Transient nanobubbles in short-time electrolysis

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Abstract
Water electrolysis in a microsystem is observed and analyzed on a short-time scale of ~10 µs. The very unusual properties of the process are stressed. An extremely high current density is observed because the process is not limited by the diffusion of electroactive species. The high current is accompanied by a high relative supersaturation, $S > 1000$, that results in homogeneous nucleation of bubbles. On the short-time scale only nanobubbles can be formed. These nanobubbles densely cover the electrodes and aggregate at a later time to microbubbles. The effect is significantly intensified with a small increase of temperature. Application of alternating polarity voltage pulses produces bubbles containing a mixture of hydrogen and oxygen. Spontaneous reaction between gases is observed for stoichiometric bubbles with sizes smaller than ~150 nm. Such bubbles disintegrate violently affecting the surfaces of the electrodes.

(Some figures may appear in colour only in the online journal)

1. Introduction

It is more than 200 years since water electrolysis was observed for the first time (see [1, 2] and references therein). Since then the process has been widely used in different applications including hydrogen production [3, 4]. Nowadays electrolysis of water also finds applications in different kinds of microdevices such as actuators [5–8], pumps [9, 10], and others [11, 12]. Fast performance of microsystems requires processing on a short-time scale. Surprisingly enough, most research on water electrolysis has dealt with macro- or microscopic systems on a time scale longer than milliseconds [9, 13]. A few papers, where shorter (microseconds) voltage pulses were considered, discussed increase of the overall efficiency [14] or optimization of the performance of electrolysis [15], but did not observe the process on the microsecond time scale.

In normal long-time electrolysis (long-time means here a time scale $\tau > 1$ ms) gas bubbles with diameters in the range of 10–1000 µm are observed [13, 16]. The maximal current density that can be reached in this case is around 1 A cm$^{-2}$ [17] and the maximal relative supersaturation is ~100 [18]. These values cannot be increased further because bubbles cover the whole surface of the electrode making it inactive [17, 19, 20].

In short-time electrolysis, say $\tau = 1–100$ µs, one could expect unusual properties of the process. This becomes obvious if we consider gas diffusion into the liquid above the electrode. For the time $\tau$ significant supersaturation is possible at a distance from the electrode $l \sim \sqrt{D\tau}$, where $D$ is the diffusion coefficient of the formed gas in the surrounding liquid. Taking as typical values $D \sim 10^{-9}$ m$^2$ s$^{-1}$ and $\tau \sim 10$ µs, one finds $l \sim 100$ nm. This means that on this time scale only nanobubbles can be formed. This is indeed the case, as we demonstrated recently [21]. Nanobubbles of 200–300 nm in diameter were observed stroboscopically above microelectrodes. These nanobubbles were formed for the first 20–50 µs then aggregated to microbubbles after 100–300 µs, but the following dynamics was very slow.
A number of observations indicate that smaller nanobubbles can exist at shorter times, $\tau \lesssim 10 \mu s$. For example, it was demonstrated that the reaction between hydrogen and oxygen can be ignited spontaneously in nanobubbles with sizes smaller than 150 nm [21]. Different manifestations of this reaction show that the reaction persists for nanobubbles as small as 50 nm or even smaller.

In this paper we describe the formation of nanobubbles on the short-time scale $\tau = 1$–100 $\mu s$. It is demonstrated that very high current densities and supersaturations can exist accompanied by the homogeneous nucleation of nanobubbles. Bubbles containing hydrogen or oxygen grow and aggregate forming micro-sized bubbles on a time scale of $\tau \gtrsim 100 \mu s$. The nanobubbles containing a mixture of the gases disappear as a result of the reaction between the gases. These are transient nanobubbles, which exist for only a short time and are difficult to observe directly. In contrast to our first report [21] we provide here a detailed description of the transient nanobubbles and pay less attention to the chemical reaction inside of these bubbles.

The nanobubbles discussed in this paper differ from surface nanobubbles, which have recently attracted considerable attention. Long-lived surface nanobubbles have been observed with different methods [22–24]. Observation with atomic force microscopes (AFM) has become especially popular (see [25] and references therein) due to its simple realization. These nanobubbles are widely discussed in the literature because of their mysterious stability. High Laplace pressure drives diffusion of gas out of the bubbles resulting in a dissolution time of $\sim 10$ $\mu s$, but not days as observed (see [26] for a review). The precise reason for this stability is not clear yet, but in a promising model [27] of ‘dynamical equilibrium’ the gas flux going out of the bubble through the spherical cap is balanced with a gaseous influx at the contact line.

