

# Dynamics of single hydrogen bubbles at a platinum microelectrode

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## Abstract

The bubble dynamics, including the formation, growth and detachment, of single H<sub>2</sub> bubbles were studied at a platinum microelectrode during the electrolysis of 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte. The bubbles were visualized through a microscope by a high-speed camera. Electrochemical measurements were conducted in parallel to measure the current transient. The periodic current oscillations, resulting from the periodic formation and detachment of single bubbles, allow the bubble lifetime and size to be predicted from the current transient. A comparison of the bubble volume calculated from the current and from the recorded bubble image shows a gas evolution efficiency increasing continuously with the growth of the bubble until it reaches 100%. Two different substrates, glass and epoxy, were used to embed the Pt wire. While nearly no difference was found with respect to the growth law for the bubble radius, the contact angle differs strongly for the two types of cell. Data provided for the contact point evolution further complete the image of single hydrogen bubble growth. Finally, the velocity field

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3      driven by the detached bubble was measured by means of PIV and the effects of the convection  
4      on the subsequent bubble were evaluated.  
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## 10      Introduction 11 12

13      The economic large-scale production of hydrogen is of high interest for both hydrogen-based en-  
14      ergy storage systems and mobility systems employing fuel cells. One important piece of technol-  
15      ogy to produce the required high-purity hydrogen consists in water electrolysis. Commercially,  
16      the technique has been used for a long time in alkaline electrolyzers, although its percentage of  
17      world production is only around 4%. The possibility to power water electrolysis with renewable  
18      energies has increased research in the field of both polymer exchange membranes (PEMs)<sup>1</sup> and  
19      alkaline electrolyzers.<sup>2–4</sup> One main challenge making water electrolysis economically competitive  
20      is to raise their efficiency by decreasing the cell voltage. In this respect, electrode coverage by  
21      gas bubbles<sup>5–7</sup> is one of the key sources which create undesired overpotentials. Thus, the efficient  
22      detachment and transport of gas bubbles away from the electrodes by a corresponding electrode  
23      design, zero-gap electrolyzers<sup>8</sup> or by external fields,<sup>9</sup> as discussed below, is important.  
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26      One precondition for efficient bubble management<sup>7</sup> is a detailed understanding of the key  
27      mechanisms of hydrogen bubble formation, growth and detachment. However, despite extensive  
28      efforts in the past, important aspects of bubble dynamics, such as the interaction and coalescence  
29      of bubbles or the different growth modi of the bubbles themselves, are not yet fully answered.  
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31      Also, new ways to get rid of large bubbles by means of magnetic fields,<sup>10–14</sup> ultrasound<sup>15</sup> or su-  
32      pergravity<sup>9</sup> mostly examine the bubble ensemble from the top and not from the side. Hence, to  
33      provide that necessary information on the bubble shape profile, including the contact line the bub-  
34      ble forms with the electrode, microelectrodes<sup>16–24</sup> are the method of choice. Here, the multiple  
35      growth of several bubbles which shade each other can be largely suppressed and single bubble  
36      behaviour can be studied in detail. To do so, acid electrolytes, e.g. based on H<sub>2</sub>SO<sub>4</sub>, are favored in  
37      contrast to alkaline ones, since highly periodic bubble formation cycles (see e.g.<sup>18,21,24,25</sup>) can be  
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observed instead of erratic ones. Despite this regularity of bubble formation in acidic electrolytes, the sequence of growth modi, typically expressed by the growth law for the radius R

$$R(t) = \beta \times t^b, \quad (1)$$

differs significantly between different studies. Agreement exists about a first, inertia-controlled sequence, during which a  $R(t) \propto t$  dependence is predicted.<sup>20,26</sup> This was observed in a number of studies,<sup>20,27</sup> although with a poor temporal resolution, restricted mainly to a few data points if at all. The  $R(t) \propto t^{1/2}$  regime, as predicted by Scriven<sup>28</sup> for a dynamics controlled by the diffusion of dissolved H<sub>2</sub> towards the bubble, was found to be a succeeding regime by other authors.<sup>16,17,20,27</sup> Other experiments<sup>18</sup> were able to convincingly show that the mass transfer of dissolved hydrogen is not the rate-limiting step and proved that their bubbles follow a  $R(t) \propto t^{1/3}$  which was also identified in the other works<sup>19,24,29</sup> in particular for high current densities. Although Westwater and co-worker in their pioneering studies<sup>16,17</sup> found the  $t^{1/2}$  dependence for the single bubbles, they also noticed an exponent close to  $t^{1/3}$  when coalescing bubbles are present.<sup>16</sup> This fact is interesting because the validity of the growth laws was believed to be restricted to cases where the adhering bubbles do not mutually interfere.<sup>30</sup> Further works, such as<sup>20,27</sup> did not only found one or two of these regimes but also reported a continuous transition  $t \rightarrow t^{1/2} \rightarrow t^{1/3}$ .

A similar diversity is found with respect to the behaviour of the contact angle during the bubble evolution. The contact angle depends on the wettability of the electrode and on the surface tension of the hydrogen-electrolyte interface. While<sup>16</sup> report on fluctuating contact angles at the Pt electrode in the range of  $\theta \sim (5\ldots15)^\circ$  together with a nil overall change,<sup>17</sup> reports a permanently decreasing contact angle with increasing bubble radius for the Ni microelectrode and comparable H<sub>2</sub>SO<sub>4</sub> concentration, also found by<sup>24</sup> for their Pt microelectrode. By contrast, for a larger transparent Pt electrode,<sup>24</sup> observed significantly higher contact angles which even slightly increases with growing R.

The present work aims to resolve some of these issues in a combination of high-speed mi-

croscopy coupled with extensive image processing and electrochemical measurements. Particular emphasis is also given to a precise description of the bubble geometry, by providing time-resolved data not yet available in the literature. Furthermore, particle image velocimetry is used to study the detachment-induced microconvection of the bubbles and their impact on succeeding bubbles.

## Experimental Methods

### Electrochemical Setup

A 3-electrode electrochemical setup was used to generate a single H<sub>2</sub> bubble in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte (Fig. 1(a)). A cuboid glass cuvette (Hellma) with the dimension of height × width × depth = 45 × 10 × 10 mm was used as the electrochemical cell. The working electrode was made from a 100  $\mu$ m Pt wire with a purity of 99.99 %. The cell was manufactured in two different versions. The first type is free of any organic components and was produced by means of burning the Pt wire into a glass capillary. This capillary was inserted into a Teflon plate. For the second type, epoxy resin was used to embed the Pt wire to prepare the working electrode. The Pt surface for both cell versions was polished with SiC paper, ending with #4000. The bottom of the glass cuboid cell was cut to mount the Teflon or epoxy plate with the Pt electrode inside. A Pt wire with a diameter of 1 mm was used as the counter electrode and the mercury/mercurous sulphate electrode (MSE) served as the reference electrode through a salt bridge. All the potentials refer to the MSE (650 mV vs. SHE). The measurements were conducted in the Pt glass cell if not otherwise noted in the manuscript.

