\times 100$ objective, zoom $\times 1.0$

electrodes for primary pH measurements, while the electrochemically coated ones yield a promising 7- to 11-fold surface increase.

Determination of the standard potential of Ag/AgCl-electrodes with electrochemically coated and sputtered platinum electrodes

In the Harned cells used for primary pH measurements, the PHE is combined with a Ag/AgCl-electrode. Once primary pH measurements require a very high accuracy, it is essential to determine the standard potential of Ag/AgCl-electrodes with a small measuring uncertainty.

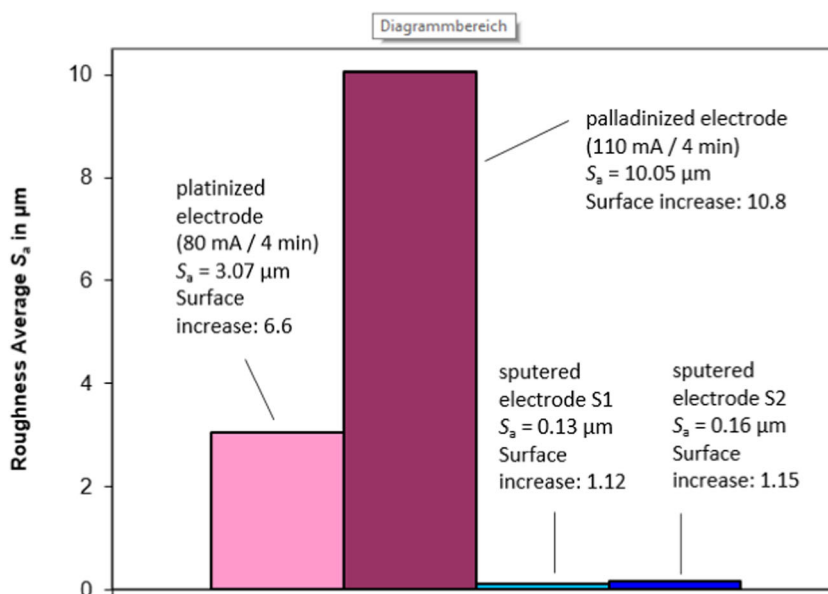
The values expected for these standard potentials at different temperatures are substantiated by theory [30] as well as by practical measurements, so, they are a

quality criterion for primary pH measurements by Harned cells.

Each electrochemically coated and sputtered Pt-electrode used in the experiments was combined with a Ag/AgCl-electrode in a Harned cell filled with 0.01 mol/kg HCl, and the cell potential was determined at 25 °C. The standard potential of the Ag/AgCl-electrodes was calculated from the cell potential according to Eq. (1):

$$E_{\text{Ag}}^0 = E + \frac{2 \cdot R \cdot T \cdot \ln 10}{F} \cdot \left[\lg(m_{\text{HCl}}) + \lg(\gamma_{\pm\text{HCl}}) + 0.25 \lg \frac{p^0}{p_{\text{H}_2}} \right] \quad (1)$$