A number of methods to generate surface nanobubbles are in use, including solvent exchange, temperature change for liquid or substrate, and liquid pressurizing [28]. The electrochemical formation of surface nanobubbles has been observed in water electrolysis for hydrogen [29] and for both hydrogen and oxygen [30] on highly orientated pyrolytic graphite. The electrochemical process is considered as a flexible way to control the bubble production (density and size) [31]. In contrast with the electrochemical process considered in this paper the electrochemical production of surface nanobubbles had a much smaller current density ($\sim 10^{-4}$ A cm$^{-2}$) and much longer time scale ($\sim 10$ s).

This paper is organized as follows. In section 2 we describe the system for observation of the short-time electrolysis, application of the voltage pulses, and the current response. In section 3 the main results obtained with the stroboscopic observations are described. Electrolysis with alternating sign pulses is described in section 4, where we present the results obtained with a stroboscope and vibrometer. We also explain modification of the electrode surface due to the process. In section 5 the evolution of the transient nanobubbles is summarized and we discuss their possible applications. Our conclusions are collected in section 6.

2. Short-time electrolysis

To analyze electrolysis on a short-time scale in a microscopic system special microchips were prepared. One of the chips is shown in figure 1. For fabrication we used wafers made of BF-33 Borofloat glass. First, a Ti sublayer was deposited on the glass (10 nm) for better adhesion, then a 100 nm thick metallic layer was sputtered. We used the wafers with different metals on top such as Pt, Pd, Au or W. The metals were patterned and covered lithographically with the insulating resist SU8 where it was necessary. Different thicknesses of the SU8 layer of 3 and 90 $\mu m$ were used. The fabricated wafers were diced into separate chips with a size of $12 \times 12$ mm$^2$. Each chip contained 16 pairs of microelectrodes of different shapes and sizes and contact pads to address a specific pair electrically. The patterned SU8 layer formed walls of open channels for a liquid. A chip filled in with the electrolyte was covered by a thin (30 $\mu m$) glass plate for observation of the electrolysis.

As the solution for electrolysis we used 15 g of Na$_2$SO$_4$ dissolved in 100 ml of deionized water. We also used the solutions of NaCl and KI in water in similar concentrations.

The process was observed with a homemade stroboscopic system [32]. In this system the light source and the electrical pulses applied to the electrodes were controlled with a time resolution of 0.1 $\mu s$. As a light source two powerful LUXEON® III green LEDs were used. With this system we were able to observe the electrodes in an optical microscope with an illumination time longer than 5 $\mu s$. 

![Figure 1](image-url)
2.1. Voltage

For a chosen pair of electrodes one was always grounded and the other one (working electrode) could be at a negative or positive potential. Hydrogen or oxygen bubbles were produced above the working electrode. We could apply voltage as a pulse of a given length from 1 to 10$^5$ µs. The pulse could be repeated with a frequency $f$. At a prescribed moment of time a short flash of light $\geq 5$ µs was switched on and an optical microscope image of the electrodes was made during the flash. The applied voltage and the resulting current through the electrodes were recorded. Alternatively, keeping one electrode grounded we applied voltage pulses of alternating polarity to the working electrode repeated with a particular frequency. In this case bubbles containing both gases H$_2$ and O$_2$ could be formed [21].

The voltage needed to start the electrolysis was always larger than that for macrosystems, $U_0 = 2.5–4$ V. The high threshold voltage has already been observed in microsystems [7, 9, 10], but the reason has not been explained. It has to be stressed that in microsystems a planar geometry is used where both electrodes are in the same plane. In this case the Ohmic losses (resistance between the electrodes) are considerable even for well conducting electrolytes. This is in contrast with macrosystems, where these losses are usually negligible. For one pair of electrodes we measured the resistance to be $R = 2.3$ kΩ, but it varied to some degree from pair to pair due to different geometries. The working current in our system, $I \sim 1$ mA, was quite large. Therefore the Ohmic polarization is estimated as a few volts (2–3 V).