Electrolysis was carried out at potentiostatic conditions with a Zahner Zennium electrochemical workstation at -1.5 V for 600 seconds with a sampling rate of 100 Hz. The glass cell and Teflon plate were cleaned with Caro's acid and rinsed carefully with deionized water before performing the first measurement. Before every further series of experiments, the cell and electrode were cleaned 3 times with distilled water and fresh electrolyte. After the experiments, the glass cell was filled with distilled water so that the Pt electrode was preserved under wet conditions. Before the

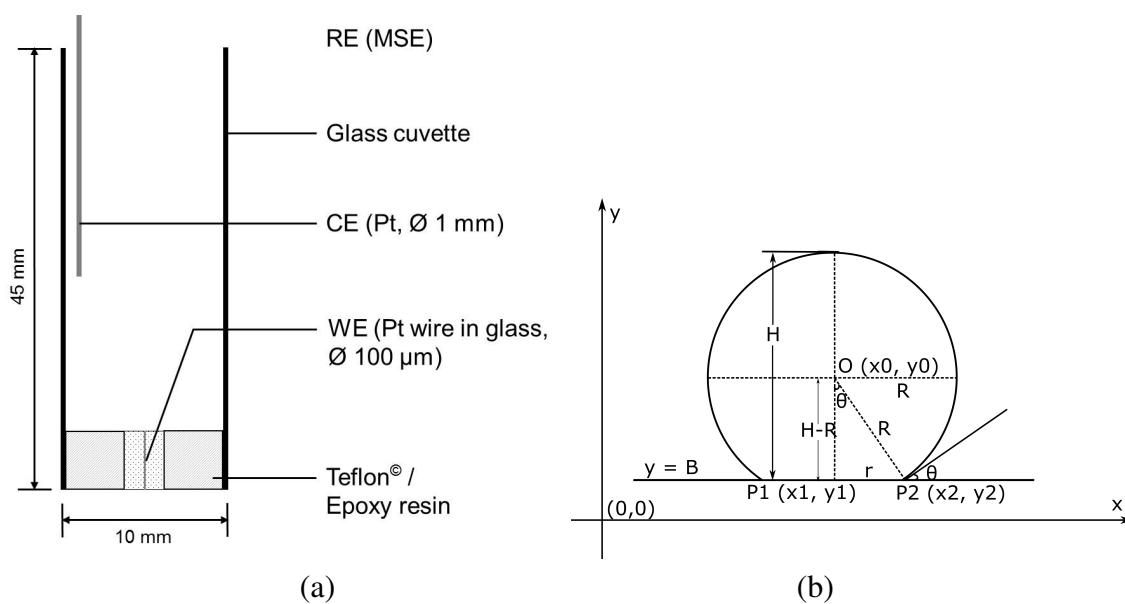


Figure 1: Sketch of (a) electrochemical cell and (b) bubble geometry.

next series of experiments the glass cell was treated with the same rinsing procedure as detailed above.

A microscope was used to visualize the gas bubble in side view with a magnification between 10 and 40. The illumination was a LED light together with a diffuser at the back of the cell. The bubble growing videos were taken by a high speed camera (IDT NX4-S1) with a frame rate from 100 to 4000 frames per second (fps) which was increased to 10000 fps in a few experiments. One video containing 1000 to 4600 frames of images was recorded in each minute throughout the measurements. The videos were then converted to images for further analysis. To visualize the flow field, tracer particle (polystyrene particles with a size of  $1 \mu\text{m}$ ) were added to the electrolyte. These experiments were performed exclusively in the Pt epoxy cell to avoid any contamination by surface-active species in the Pt glass cell.

## Description of the bubble geometry

The extraction of the bubble geometry, depicted in Fig. 1, as a function of time was done via image processing of the high-speed movies and is detailed in the Supporting Information. Three different strategies to assess the key quantity, the bubble radius  $R$ , were adopted: (i)  $R$  was determined via

the Feret diameter, defined as the longest distance between two points in the selected area, using ImageJ "analyze particle" method. (ii)  $R$  was obtained by direct measurement in the gray-value image and assuming that the maximum width of the bubble equals the diameter of the bubble. (iii) Fitting of the bubble interface assuming the bubble as a part of a sphere. For this purpose, a circular fit of the bubble interface by Matlab was performed to obtain the equation of a circle for the interface of the hydrogen bubble, given by

$$(x - x_0)^2 + (y - y_0)^2 = R^2 \quad (2)$$

To speed up the number of iterations and the accuracy of the fitting procedure of  $R$  and the bubble center  $(x_0, y_0)$ , initial values of the three quantities were determined by measurement in the gray-value image (see Supporting Information).

From the fit, the height,  $H$ , of the bubble can be derived

$$H = (y_0 - B) + R. \quad (3)$$

The volume  $V$  of the hydrogen bubble then follows via

$$V = \pi \times H^2 \times (R - H/3) \quad (4)$$

One example to compare the three methods is shown in the Supporting Information. The Feret diameter is bigger than the real value due to the difficulty in distinguishing the bubble by simple threshold analysis. Furthermore, it is clearly seen that the width of the bubble, directly measured in the gray-value image, fits well to the diameter calculated by the circular fit.

Further important quantities of the bubble are the location of the contact line where the bubble forms on the electrode, and the corresponding contact angle, cf. Fig. 1b. Both quantities can be

readily derived when the equation for the electrode position,

$$y = B \quad (5)$$

is given together with the equation of the circle.

To do so, we substitute Eq.5 into Eq.2 and solve for the zeroes

$$x_{1,2} = x_0 \pm \sqrt{R^2 - (B - y_0)^2} \quad (6)$$

The two solutions  $x_1$  and  $x_2$  are the x coordinates of contact points  $P_1$  and  $P_2$  in Fig. 1. The diameter  $d$  of the circular contact line which encompasses that area of the electrode covered by the hydrogen bubble is given by

$$d = x_2 - x_1. \quad (7)$$

The contact angle which the liquid-gas interface forms with the Pt electrode can be determined from the slope  $dy/dx$  obtained upon differentiating eq.(2) with respect to x to obtain  $dy/dx = -(x - x_0)/(y - y_0)$ . The contact angle,  $\theta$ , then follows via  $\theta = atan(x_1 - x_0)/(y_1 - y_0)$ . Alternatively, the contact angle can be calculated based on the  $H$  and  $R$ , obtained as described above:

$$\theta = acos \frac{H - R}{R} \quad (8)$$

In the Supporting Information one example compares the two methods of contact angle determination. The result showed a good agreement of both methods for most of the time, but the circular-fit method showed fewer variations from the mean value.

Frequently, another method is used in the literature,<sup>24</sup> termed "footprint method",

$$\theta = asin \frac{r}{R} \quad (9)$$

in which  $R$  and  $r$  are the radii of the bubble and of the contact line, respectively. This method needs

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3 to measure the footprint of the bubble, which was possible in<sup>24</sup> by using a transparent substrate. In  
4 the standard case of a non-transparent electrode, in particular when small coalescing bubbles are  
5 generated at the rim of the larger bubble, this method is difficult to apply.  
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8 Based on the issues discussed above, the circular fit method turns out to be the method of  
9 choice in the automated processing of large numbers of bubble images. It is therefore used for  
10 both radius and contact angle determination if not indicated otherwise. Before doing this, we  
11 checked the accuracy of the method by determining the  $R$  and  $\theta$  of synthetic bubbles, supposed to  
12 grow via  $R(t) = \beta t^{1/3}$  (see Supporting Information). Here it turned out that the accuracy of the  $R$   
13 determination is better than 0.5 pixels. However, the determination of the contact line diameter is  
14 affected with a typical error of  $\pm 10$  pixels, related to the uncertainty in the determination of the  
15 bubble center. Therefore, the uncertainty of the  $\theta$  determination is  $\pm 2^\circ$ .  
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## 28 Results

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32 The experiments were conducted over a timespan of 600 s during which electrochemical and mi-  
33 croscopic measurements ran in parallel. At the given potential, E=-1500 mV, applied at the Pt  
34 microelectrode, the current-time transient passes periodic current oscillations. A subsequence con-  
35 taining 15 oscillations is depicted in Fig. 2(a). Parallel microscopic observation, shows that each  
36 period of the current oscillation is the manifestation of a hydrogen bubble cycle, starting with the  
37 formation of the bubble and terminating by its detachment from the electrode. In Fig. 2(b) we  
38 compare the lifetime  $\tau$  of the gas bubble, determined via microscopy, to the period,  $\tau_{EC}$ , of the  
39 current-time plot, calculated by Matlab. The lifetime provided by both techniques differs by not  
40 more than 20 ms (3%) at maximum. Fig. 2(b) shows that the lifetime increases with progressing  
41 time. The origin is seen in a change of the electrode conditions due the adsorption of H atoms and  
42 other species at the Pt surface at longer operation time.  
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54 Before going into the dynamics of the bubble cycles, it is worth commenting on the waiting  
55 time,  $\Delta t_w$ , until the first hydrogen bubble is formed.  $\Delta t_w$  was discussed by Glas and Westwater<sup>17</sup> for  
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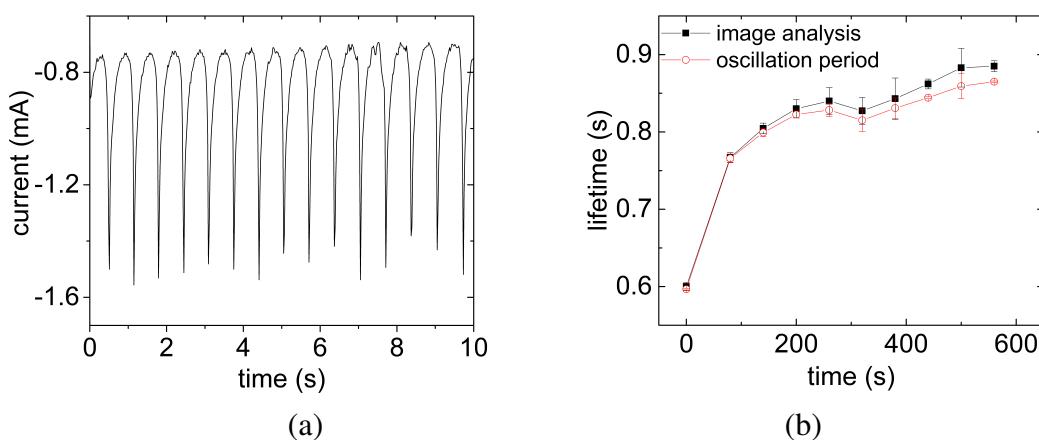