Fig. 8 Roughness average S_a of investigated platinum electrodes



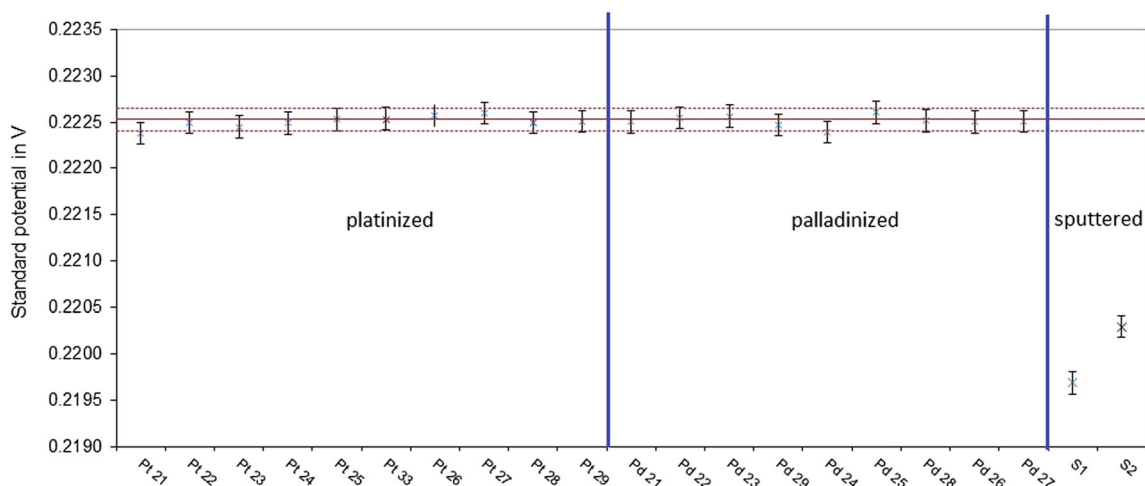


Fig. 9 Standard potentials of Ag/AgCl-electrodes determined at 25 °C using differently electrochemically coated and sputtered Pt-electrodes

with

E	Measured cell potential in V
T	Thermodynamic temperature in K
m_{HCl}	Molality of hydrochloric acid in mol kg ⁻¹
$\gamma_{\pm\text{HCl}}$	Mean activity coefficient of hydrochloric acid
p^0	Atmospheric pressure under standard conditions in Pa
p_{H_2}	Partial pressure of hydrogen in Pa

The partial pressure of hydrogen is the difference between the atmospheric pressure p_{at} and the vapor pressure of the solution [31].

In case of dilute aqueous solutions, the vapor pressure is estimated to be equal to that of pure water $p_{\text{H}_2\text{O}}$. Furthermore, the hydrostatic pressure p_{hy} has to be considered, in dependency from the immersion depth of the hydrogen inlet in the solution.

The partial pressure of hydrogen is calculated according to Eq. (2).

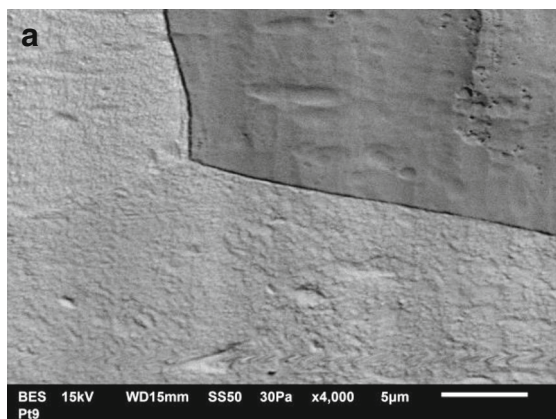
$$p_{\text{H}_2} = p_{at} - p_{\text{H}_2\text{O}} + p_{hy} \quad (2)$$

The influence of the hydrostatic pressure is empirically investigated for aqueous solutions [31, 32]. The partial pressure of the saturated water vapor can be calculated by Wagner equation [31, 33].

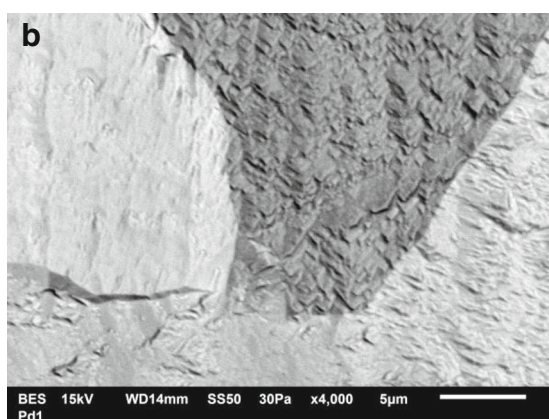
The given Eq. (1) is the basis for the calculation of the expanded measurement uncertainty of the standard potentials determined.

The expanded measurement uncertainty amounts to $U(k=2) = 0.00012$ V.