By agreement we defined the threshold for the electrolysis by applying different voltages for 5 ms and observing the gas formation. At $U = U_0$ the first gas was visible in the system. For example, for the same pair of electrodes, for which the resistance was measured, we found $U_0 \sim 3.2$ V. In some cases $U_0$ was as large as 6 V or so, but we found out that this was due to the potential drop on the electrode surface. Treatment of such chips in O$_2$-plasma significantly reduced $U_0$. Probably a film (hydrocarbons) was formed on top of the electrodes during the fabrication process. It should be stressed that the absolute values of the potential have to be taken with care because we are dealing with a two-electrode system and there is uncertainty in the potential of the working electrode, in contrast with a three-electrode system.

2.2. Current

The current response to square voltage pulses applied to the working electrode is shown in figure 2. The response is in accordance with expectations. One can separate two components in the current. The first one is the Faradaic current $I_F$ that does not depend on the time $t$ for square voltage pulses. The second component is responsible for the charging–discharging of the double layer on the electrode surface and is not related to the electrochemical reaction. It behaves as $I_L e^{-t/\tau_c}$, where $I_L$ is a constant and $\tau_c$ is the relaxation time related to the capacitance of the double layer.

As a result we fitted the current response on the square voltage pulse by a function of three parameters,

$$I(t) = I_F + I_L e^{-t/\tau_c}. \quad (1)$$

It has to be stressed that typically in macro- and microsystems considered on the long-time scale the Faradaic current $I_F$ depends on the time because it is diffusion limited. For parallel electrodes the current is proportional to $\sqrt{\tau_D/\tau}$ in accordance with the Cottrell equation [33], where $\tau_D$ is the diffusion time for the electroactive species in the solution. In our case the diffusion time is too long to play any role. Roughly, it can be estimated as $\tau_D \sim L^2/D \sim 100$ ms, where $L \sim 10 \mu$m is a typical size of our electrodes and $D \sim 10^{-9} \text{ m}^2 \text{ s}^{-1}$ is a typical diffusion coefficient of the electroactive species in water.

We used equation (1) to fit the current response, as shown in figure 2. The quality of the fit can be seen in the insets. The Faradaic current can be well approximated by a constant in the investigated time domain $t < 100$ µs. For alternating pulses the positive $I_p(t)$ and negative $I_n(t)$ halves of the pulse are symmetric, as shown in the bottom inset. For single polarity pulses the relaxation time $\tau_c$ is larger for the negative half of the pulse (4.9 against 1.3 µs), reflecting dependence of the double layer capacitance on the potential [33]. For the alternating polarity pulses in figure 2 we found from the fit $\tau_c = 4.0$ µs. With frequency increase the relaxation time decreases slowly, indicating that not all adsorption states can be filled for a short time. It has to be noted that the Faraday component of the current persists up to the shortest pulses of 1 µs ($f = 500$ kHz) that we investigated. The presence of this component signals formation of gases on this shortest time scale that was directly observed with the stroboscope.

The Faradaic current reaches rather large values. For the case shown in figure 2 it is $I_F = 0.80 \pm 0.07$ mA for the single polarity pulses and $I_F = 1.08 \pm 0.03$ mA for the alternating polarity voltage pulses. Keeping in mind that the open area
of the electrode was around 1260 $\mu$m$^2$ one finds that the current density was $j_F \approx 80$ A cm$^{-2}$. This is the average value of the current density but locally it can be five times larger (see section 3.1). This value is much larger than the maximal value $\sim 1$ A cm$^{-2}$ [17] that can be reached in the long-time electrolysis.

The most important conclusions that can be drawn from the current–voltage behavior of the microsystem on the short-time scale are the following. (i) The electrolysis persists normally up to the shortest investigated time of 1 $\mu$s. (ii) The current density is at least two orders of magnitude larger than was previously observed in macrosystems.

3. Stroboscopic observations

The stroboscopic technique gives images that were made for different runs. To draw conclusions from these images the system has to behave reproducibly from run to run. For our system this condition was fulfilled. The images made at the same moment for different runs were hardly distinguishable on the short-time scale and varied slightly on the long-time scale, $>1$ ms. In the latter case, the positions and sizes of separate bubbles were slightly different, but qualitatively the pictures were the same. For good visibility we used typically a 10 $\mu$s long flash of green light that was delayed for different times from the beginning of the voltage pulse. The camera collected the light from the microscope during the flash. The estimated time uncertainty in 5 $\mu$s is reasonably small, although comparable with the time scale. The gas produced by a series of pulses in most cases disappeared diffusively in less than 1 s. Sometimes, when the amount of produced gas was large, a stable (pinned) bubble formed. In this case we have to refill the chip for further use. Due to evaporation we were able to operate with a filled chip for 15 min.