Figure 2: (a) A 10 second section taken from the current-time behaviour over 600 s at  $E = -1.5$  V. (b) The change of period  $\tau_{EC}$  of the current oscillations obtained from (a) in comparison to the bubble lifetime  $\tau$  determined by microscopy as a function of time. All experiments were performed in the Pt-glass cell.

different electrode materials. For hydrogen bubbles evolving at Ni electrode, a  $\Delta t_w$  up to 30 s was observed for  $j = 400 \text{ A/m}^2$ . Actually, there was no measurable waiting time in our experiments. Indeed, microscopic inspection with a high frame rate (10000 fps) shows that the first bubbles form in less than  $\Delta t_w < 0.1$  ms after the potential was applied at the Pt microelectrode exposed to a fresh electrolyte. This signals the existence of a sufficiently large number of nucleation sites at the electrode.

With a given hydrogen diffusivity  $D$  ( $D = 4.2 \times 10^{-9} \text{ m}^2/\text{s}$ )<sup>31</sup> in the electrolyte, the front of dissolved hydrogen travels over a distance  $\delta \sim \sqrt{D \times \Delta t}$ . To estimate the resulting average concentration of dissolved hydrogen  $c_{H_2}$  we consider a small hemispherical volume  $V_c$  of a radial extension  $R_0 + \delta$  and a height  $\delta$  above the electrode. Applying eq. (4) under the constraint of  $R_0 \gg \delta$ , we obtain  $V_c = 2\pi R_0^2 \times \delta$ . The concentration  $c_{H_2} = \dot{n}_{H_2} \Delta t_w / V_c$  is then given by

$$c_{H_2} = 2I\sqrt{\Delta t_w} / (zF\pi R_0^2\sqrt{D}) \quad (10)$$

using Faraday's law.  $\dot{n}_{H_2}$  is the number of moles of dissolved hydrogen generated per time;  $I$ ,  $F$  and  $z$  refer to the current, the Faraday constant,  $F = 96500 \text{ C/mol}$  and the number of electrons

involved ( $z = 2$ ).  $c_{H_2}$  scales with  $\sqrt{\Delta t_w}$ . Setting  $I \sim 1.5$  mA and  $\Delta t_w \sim 10^{-4}$  s, in accordance with our experimental conditions, we obtain  $c_{H_2} = 0.3$  mol/l.

Taking into account the saturation concentration  $c_{H_2}^s$  of  $H_2$  of approx  $0.75 \times 10^{-3}$  mol/l (28°C),<sup>17</sup> the supersaturation is  $\Delta c_{H_2} = c_{H_2} - c_{H_2}^s \sim 0.29$  mol/l. This value slightly exceeds the values in the literature.<sup>17,31,32</sup> Vogt<sup>31</sup> was able to show that the rather different values of  $\Delta c_{H_2}$  in 1M  $H_2SO_4$  reported by<sup>32</sup> (0.1 mol/l for  $j = 10^4$  A/m<sup>2</sup>) and<sup>17</sup> (0.05 mol/l, same current) belong to different regions, the electrode and bulk, respectively. Hence, in view of the rather high current density, the estimated supersaturation close to the electrode is sufficient to achieve bubble nucleation even for very short  $\Delta t_w$ .

## H<sub>2</sub> bubble cycle

To analyse the bubble cycle in more detail, Fig. 3 shows a zoom into one period of the current oscillations together with representative stages (A-F) of the corresponding bubbles gained from microscopy. The synchronization between the application of the electric potential and the video signal reveals the coincidence of the moment of bubble detachment and the minimum of  $I$ . Thus, every bubble cycle starts with a high current when the large precursor bubble has just detached from the electrode and the latter is only covered by the first few small hydrogen bubbles. Point A shows an image close to this moment. As the growing bubble increases in size (points B-C), the total current decreases, reaching a minimum at about 60% of  $\tau$  ( $0.6 \times \tau$ ) around point D. Before the bubble detaches (point F), the current increases again (point E). This interesting but surprising behaviour is very robust. It is correlated by a small translation of the bubble along the electrode. This leads to a reduction of the covered electrode area, as will be shown later on. The process of detachment is always accompanied by the immediate formation of small bubbles. They rapidly coalesce to form the next larger bubble, the growth of which then dominates the bubble cycle.

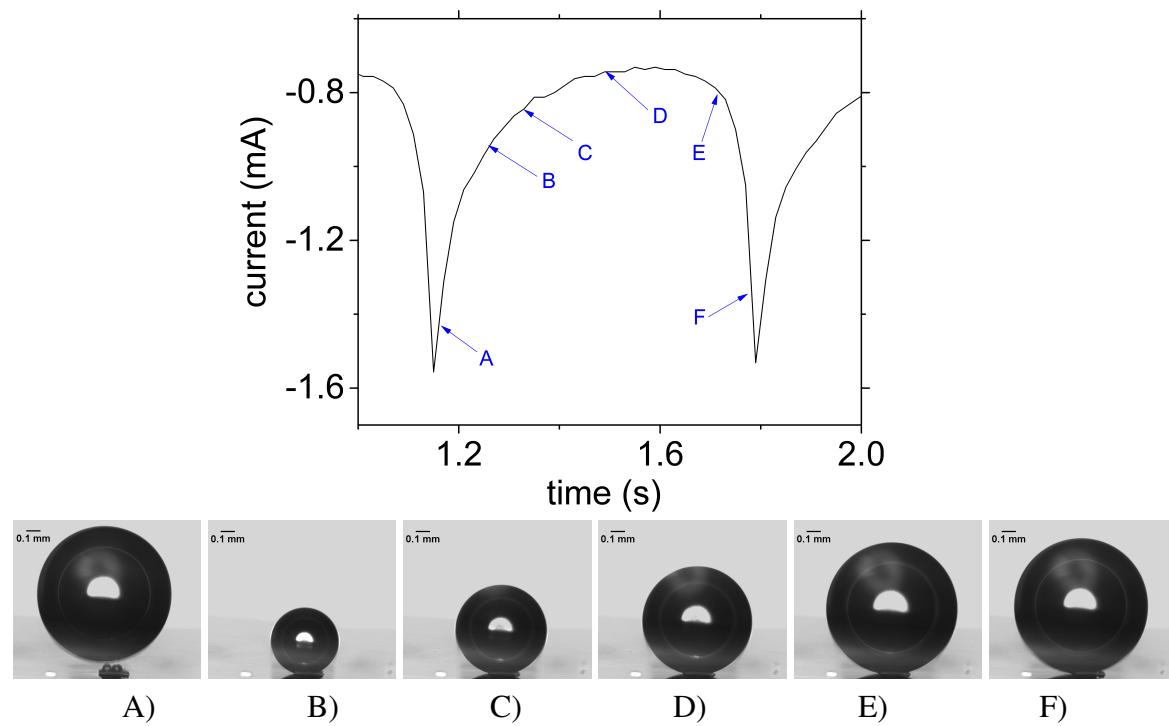


Figure 3: Zoom into a period of the current-time behaviour at  $E = -1.5$  V with peaks in the current ( $-1.55\text{ mA}$ ) occurring at  $t_0 = (1.15 \pm 0.01)$  s and  $t = t_0 + \tau$ . Characteristic stages of the bubble evolution, denoted by A-F (from left to right), are shown below. Frame A was taken at  $t=t_0 + 0.01\text{ s}$ . All experiments were performed in the Pt-glass cell.