The following figures show a comparison of the standard potentials, which were determined using a combination of



SEM image of a new uncoated platinum electrode (4000 x magnification)



SEM image of a multiply used, uncoated platinum electrode (4000 x magnification, too)

Fig. 10 **a** SEM image of a new uncoated platinum electrode ($\times 4000$ magnification). **b** SEM image of a multiply used, uncoated platinum electrode ($\times 4000$ magnification, too)

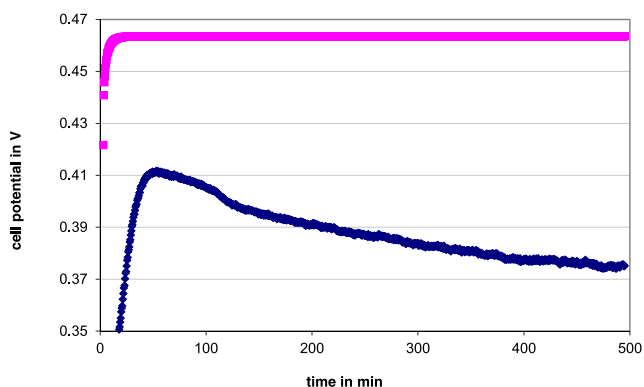


Fig. 11 Cell potential of a new, uncoated electrode (lower graph, dark blue) and a multiple-used (aged) (upper graph, magenta), uncoated platinum electrode, combined with Ag/AgCl-electrodes in 0.01 mol/kg HCl in a period of 500 min

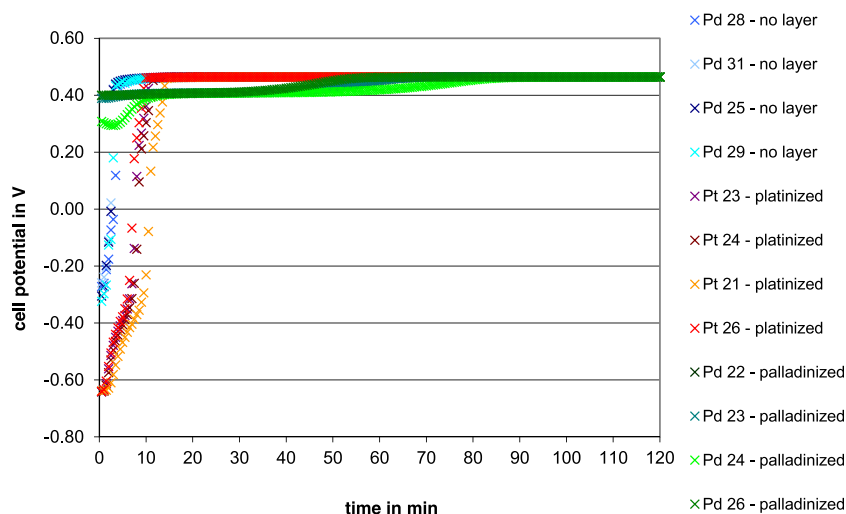
platinum electrodes (see supplementary information, Table 2) and a Ag/AgCl-electrode.

The investigations of the electrodes no. Pt 22 (platinized) and Pd 23 (palladinized) using SEM showed an almost homogenous surface. For this reason, the standard potentials of these electrodes were used as reference values, for a comparative depiction of the measuring results. In the diagram in Fig. 9, this reference value is depicted as a red line. The measurement uncertainty is depicted as tolerance range (broken line) around the reference value.

For each experiment, usually two electrodes were used. Up to five measurements have been carried out with each investigated electrode. The mean values of the measurement results built the basis for the evaluation of investigation.

The results shown in Fig. 8 evidence for the electrochemically coated Pt-electrodes in the range investigated to yield comparable results which confirm the reference value within the measurement uncertainty.