Figure 3 shows the electrodes at different moments of time. A positive or negative voltage pulse 50 $\mu$s long was applied to the electrodes. The left image shows both electrodes 20 $\mu$s after the beginning of the positive voltage pulse. Oxygen and hydrogen are formed above the working electrode and grounded electrode, respectively. All the other images show the working electrode with hydrogen at different moments during the negative voltage pulse.

Indeed, the periphery of the electrode is a preferable place for bubble nucleation, but one can see some haze in the inner part of the electrode. With our microscope we can reliably resolve bubbles with a diameter of 500 nm. The bubbles forming the haze are smaller. We are able to see them because they strongly scatter the light. The diameter of these scattering centers is estimated as $d > \lambda/\pi \approx 170$ nm [34], where $\lambda = 520$ nm is the wavelength of the LED used. These scattering centers fill the inner part of the electrode densely and grow with time.

3.1. Supersaturation

Let us make some simple estimates. For the time $\tau = 20$ $\mu$s the gas molecules can diffuse in the vertical direction off the electrode for the distance

$$l_{H_2} \sim \sqrt{D_{H_2} \tau} \approx 300 \text{ nm}, \quad l_{O_2} \approx 200 \text{ nm}, \quad (2)$$

where $D_{H_2} = 4.5 \times 10^{-9}$ m$^2$ s$^{-1}$ and $D_{O_2} = 2.0 \times 10^{-9}$ m$^2$ s$^{-1}$ are the diffusion coefficients of hydrogen and oxygen in water. These values of the diffusion length have to be considered as the upper limits on the bubbles that can be formed during the time $\tau$. Therefore, it is natural that we can see only nanobubbles during the first 20 $\mu$s of electrolysis.

The relative supersaturation for $H_2$ or $O_2$ molecules can be found as follows. The concentration of the $n$th gas in the diffusion layer is $n_i = N_i/A$, where $A$ is the area of the working electrode and $N_i$ is the number of molecules produced by the electrolysis. This number is related to the Faraday current as $N_i = I_F/2|e|$ (for $H_2$), where $e$ is the electron charge. The relative supersaturation is the ratio of the gas concentration to the saturated concentration $n_i^{(s)}$, which at normal conditions is $4.7 \times 10^{17}$ cm$^{-3}$ or $7.7 \times 10^{17}$ cm$^{-3}$ for hydrogen or oxygen, respectively. Then we find for the supersaturation

$$S_{H_2} = \frac{j_F}{2|e|n_{H_2}^{(s)}} l_{H_2}, \quad S_{O_2} = \frac{j_F}{4|e|n_{O_2}^{(s)}} l_{O_2}, \quad (3)$$

where $j_F = I_F/A$ is the current density.

The Faradaic current recorded together with the images in figure 3 was $I_F \approx 1.5$ mA. However, it is not straightforward to estimate the current density because it is highly nonhomogeneous for planar electrodes. We have already analyzed the current distribution over the electrode (see [21] Supplemental), extracting the information from the observed ‘wear’ of the electrodes. It was found that the current density over the electrode surface can be presented as $j_F(x, y) = j_{m} f(x, y)$, where $x$ and $y$ are the coordinates of a point on the electrode and $j_{m}$ is the maximal current density. The function $f(x, y)$ has an average value over the electrode of $\bar{f}(x, y) \approx 0.2$. The area of the electrode was $A \approx 1260 \mu$m$^2$ and we find $j_{m} \approx 600$ A cm$^{-2}$. This is an extremely high value in comparison with usual electrolysis and it is realized in the
area of active bubble formation, as can be seen in figure 3. The supersaturation in this area for the time \( \tau = 20 \mu s \) is estimated as

\[
S_{H_2}^m \approx 2700, \quad S_{O_2}^m \approx 1200.
\] (4)

These are incredibly large values.