### Growth mode of the bubbles

Following Darby & Haque<sup>18</sup> the temporal change,  $\dot{n}_{H_2}$ , of the moles of dissolved hydrogen in the electrolyte (volume  $V_l$ ) between the electrode and bubble is given by the difference between the production of hydrogen per second at the electrode,  $\dot{n}_I$ , and the consumption,  $\dot{n}_b$ , by the growing bubble (volume  $V$ ):

$$\dot{n}_{H_2} = \dot{n}_I - \dot{n}_b \quad (11)$$

$$\frac{1}{V_l} \partial_t C_{H_2} = \frac{I}{zF} - \frac{p}{R_g T} \partial_t V \quad (12)$$

The ideal gas equation  $pV = n_b R_g T$  was invoked in the second term of eq.(12) to relate  $n_b$  to the volume of hydrogen produced under a pressure  $p$  and a temperature  $T$  at a given gas constant  $R_g$ . For the pressure  $p = p_0 + \rho gh + 2\sigma/R$  holds, where  $p_0$ ,  $\rho gh$  and  $2\sigma/R$  refer to the atmospheric pressure ( $p_0 = 101325$  Pa), the hydrostatic and the Laplace pressure, respectively. Note that even for the smallest bubble size,  $R = 20 \mu\text{m}$ , observed in the experiments, the relation  $2\sigma/R = 0.04 p_0$  holds. Hence, the Laplace pressure can safely be neglected during most of the bubble evolution. The same holds for the hydrostatic pressure in view of the small electrolyte height ( $h=0.03$  m), i.e.  $\rho gh = 0.003 p_0$ .

Based on the fact that the bubble diameter soon becomes larger than that of the electrode, we assume that the change in the hydrogen concentration around the bubble is nil, i.e.  $\frac{1}{V_l} \partial_t C_{H_2} = 0$ . Thus, we test the validity of the assumption that the hydrogen produced at the electrode directly diffuses into the bubble. This diffusion can only proceed via the thin electrolyte wedge at the foot of the bubble. This wedge starts at the triple point where the three phases (Pt, H<sub>2</sub> and electrolyte) are simultaneously present. The bubble growth law under this condition is then given by

$$\frac{\partial V}{\partial t} = \frac{4\pi}{3} \frac{d(R^3)}{dt} = \frac{IR_g T}{2F p_0} \quad (13)$$

Integration of eq.(13) over time delivers

$$V_{EC} = \frac{R_g T}{2F p_0} \int_0^t Idt, \quad (14)$$

where the integral  $Q = - \int Idt$  was computed with a time resolution of  $dt = 0.01s$ . The resulting  $V_{EC}$  refers to the volume obtained by measuring the current transient under the assumption of a 100% conversion of the electric current into hydrogen.  $V_{EC}$  is plotted as the black curve in Fig. 4. Assuming, for the sake of simplicity, a roughly constant current  $\bar{I}$  during bubble growth, integrating eq.(13) delivers in terms of the bubble radius

$$R = \left( \frac{3\bar{I}R_g T}{8\pi F p_0} \right)^{1/3} t^{1/3} = \beta t^{1/3}, \quad (15)$$

i.e. the growth law for high current densities as already introduced in the Introduction.  $V_{EC}$  is

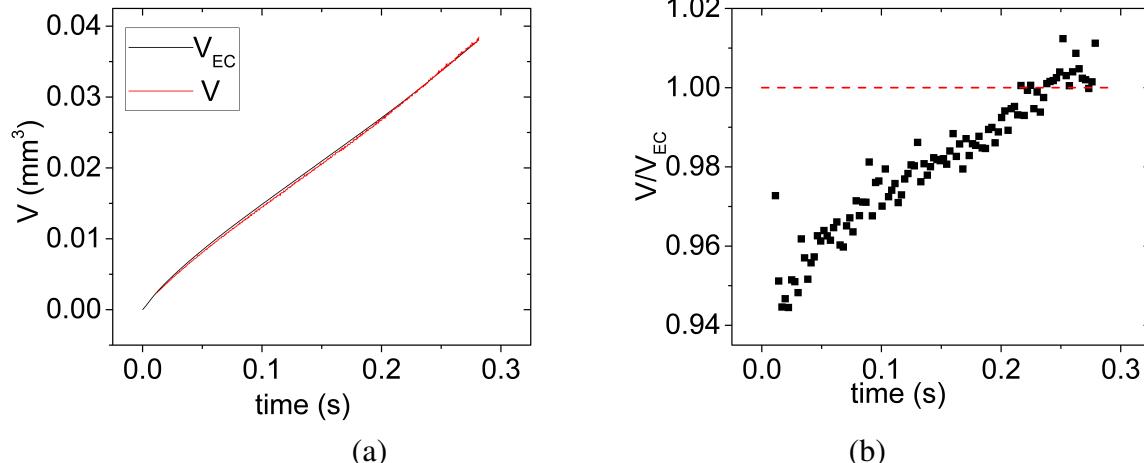


Figure 4: (a) Comparison between the bubble volumes determined by image analysis,  $V$ , and calculation,  $V_{EC}$ , according to eq. (14).  $t=0$  s corresponds in (a) to the time when the current reaches the peak current, and in (b) to the time when the new bubble forms after the previous one has just detached. (b) Ratio  $V/V_{EC}$  between the image analysis and calculated bubble volumes; the red dashed line corresponds to  $V/V_{EC} = 1$ . The measurement was done in the glass cell with a frame rate of 4000 fps.

faced with the volume  $V$ , as obtained by microscopy and applying eq.(4), which is plotted as the red curve in Fig. 4a. Obviously, the two volumina correspond very well for most of the time.

To underline the differences, in Fig. 4b we plot the ratio  $V/V_{EC}$ , frequently denoted as the gas evolution efficiency. Even at the beginning the gas efficiency is higher than 0.94 and increases continuously. It reaches unity after approx. 80% of the bubble period. Hence, it is reasonable to assume that nearly 100% of the hydrogen is converted into gas injected into the bubble at its foot. Thus, hydrogen diffusion from the bulk, which would lead to  $R \propto t^{1/2}$ , does not take place.

A special feature of all experiments in both the Pt glass and the Pt epoxy cell is the fact that the bubble growth also proceeds via coalescence with small hydrogen bubbles. They form in vicinity of the contact line of the large bubble as documented in Fig. 5. This observation differs from the experiments of Kristof & Pritzker<sup>21</sup> who found no coalescence at all in 1 M  $H_2SO_4$ . In our case, one could assume that the growth law, eq.(13), should be modified into  $\partial_t V_b \approx \sum_i qV_s f_{co}$ , where  $q$  refers to the number of small bubbles with a volume  $V_s$  which coalesces with a rate  $f_{co}$ . The experiments show that the size of the small bubbles is about 20  $\mu\text{m}$ . Approximately three small bubbles ( $q \sim 3$ ) seem to coalesce within 1 ms. However, to create the volume increment of Fig. 4, approximately 15 bubbles of this size are necessary. Hence, it is unlikely that the bubble will be totally pumped up via coalescence with small bubbles. But we are faced up to the interesting situation in which the bubble is fed by two different mechanisms at a comparable extent, coalescence and diffusion of hydrogen via the electrolyte wedge. In the next section we will also see whether this has an impact on the growth law, eq.( 1).

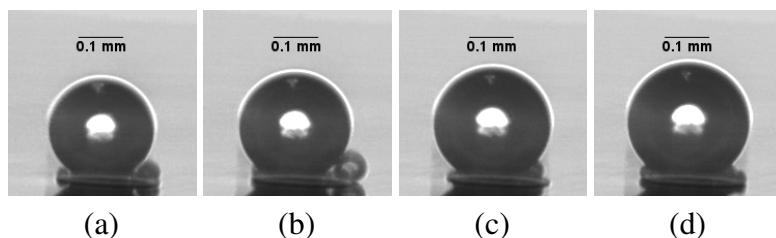


Figure 5: Coalescence of small bubbles with the main bubble; frame rate: 1000 fps. (a)  $t_0$ , (b)  $t = t_0 + 1$  ms, (c)  $t = t_0 + 2$  ms, (d)  $t = t_0 + 3$  ms. All experiments were performed in the Pt-glass cell.