Fig. 12 Development of the cell potential of platinum electrodes, combined with Ag/AgCl-electrodes, in the first 120 min after starting hydrogen flow



The results of the sputtered electrodes no. S1 and S2 are significantly different from the standard potentials expected. These results confirm the sputtered electrodes not to be suitable for primary pH measurements using the PHE under the conditions given. Moreover, the tests confirm the function as PHE not to be significantly affected by the conditions of the electrochemical deposition, even though the conditions applied for the electrochemical deposition of platinum electrodes are defined slightly differently in different institutes.

However, it is very important to keep the once defined parameters very exactly and to control them so as to ensure the required reproducibility of the method.

Investigation of shiny (uncoated) platinum electrodes

From literature [34–36], it is known that many experiments with shiny platinum surfaces under current conduction have been carried out. This was the reason why the investigations of this work were extended to shiny (uncoated) Pt-electrodes. In these tests, it was differentiated between new platinum electrodes which have never been used before and platinum electrodes which have been platinized, used for measurements, and cleaned multiple times in the past. Figure 10a, b shows a comparative image of two shiny Pt-electrodes. In Fig. 10a, the surface of a new, unused platinum electrode and, in Fig. 10b, a platinum electrode which has multiply been platinized, used for primary pH measurements and then cleaned using aqua regia, are shown.

The images reveal the surface character of new, shiny platinum electrodes to be different from the surface character of multiple-used platinum electrodes. From these results, it can be concluded that the surface of a platinum electrode cannot be brought back to the initial state again after multiple platinizing and cleaning. We could talk of a “conditioning” of the platinum electrode. For a characterization of the influence of

the surface character of the Pt electrodes on their performance, a new platinum electrode and a multiply used one were, each, combined with a Ag/AgCl-electrode, and the cell potential was determined in a 0.01-mol/kg HCl.

Figure 11 depicts the cell potential measured with both electrodes over a period of 500 min.

After a short while, the multiple-used, shiny Pt-electrode reaches a value close to the expected cell potential of about 0.463 V. The new, shiny Pt-electrode shows an increase of the cell potential up to a value of 0.41 V and then a steady decrease.

The multiple used, shiny Pt-electrode provided unexpected results. To substantiate the results, further tests of multiple-used Pt-electrodes compared to electrochemically coated Pt-electrodes were carried out. To do this, four multiple-used, shiny (uncoated) Pt-electrodes, four platinized Pt-electrodes, and four palladinized Pt-electrodes were investigated. The platinized and the palladinized electrodes were electrochemically coated under the conditions chosen and defined on the basis of previous SEM examinations.

The Pt-electrodes were used to determine the standard potential of Ag/AgCl-electrodes in a 0.01-mol/kg HCl to examine and compare the response times of the electrodes. These tests were followed by measurements over a period of 600 min. In Fig. 12, results for the beginning of the long-term investigation (the first 120 min) are shown.

The platinized and the palladinized, as well as the uncoated, shiny Pt-electrodes, show similar responding characteristics. The multiple-used, shiny Pt-electrodes and the platinized Pt-electrodes reach the expected value after more than 15 min. With the palladinized Pt-electrodes, the expected cell potential was reached after about 100 min only.

In principle, this is not a critical aspect in the primary pH measurements with Harned cells because an equalization time of about 120 min is provided, anyway, before the measurement is started.

In Fig. 13, the cell potential of the four multiple-used, uncoated platinum electrodes is compared to a platinized and a palladinized Pt-electrode.

The time period shown in Fig. 13 represents the usual duration of primary pH measurements with Harned cells. The standard deviation for each platinum electrode investigated within in the selected period was calculated from the cell potential measured. The assessment of the measurement results revealed a very stable cell potential for the platinized as well as the palladinized Pt-electrode. The standard deviation of the cell potential is $1 \cdot 10^{-6}$ V; thus, it is negligibly small. The four multiple-used, shiny (uncoated) Pt-electrodes show a significantly higher standard deviation of up to $6 \cdot 10^{-5}$ V and a drift behavior which was continued until the end of the measurement period of 600 min.