3.2. Homogeneous bubbling

Observation of the haze far from the electrode periphery is a signal of homogeneous nucleation of small bubbles. Our estimates of the supersaturation (4) also support this idea. In the classical theory of homogeneous nucleation [35, 36] the probability to create a bubble of the critical size \( r_c \) is given by the exponent

\[
w \sim \exp \left\{ -\frac{4\pi r_c^2 \gamma}{3kT} \right\}, \quad r_c = \frac{2\gamma}{\Delta P},
\] (5)

where \( \gamma \) is the surface tension of the liquid and \( \Delta P \) is the pressure difference between the gas and the liquid. The pressure in the gas \( P_g \) must support the high supersaturation in the liquid. It is defined as \( P_g = SP_i \), where \( P_i \) is the saturated pressure for a gas at normal conditions. For both \( H_2 \) and \( O_2 \) gases \( P_i \approx 1 \text{ atm} \) and we find \( \Delta P_i \approx P_i(S_i - 1) \) for the \( i \)th gas.

For small supersaturation, \( S - 1 \sim 1 \), the critical size \( r_c \sim 1 \mu m \) is large and the exponent in (5) is incredibly small. For high supersaturation, \( S \sim 1000 \), the critical size \( r_c \sim 1 \text{ nm} \) is small and the probability to create a critical bubble, which is able to grow, becomes appreciable. It is hardly reasonable to make more detailed estimates. This is because a number of important corrections have to be included in the classical nucleation theory [35, 37, 38]. It has to be noted that according to (3) \( S_i \) increases with time as \( \sqrt{T} \). Therefore, starting from some moment after the beginning of the electrolys, homogeneous bubble formation is expected. With temperature increase as one can see from (5) that homogeneous bubbling must start earlier and due to the exponential dependence this tendency must be well pronounced. This prediction is very easy to check experimentally by carrying out water electrolysis at elevated temperatures.

For this experiment we heated the chip by a flat resistor and controlled the temperature by a thermocouple. A 20 \( \mu s \) long negative voltage pulse was applied to the electrode. Hydrogen nano- and microbubbles are visible.

Figure 4. Images of the electrode at \( t = 17 \mu s \) (top row) and \( t = 27 \mu s \) (bottom row) taken at different temperatures. A 20 \( \mu s \) long negative voltage pulse was applied to the electrode. Hydrogen nano- and microbubbles are visible.

measuring the conductivity of the bulk solution with a Mettler Toledo SevenMulti conductivity meter. We found that the conductivity can be well described by the linear behavior \( \sigma(T) = \sigma_0 [1 + \alpha(T - T_0)] \), where \( \sigma_0 \) is the conductivity at temperature \( T_0 \). The thermal coefficient was found to be \( \alpha = 0.024 \text{ K}^{-1} \). This value is in good agreement with the value of 0.028 \text{ K}^{-1} found from the current increase on the chip and with the values reported in different literature sources.

Comparing the images in the top row of figure 4 one can see that many more nanobubbles become visible with the temperature increase. On the other hand, the gas volume at \( T = 53^\circ C \) must be approximately two times larger than that at \( T = 23^\circ C \), as follows from the current increase. This has the following explanation. At higher temperature the nucleation of critical bubbles occurred earlier and up to the moment \( t = 17 \mu s \) many more bubbles had enough time to grow to a visible size. At \( T = 23^\circ C \) most of the bubbles are small enough to be invisible.

This becomes even more clear when one compares the top and bottom rows. For example, the bottom image at \( 23^\circ C \) contains much more visible gas than the top image. However, when the pulse is over there is no gas production anymore and one would expect the equal or opposite relation between the gas volumes. There is a very simple and natural explanation for this phenomenon. The voltage pulse produces a certain amount of gas. This gas can exist in three forms: molecules dissolved in the liquid, nanobubbles larger than the critical size but smaller than needed to be visible with the stroboscope, and visible nano- or microbubbles. If homogeneous nucleation of bubbles occurs, then at a certain moment a significant volume of gas is collected in the invisible nanobubbles. These nanobubbles grow with time and become visible with a delay, producing the phenomenon of gas appearing from nothing.

We consider figure 4 and the explanations above as strong support for the idea that in the short-time electrolysis we observe homogeneous formation of bubbles.
3.3. Transition to long-time dynamics

Let us consider now how transition to the usual long-time electrolysis occurs. A negative or positive voltage pulse 100 $\mu$s long was applied to the working electrode. The electrode was observed at different moments of time when the pulse was already switched off. Some results are shown in figure 5.