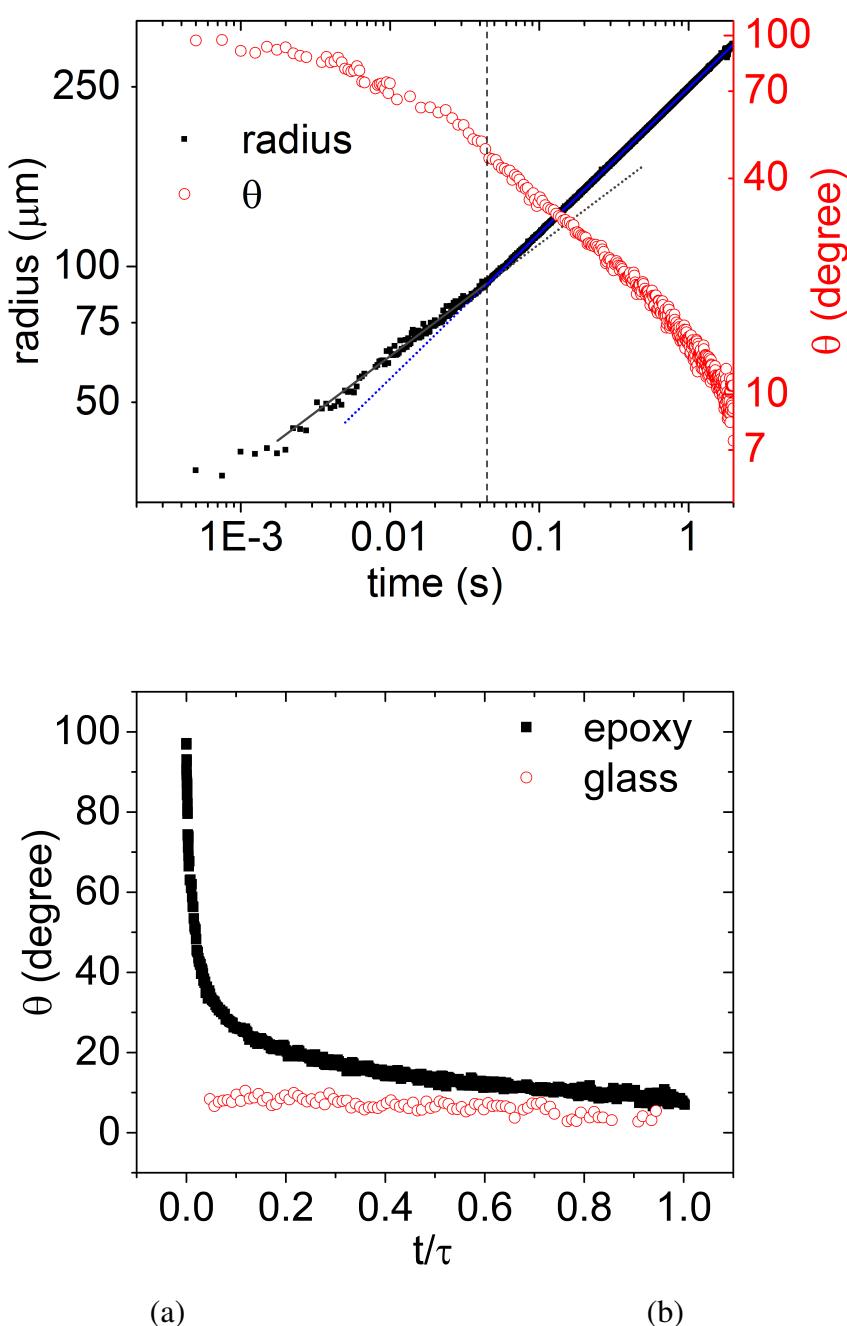


Figure 6: (a) Radius and contact angle versus time during the entire experiment time (epoxy cell, frame rate: 4000 fps). The solid lines in the plot show the linear fit of the radius. The fits are prolonged (dotted lines) to clearly indicate the two different slopes separated by the dashed vertical line. (b) Comparison of the contact angle evolution of the  $H_2$  bubble between the glass (frame rate: 4000 fps) and the epoxy cell.

## Evolution of bubble geometry

To analyse the growth of the single hydrogen bubbles we next examine the bubble radius  $R$ , the contact angle  $\theta$  and the radius of the contact line  $r = d/2$  as a function of time. Fig. 6a shows  $R$  and  $\theta$ , captured with a frame rate of 4000 fps, versus time in double logarithmic form for the Pt epoxy-cell. The Pt glass and Pt epoxy differ mainly in the evolution of the contact angle (Fig. 6b), while the radius evolution proceeds very similarly. Two ranges of radius evolution  $R(t)$ , eq. (1), can be identified, characterized by different slopes as indicated in Fig. 6a. The first range captures the early and the intermediate phases of the growing bubble. In contrast to other works,<sup>20,27</sup> we could not identify the linear scaling  $R(t) \propto t$  in the early phase as predicted by Rayleigh's equation,  $R(t) = \sqrt{2\Delta p/3\rho_l} \times t$ , where  $\Delta p$  and  $\rho_l$  refer to the capillary pressure and density of the electrolyte. Although the initial phase until approx  $t \sim 3$  ms can be linearly fitted according to  $R = a \times t$ , the slope  $a$  does not match the coefficient of the Rayleigh equation. This behavior is plausible since after 0.1 ms numerous small bubbles are already present. They coalesce in some milliseconds to form a bigger bubble with a radius of about  $40\mu\text{m}$ , which is far too large to still obey Rayleigh's equation. During the first regime the scaling exponent changes smoothly to reach  $b = 0.24 \pm 0.02$  at the end.

The second regime is marked by an increase in the slope towards  $b = 0.30 \pm 0.02$ . This is close to the  $R(t) \propto t^{1/3}$  law, discussed above, which follows for the direct diffusion of the hydrogen produced into the bubble via the thin electrolyte wedge at the bottom. An exponent close to  $1/3$  was already found in the previous works.<sup>18,19,24,27</sup> However, our experiments differs in two aspects from former works. First, as already mentioned before, the growth of the bubble proceeds by two modi, coalescence with small bubbles and diffusion of dissolved  $H_2$ . Since the ratio between the volume of the large bubble to that of the small one is much larger than unity, the impact of coalescence on the large bubble remains weak. Under these circumstances, it obviously does not matter from which source hydrogen enters the bubble. Hence, the joint action of both mechanisms leads to a scaling exponent close to  $1/3$  at high current densities.

Second, different to,<sup>16,17,20,27</sup> a diffusion-controlled regime characterized by a scaling expo-

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nent of 1/2 was not observed. We believe that the lack of the diffusion-controlled regime is a natural consequence of the nearly vanishing waiting time until a bubble is formed, both in the fresh electrolyte and after detachment of the forerunning bubble. Hence, in view of the rapid nucleation of hydrogen bubbles, there will be no significant diffusion of dissolved hydrogen into the bulk electrolyte. Thus, it is unlikely to have a regime where the diffusion of dissolved hydrogen from the bulk limits the growth of the bubble.