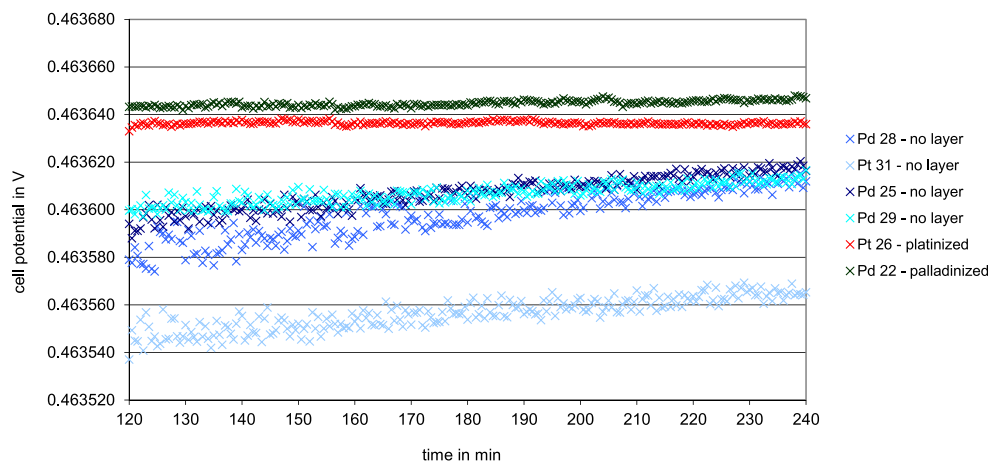
For a complete assessment of the measurement results, the measurement uncertainty for primary pH measurements using multiple-used, shiny platinum electrodes was estimated. This revealed an expanded measurement uncertainty of $U(k=2) = 0.005$ at 25 °C. The measurement uncertainty which can be obtained using electrochemically coated Pt-electrodes was $U(k=2) = 0.0025$ at 25 °C. According to these investigation results, shiny platinum electrodes are not suitable for primary pH measurements with Harned cell with least measurement uncertainty.

Conclusions

The surface structures of electrochemically platinized and palladinized Pt-electrodes were assessed by scanning electron microscopy, optical microscopy, and confocal laser scanning microscopy. Based on the investigation results, parameters for the treatment of platinum electrodes by electrochemical deposition were derived.

Optimal conditions for platinized Pt-electrodes are constituted at a current density of 80 mA and a duration of 4 min as

Fig. 13 Cell potential of four used, uncoated Pt-electrodes (blue) in comparison with a platinized (red) and a palladinized (green) Pt-electrode (measured with Ag/AgCl-electrodes in 0.01 mol/kg HCl, the figure shows time frame from 120 to 240 min after the inlet of hydrogen was started)



well as at a mass fraction of 0.01% of lead acetate in the electrolyte. For palladium-coated platinum electrodes, a current density of 110 mA is to be used.

Based on measurements with Harned cells, it was revealed that slightly different conditions of electrochemical deposition do not have a significant effect on the measuring results.

However, it is very important to exactly comply with the defined deposition parameters to ensure the required reproducibility of the primary method.

The investigations presented in this work do not allow any statement about a possible difference of layer formation during electrochemical deposition between new and aged platinum electrodes. This aspect should be considered for further investigations.

The examinations on sputtered electrodes revealed that the surface increase required for the realization of a platinum hydrogen electrode could not be achieved under the given sputtering conditions.

The examination of shiny (uncoated) platinum electrodes revealed a significant difference between multiple-used shiny platinum electrodes and new, shiny platinum electrodes.

The new, uncoated electrodes did not reach the expected value of the cell potential. Measurements with multiple-used and uncoated Pt-electrodes showed that the uncertainty is twice as high as the one for measurements with platinized Pt-electrodes applying electrochemical deposition.

Thus, a treatment of platinum electrodes by electrochemical deposition under defined conditions is required to obtain reliable and reproducible results of primary pH measurements using Harned cells.

These investigations revealed deposition parameters suitable as a basis for the standardization of the primary method using Harned cells at up to 90 °C.

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