It was already clear from figure 4 that nanobubbles growing from the nucleus start to coalesce at some moment of time and form microbubbles (see the bottom row in figure 4). Fast aggregation becomes possible due to the high density of nanobubbles. Now, from figure 5 one can see that significant changes occur between the images taken at 100 and 300 $\mu$s. The following dynamics becomes very slow. This is especially clear for the images at 0.5 and 5 ms. It is expected that the long-time dynamics is controlled by the slow diffusion and slow coalescence.

The main conclusion that one can make from the short-time stroboscopic observations is that the nanobubbles are densely produced in the homogeneous nucleation regime. They exist for some time in the ‘invisible’ form where they are too small to scatter light significantly but are invisible to the stroboscope. At later moments they become visible but still exist as separate nanobubbles. Later they start to aggregate to form microbubbles that are usually observed in electrolysis. Extremely high current densities and relative supersaturations are observed.

4. Alternating sign pulses

Up to now we have discussed only hydrogen and oxygen bubbles that are formed on different electrodes when a negative or positive voltage is applied to the working electrode. However, there is a simple but effective procedure that allows formation of bubbles containing a mixture of H$_2$ and O$_2$. Moreover, the gas composition can be controlled electrically. The idea is to use pulses of alternating polarity [21]. In this case hydrogen and oxygen will be produced locally above the same spot on the electrode. If the pulses are short enough that the gas redistribution due to diffusion can be neglected, one can expect formation of bubbles containing both gases.

For homogeneous nucleation formation of a bubble containing both gases is favorable in comparison to two bubbles containing different gases. This is because even in the regime of homogeneous nucleation there is an energetic barrier to forming the critical nuclei. For the second gas it is easier to diffuse inside the existing bubble than to overcome the barrier and form a new nucleus.

4.1. Reaction inside nanobubbles

While the frequency of the alternating pulses is not very high the process proceeds similarly to that for single polarity pulses. However, when the frequency is higher than $f = 20$ kHz (at room temperature) the visible gas suddenly disappears. This can be clearly seen in figure 6. The figure shows gas developed in the system after 1 ms of electrolysis. Negative potential pulses applied to the working electrode (at the bottom in each image) result in H$_2$ formation above this electrode at different frequencies (right column). No significant dependence on the frequency is observed. Oxygen formed above the working electrode for positive pulses also does not show frequency dependence (middle column). The left column shows the situation for the alternating pulses applied to the working electrode. In this case we observe strong dependence on frequency. Alternating pulses repeated with a frequency of $f = 20$ kHz produce significant amount of gas. One can see that this gas is collected in bubbles that differ from those in the middle and right columns. Already at $f = 50$ kHz only a small volume of gas is observed. At $f = 100$ kHz practically no gas is visible.
Figure 6. Gas production with negative pulses (right column), positive pulses (middle column) and alternating polarity pulses (left column) at different frequencies. For the alternating pulses the visible gas production disappears suddenly at higher frequencies.

Where has the gas disappeared to? The Faraday component of the current depends on frequency very weakly if it depends at all. Because pulses of single polarity produce gas at all frequencies it is difficult to assume that Faraday’s law breaks down at higher frequencies. Experimentally, we established that the disappearance of the gas is related to the stoichiometric production of hydrogen and oxygen. There is no visible gas production when the positive and negative halves of the pulse have the same duration. In this case two $H_2$ molecules are produced for one $O_2$ molecule. If we change the relative durations of the positive and negative parts of the pulse then the stoichiometric balance will be broken. In this case the gas reappears in the system, as shown in figure 7. In this figure $D$ is the duty cycle of the pulse, that is the fraction of time when the voltage on the working electrode is negative.

It seems reasonable to assume that the gas disappears due to a chemical reaction between gases occurring in the solution. Reaction is hardly possible between separate dissolved gas molecules. For high supersaturation the molecules exist in the solution for only a short time before entering nanobubbles, as one can see in figures 3 and 4. It is possible that the reaction proceeds in nanobubbles containing a stoichiometric mixture of $H_2$ and $O_2$. Of course, a bulk mixture of gases at room temperature and normal pressure will not react, but gases confined in a small volume could behave differently. It is known that below a certain size, material properties can change drastically [39]. For example, surface tension can support metastable phases of nanocrystals [40] that exist only at high pressure for bulk materials. In liquids the surface tension results in significant pressure inside nanobubbles. This pressure can shift the chemical equilibrium [41] and it is known also that fast dynamical processes play a role for ignition of the reaction on the macroscale [42–44]. Nevertheless, the precise mechanism of the reaction is not clear at this moment.