While  $R(t)$  is governed by  $j$ , eq. (15), the contact angle  $\theta$ , Fig. 6b, is largely determined by the substrate in which the Pt wire is embedded. The hydrophobic epoxy substrate has a surface energy of about  $0.046 \text{ N/m}^{33}$  while that of the hydrophilic glass is about 10 times larger. Hence, the wetting of the hydrophobic epoxy substrate by the acidic electrolyte with its high surface tension ( $0.073 \text{ N/m}^{34}$ ) is energetically not favorable. Therefore, the contact angle in the epoxy cell is significantly higher than that in the glass cell. As the bubble grows in size,  $\theta$  showed a power law decrease in the Pt epoxy cell towards the contact angle of the bubble in the glass cell close to detachment. The decreasing  $\theta$  with increasing  $R$  in the epoxy cell, in comparable manner seemingly also found on hydrophobic electrodes,<sup>35</sup> seems to be a logical consequence of the scaling of  $R(t) = \beta t^b$  under the condition that  $r/R$  is small. In this case,  $\theta = \arcsin(r/\beta t^b) \approx (r/\beta)t^{-b}$ . Given the growth law,  $R(t) = \beta t^{0.28}$  for the particular experiment in the Pt-epoxy cell, on fitting the measured  $\theta(t)$  we recover  $\theta \approx (r/\beta)t^{-0.28}$ . By contrast, in the Pt glass cell  $\theta$  is with  $(10 \pm 2)^\circ$  significantly smaller and decreases much less towards  $\theta = (4 \pm 2)^\circ$  close to detachment. In this way, our experiments in the Pt glass cell are in agreement with<sup>16</sup> who found nearly constant  $\theta \sim (5 \dots 15)^\circ$  with a comparable Pt microelectrode. By contrast, a behaviour comparable to our experiments in the Pt epoxy cell was found for similar  $\text{H}_2\text{SO}_4$  concentration in<sup>17</sup> for a Ni microelectrode and<sup>24</sup> for a Pt microelectrode. Meanwhile, with larger planar Pt electrodes, higher and even slightly increasing contact angles were measured.<sup>24</sup>

Returning to the Pt glass cell, the circular fit gives access to the contact points P1 and P2, by means of eqs.(6-7), cf. Fig.1. These points are part of the contact line given by the intersection between the liquid-gas interface and the electrode. Fig. 7a (bottom) shows the change in their

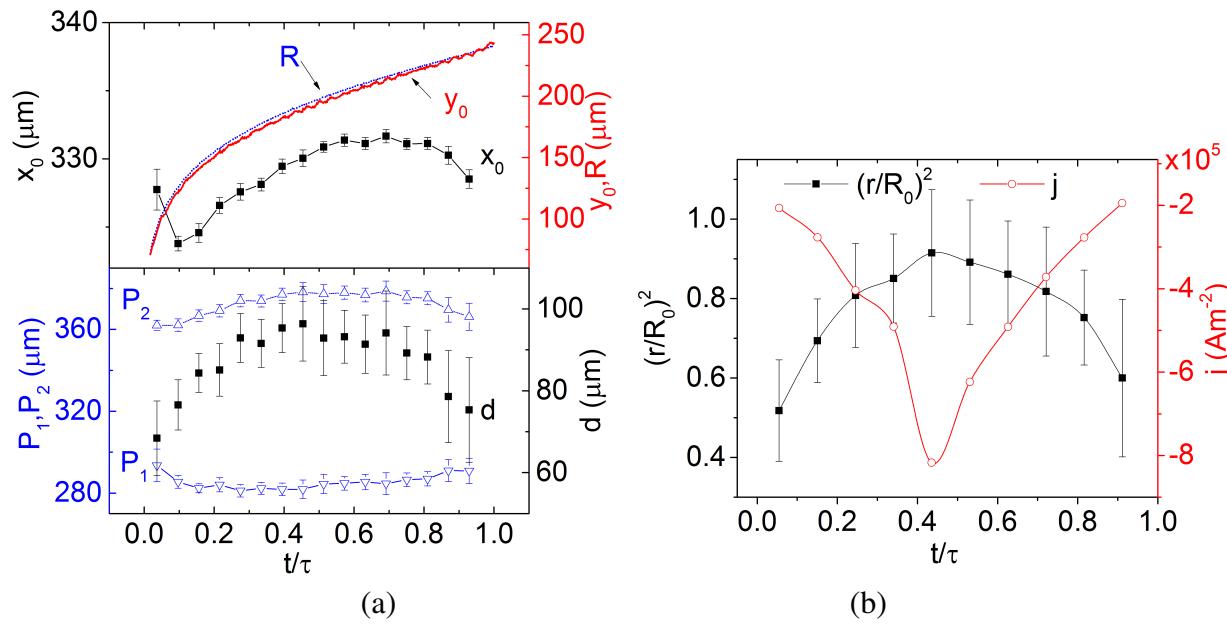


Figure 7: (a) x-position of contact points,  $P_1$  and  $P_2$ , and the resulting contact line diameter (bottom). The top figure shows the center of the bubbles,  $x_0$  and  $y_0$ , together with the bubble radius  $R$  as a function of time. (b) Ratio between the electrode area covered by the bubble to the entire electrode area superimposed with the current density  $j$ . All experiments were performed in the Pt-glass cell at 1000 fps.

x-position over time together with the resulting diameter of the contact area,  $d$ . Additionally, the x- and y-position of the bubble center,  $x_0$  and  $y_0$ , is plotted in Fig. 7a (top). As already mentioned above, the error in determining the diameter of the contact circle,  $d$ , is 10 pixels (11  $\mu\text{m}$ ) due to an uncertainty in the x-position of P1 and P2 of  $\pm 5$  pixels. Interestingly, the shape of the  $d$  curve shows a fingerprint of the I-t curve, Fig. 3a.  $d$  rises until the middle of the period to reach an intermediate plateau value which corresponds approximately to the electrode diameter of 100  $\mu\text{m}$ . At times larger than  $t/\tau = 0.7$  it decays again to reach approx. 75  $\mu\text{m}$  at detachment. This period of decreasing  $d$  is accompanied by a small drift of the  $x_0$  value of the bubble center by about 10 pixels (11  $\mu\text{m}$ ) towards smaller x-values along the electrode, which is clearly visible in the videos even to the naked eyes. At the same time, a small lift of the bubble occurs; note the stronger increase of  $y_0$  compared to that of the radius  $R$ . In Fig. 7b we translate this information into the surface coverage of the electrode by the gas bubble, given by the ratio between contact to electrode area. Notably, this ratio starts to decrease again at about  $0.7\tau$  in every bubble cycle. We have superimposed the current density obtained by  $j = I/(1 - (r/R_0)^2)A_0$  where  $A_0 = \pi R_0^2$ . We see a significant rise in the current density from  $2 \times 10^5 \text{ A/m}^2$  to  $8 \times 10^5 \text{ A/m}^2$ , i.e. achieved at maximum coverage of the electrode by the bubble.

## Detachment diameter and lifetime of the bubbles

Next, the growth dynamics of the bubbles was studied in dependence on the saturation of the electrolyte with dissolved hydrogen. Successive measurements were carried out without changing the electrolyte after 600 s of H<sub>2</sub> electrolysis. Fig. 8a-b shows the lifetime and detachment radius for the three successive measurements over 600 s, where the pause between these measurements was 60 s. The bubbles shown in both subfigures are from the 10 videos, taken during the 600 s duration, where each video contained approx. 15 bubbles. The lifetime of the bubble increases by about 15% over the duration of the experiment, while the detachment radius decays with time until a steady value is reached. There is only a scatter of 4% in the detachment radii of the three experiments.

The histograms of these 3 experiments are summarized in Fig. 8c-d. In contrast to (a-b), these data were extracted from the current-time transient and include all bubbles, ca. 600-750 as discussed before. Fig. 8d shows a narrow radius distribution with a standard deviation of  $1.7 \mu\text{m}$ . The histogram of the lifetimes does not obey a Gaussian distribution. We assume that the surface of the Pt electrode changes with time by ad- and absorption of atomic hydrogen during the discharging process. As a result, a slight increase in the overpotential may occur. Due to the charge-controlled mechanism, the absolute value of the current decreases on average, which leads to a slower growth rate, i.e. longer lifetime. This finding is supported by the fact that the bubble growth coefficient  $\beta$  in eq. (15) becomes smaller.