We also investigated the effect of gas disappearance in different solutions such as $Na_2SO_4$, $NaCl$ and $KI$ dissolved in deionized water to similar concentrations ($\approx 1$ M). The results of alternating pulse electrolysis in these solutions are shown figure 8. In the case of $NaCl$, hydrogen and chlorine are produced. These gases can react with each other in an exothermic reaction with an enthalpy, $\Delta H = -92 \text{ kJ mol}^{-1}$, considerably smaller than that for hydrogen and oxygen, $\Delta H = -242 \text{ kJ mol}^{-1}$. One can see that the amount of visible gas decreases with frequency increase but it does not disappear completely. This means that the reaction starts spontaneously in smaller bubbles than for $Na_2SO_4$ solution.
Nanobubbles with a size $d < \lambda/\pi$, where the stroboscope fails. The vibrometer is sensitive to variations of the optical path $\Delta d(t)$ of the laser beam with time. The optical path is defined by the change of the refractive index $\Delta n$ due to the presence of gas in the solution. If we assume that within the laser beam the lateral distribution of gas is homogeneous then

$$\Delta d = \int_0^\infty dz [\Delta n_1(z) + \Delta n_2(z)], \quad (6)$$

where $z$ is the vertical coordinate counting from the electrode surface, and $\Delta n_i(z)$ is the change of the refraction index due to gas $i$. Note that $\Delta d$ does not change if the gas molecules redistribute along $z$ but their number stays the same.

The refractive index of a liquid containing dissolved gas or gas collected in very small bubbles can be calculated using the Bruggman effective medium approximation [45]. If the volume fraction of gas is small, $f_i \ll 1$, then

$$\Delta n_i \approx \frac{3n_0(1 - n_i^2)}{2(1 + 2n_0^2)} f_i, \quad (7)$$

where $n_0 \approx 1.34$ is the refractive index of the solution at $\lambda = 633$ nm. The volume fraction of gas is expressed as $f_i = N_i / N_{\text{sol}}$, where $N_i$ is the concentration of the $i$th gas and $N_{\text{sol}} \approx 3.4 \times 10^{22}$ cm$^{-3}$ is the concentration of the solution. If the gas in the volume cannot disappear, for example, due to chemical reaction, then the vibrometer signal must be proportional to the total gas flux produced by the Faraday current [21],

$$v(t) = -\frac{\partial \Delta d}{\partial t} \approx \frac{0.35}{N_{\text{sol}}} [J_1(t) + J_2(t)], \quad (8)$$

where $v(t)$ is the signal of the vibrometer and its opposite sign is defined by the instrument. The total flux of the produced molecules, $J_{\text{tot}} = J_1 + J_2$, is a non-decreasing function of time.

We observed the process with a Polytec MSA-400 instrument. The laser beam ($\lambda = 633$ nm), with a diameter of 1.5 $\mu$m, was focused on the electrode at its center at a small distance from the edge. The signal is presented in figures 9(a) and (b). When the frequency of the alternating sign pulses is low, large bubbles can be formed that scatter light significantly. In this case one cannot extract helpful information from the signal, as shown in figure 9(a) for $f = 20$ kHz. However, for higher frequencies bubbles small in comparison with $\lambda/\pi$ are formed and one can clearly see the signal (see figure 9(b)). The signal becomes weaker at the inner areas of the electrode in accordance with the current distribution. It disappears altogether outside the electrodes. The latter demonstrates that the signal cannot be related to any kind of vibration. Integration of the signal over time gives the variation of the optical path $\Delta d(t)$. The integrated signal is presented in figure 9(c).

The function $\Delta d(t)$ demonstrates prominent maxima that are in phase with the voltage pulses. These maxima mean periodic decrease of the gas concentration in the liquid. The only reasonable explanation for this decrease is the reaction between hydrogen and oxygen. Of course, the vibrometer
signal is sensitive only to the overall concentration of gas in the liquid. It is not possible to say whether the gas interacts as dissolved molecules or inside nanobubbles. However, from observations of hydrogen and oxygen on the same time scale we know that each gas is collected in nanobubbles. It is hardly possible that the gases produced by alternating polarity pulses will behave differently.