Measurements between different days lead to a modified distribution of the lifetime and radius, see Fig. 8e-f, even when the electrode/cell assembly is treated as described in the Experimental section. We note a shift of up to 20% in the detachment radius and of about 50% in the lifetime of the bubbles. However, the bubble dynamics is identical to that described before; only the absolute values are shifted. To reduce this scatter, most previous works<sup>17,18,21</sup> were carried out under galvanostatic instead of potentiostatic conditions, as in<sup>16</sup> and in the present work. However, the potentiostatic mode of measuring single bubble nucleation, growth and detachment is the manner of choice because it delivers information on how surface conditions change at the Pt electrode. As already pointed out in,<sup>36</sup> the bubble dynamics at a given potential depends on the polishing quality of the electrode surface and on the history of the electrode with respect to hydrogen penetration into the electrode or aging effects which modify the properties of the surface. Evidence was also found at Pt nanoelectrodes that hydrogen atoms diffuse along the Pt surface towards the Pt glass interface,<sup>37</sup> thereby increasing the effective surface area. Hence, one can safely say that the chemical potential at the Pt surface is changed with time by adsorbed H atoms<sup>38</sup> and other species such as  $\text{OH}^-$ , and  $\text{H}_2\text{O}$ . This is presumed to be the origin of a changed open-circuit potential. The resulting different overpotentials are the source for the shift in Fig. 8e-f.

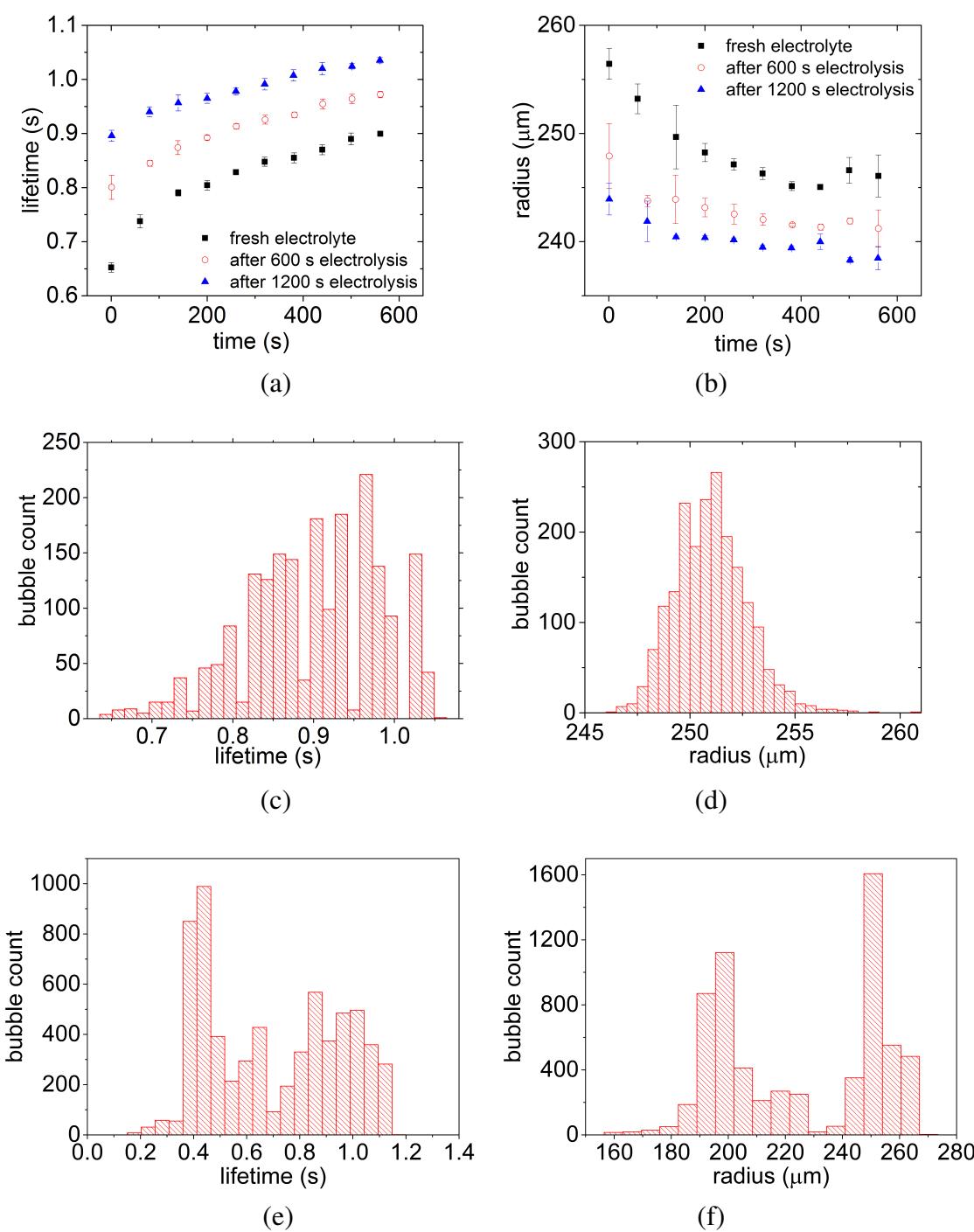


Figure 8: (a-b) The lifetime and the detachment radius of the bubble as a function of time for three subsequent experiments, as indicated in the figure legend. (c-d) Corresponding histograms including all three sequential measurements in (a) and (b). (e-f) Histograms of lifetime and the detachment radius of the bubble on two different days. All experiments were performed in the Pt-glass cell.

### Bubble detachment and associated flow

It is worth looking into the immediate process of the bubble's detachment from the electrode. Five characteristic stages are depicted in one-millisecond intervals in Fig. 9. Additionally, we have inserted the bubble's aspect ratio defined as the bubble height H divided by the bubble width W. The bubble shape remains very close to that of a sphere, as indicated by a height-to-diameter-ratio

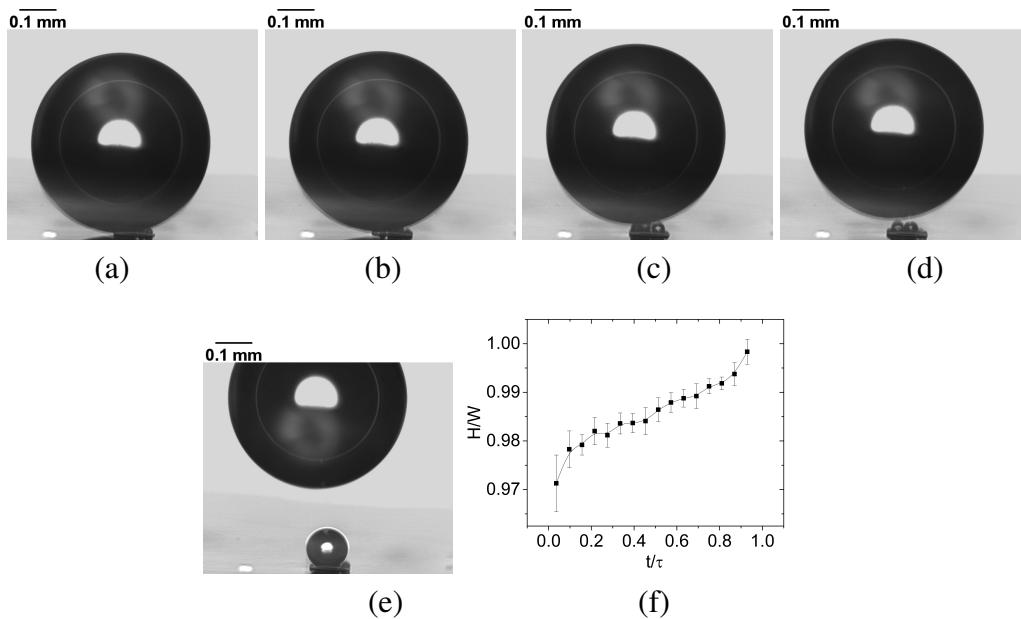


Figure 9: (a-e) Detachment process of the bubble from the electrode in the Pt-epoxy cell, frame rate: 1000fps. The time step between consecutive images is 1 ms. (f) Height-to-width ratio of the bubble versus time.

which stays close to unity during the entire bubble cycle. Most of the time, the bubble height is slightly smaller than the diameter. With increasing time, the ratio converges to unity. Only in the very last instant of time does a slight increase above unity occur during the detachment. In the present case, the process of the bubble's detachment from the electrode differs clearly from that of a bubble emerging from an orifice, and hence from other electrolysis experiments showing elongated bubbles.<sup>30,35,39</sup>

In view of the periodic formation of bubbles, the question arises as to whether the detachment of one bubble has an impact on the growth of the successor bubble. This kind of interaction may arise via the flow field which the bubble generates during detachment and lift off, by viscously

dragging the initially stagnant electrolyte. Fig. 10(a-d) shows several characteristic stages of the

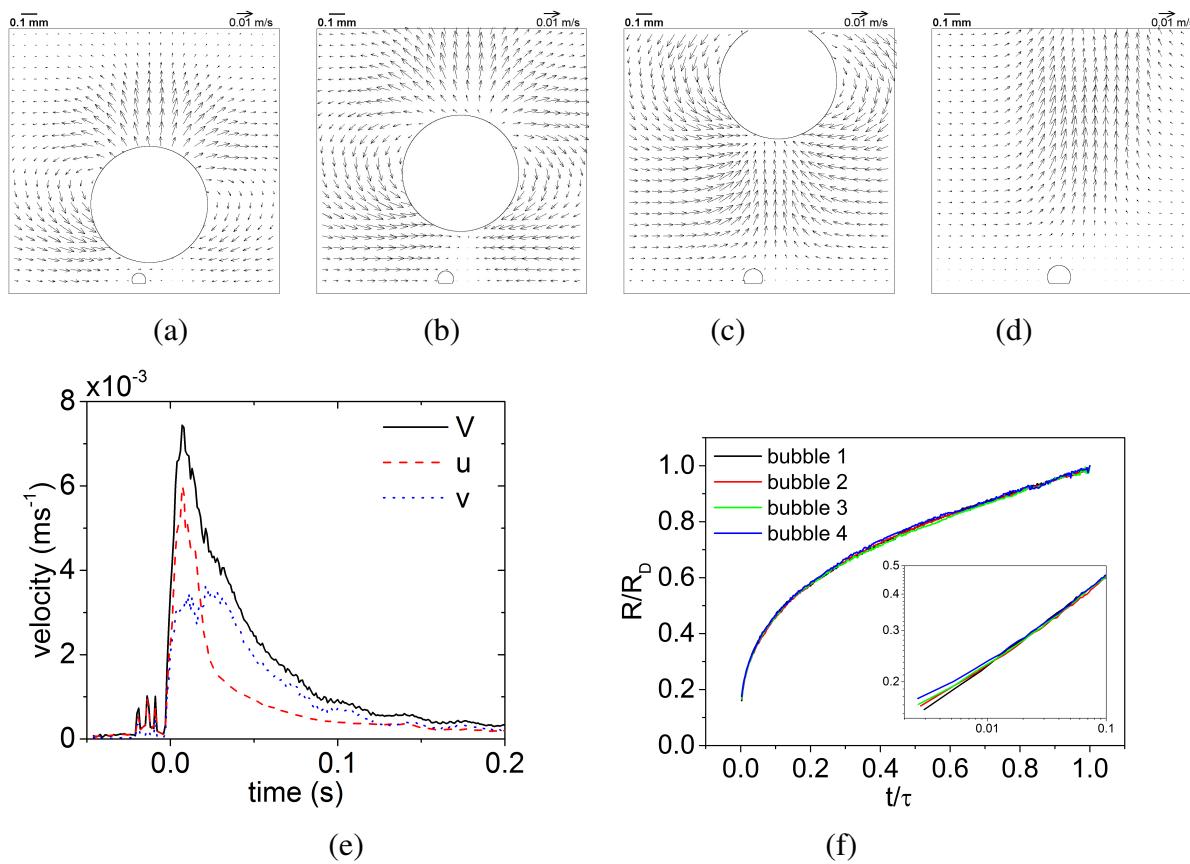


Figure 10: (a-d) Characteristic stages of the flow field during the detachment of a hydrogen bubble. The position and size of the bubble were redrawn in the figures with reference to the real bubble images. (e) Averaged velocity as a function of time. The time when the bubble was detached was set to be zero. (f) Normalized bubble size as a function of time for 4 different bubbles generated at different times after the potential was applied. Bubble 1 was the first when the potential was applied and bubbles 2, 3, 4 were the immediately following bubbles. The inset shows a zoom into the very early stage of bubble generation where a logarithmic scale was used for a better resolution. The measurement was carried out in the epoxy cell with a frame rate of 1000 fps.

flow field during bubble detachment. Upon detachment, the bubble rises through the field of view with a velocity of about  $(120 \pm 20)$  mm/s as determined by tracking the bubble. During this rise, the bubble displaces electrolyte at its front side which has to be replaced by electrolyte at its rear side. As a result the new, small bubble which grows at the electrode is impinged upon by a fluid flow. The advection of dissolved hydrogen by this flow strongly depends on the level of hydrogen saturation in the local environment of the electrode and hence on the time history of the experiment. However, the duration of this detachment-induced flow is limited to a short time interval of about

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3 100 ms, as indicated by Fig. 10(e). This figure plots the start-up and decay of this convection. To  
4 do so, the components  $u$  and  $v$  of the velocity vector  $\vec{v} = (u, v)$  in the entire area of (a-d) are area-  
5 averaged every time step (cf. Yang et al.<sup>40</sup>), and the average of both as well as of the magnitude of  
6 the velocity vector  $V = \sqrt{u^2 + v^2}$  is plotted versus time in (e).  
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10 Fig. 10(f) examines the evolution of the radius of subsequent bubbles, normalized to the cor-  
11 responding final detachment radius, versus time, again normalized with the corresponding period  
12  $\tau$ , for the first four bubbles. Also, the very first bubble which formed in the fresh electrolyte is  
13 included. We note that the growth dynamics differ only in the initial phase. Here, we see that the  
14 later bubbles are slightly larger at the beginning. However, at the time scale where the detachment-  
15 induced convection vanishes, i.e. at around 0.1 s, the curves do again collapse to form one line. For  
16 a bubble lifetime of about 0.8 s, we can conclude that the bubble growth in the present Pt micro-  
17 electrode configuration is only weakly influenced in the very first phase by the detachment-induced  
18 convection, but then with almost no impact from the foregoing bubble.  
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## 32 Conclusion

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35 This study examined the dynamics of single H<sub>2</sub> bubble generated by water electrolysis in acidic  
36 electrolyte on a Pt microelectrode under potentiostatic conditions. Different image analysis meth-  
37 ods to investigate the bubble geometry were introduced and compared, among which the self-  
38 developed Matlab code provides a fast and automated way to determine the geometry parameters  
39 such as the bubble radius, bubble position and the contact angle. The growth of the single bubble  
40 was investigated and compared on two different substrates, glass and epoxy, used to embed the Pt  
41 electrode. Nearly independently of the substrate, the bubble radius follows a  $R(t) \propto t^{(0.30 \pm 0.02)}$  law.  
42 Hence, the exponent is close to 1/3, as expected for the direct diffusion of the hydrogen produced  
43 into the bubble at its foot.

44 In contrast to  $R$ , the contact angle  $\theta$  of the bubble depends strongly on the material embedding  
45 the Pt electrode. It shows an exponential decrease at the hydrophobic epoxy material, while  $\theta$  with  
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hydrophilic glass shows a much weaker change and stays at low values between (3...12)°.

During the potentiostatic measurements of water electrolysis, the surface conditions of the Pt electrode obviously change. This is mapped by an increase in the bubble lifetime at decreasing detachment radius during the long-term measurement and by a certain shift in both quantities in measurements on different days following otherwise the same dynamics.

In contrast to bubbles detaching from orifices, the hydrogen bubbles are close to sphericity during their entire evolution. If the bubble detaches, a torus-like vortex is formed as the bubble rises. However, at bubble lifetimes of about 0.5 s, hence hydrogen bubble frequencies of about 2 Hz, the wake of this vortex influences the subsequent bubble only marginally during the very first part of its evolution.

Our results have shown that the coalescence of the smaller bubbles at the foot of the bigger bubble is also an important growth mechanism for the present single hydrogen bubbles. A more detailed investigation, in particular with a much higher temporal and spatial resolution, is necessary to shed more light on this problem.

## Acknowledgement

Financial support by DFG (Ec201/4) is gratefully acknowledged. We thank K. Hennig for her support and Dres. G. Mutschke, K. Tschulik, Ch. Cierpka and D. Baczymalski for fruitful discussions.

## Supporting Information Available

Image processing procedure to obtain the bubble geometry and a comparison of the different methods. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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## Graphical TOC Entry