The linear trend in $\Delta d(t)$ means that not all produced gas is burned in the reaction, but a small part is left after each period. This residual gas exists mainly in the form of dissolved molecules. When the gas production is switched off the residual gas disappears. To all appearances it disappears also as the result of reaction because reduction of the gas concentration due to diffusion has to proceed more slowly than observed. However, this point needs more attention.

4.3. Modification of the surfaces of the electrodes

The effect of disappearance of the gas is accompanied by modification of the electrode surface (see figure 10). We call this phenomenon ‘wear’ of electrodes. It has never been observed for single polarity electrolysis but is well visible for alternating polarity processing. The effect is observed for all investigated materials, Pt, Pd, W and Au, but manifests itself to a different degree. The strongest effect is observed for gold and the weakest one is for tungsten. This is in correlation with the material yield strength. The effect increases with the processing time, as shown in the bottom row of figure 10.

A chemical origin of the surface modification can be excluded because it is observed for different metals. On the other hand, we can exclude an electrochemical origin of the modification because it is not observed for single polarity pulses. We think that the surface modification occurs as the result of local release of energy from the exploding nanobubbles that mechanically modifies and shifts the material of the electrodes. This assumption naturally explains the correlation with the material yield strength.

We observed only weak modification of the electrodes for the alternating pulse electrolysis in the NaCl solution. In the KI solution there was no visible modification of the electrodes at all. These facts are in good agreement with the enthalpy of the reactions between $H_2$ and $O_2$, $Cl_2$ or $I_2$: the larger the enthalpy the stronger the modification of the surface.

The assumption of mechanical modification is supported by the analysis of the modified surface with an atomic force microscope (AFM). The AFM scan of the modified electrode is shown in figure 11. One can see significant displacement of the material in figure 11(b), but what is most important is that the process changes the roughness topography of the original platinum film completely, as one can see in figures 11(c) and (d).

The experimental information collected so far on the alternating pulse electrolysis (see also [21]) provides strong evidence that bubbles containing a stoichiometric mixture of $H_2$ and $O_2$ gases explode as a result of a spontaneous reaction between the gases if the bubble size is smaller than 100–200 nm. For pulses of low frequency the stoichiometric composition is reached for larger bubbles, which survive and can be observed with the stroboscope. The mechanism of the reaction in small bubbles is still not clear.
Homogeneous bubble production is closely related to the high current density that results in a huge supersaturation within the diffusion layer. The observed current density is large because we consider the system on the short-time scale $\tau \sim 10 \mu s$. In this case the current is not restricted by the diffusion of electroactive species to the surface as occurs for long-time electrolysis.

For single polarity pulses the critical nuclei are produced by density fluctuations that are possible because of very high electrolysis. In this case the current is not restricted by the diffusion of electroactive species to the surface as occurs for long-time electrolysis.

At higher temperature the microbubbles appear already at $\tau \sim 30 \mu s$ or even earlier.

When all the gas is collected in microbubbles the supersaturation in the surrounding liquid is low and the process becomes very slow. The microbubbles slowly dissolve diffusively. For example, a bubble of 10 $\mu m$ in diameter will dissolve for a time of the order of 100 ms.

The bubbles produced by the alternating polarity pulses evolve differently. The first half of the pulse produces high supersaturation of one gas, for example, H$_2$. Nuclei of hydrogen are formed homogeneously and grow diffusively. The second half of the pulse produces O$_2$ molecules in the same location above the electrode, but for oxygen it is energetically preferable to diffuse in the existing hydrogen bubble rather than to form a new O$_2$ bubble. This is why the alternating polarity pulses produce bubbles containing a mixture of hydrogen and oxygen. This mixture is stoichiometric if the positive and negative halves of the pulse have the same duration.

If a hydrogen bubble has grown large enough before oxygen starts to diffuse inside, then such a bubble evolves similarly to the bubbles containing only one gas. The lower the frequency of the alternating pulses is the longer time a bubble has for its growth. The critical frequency is around 20 kHz. The critical size of the bubble cannot be estimated very precisely from the experiment, but it is roughly around $d \approx 150$ nm [21]. For high frequency, $f > 20$ kHz, a bubble has no time to grow large. The gas mixture in the bubble becomes stoichiometric while its size is still under 150 nm. It was established (see also [21]) that in such a bubble the hydrogen and oxygen react spontaneously with bubble disintegration due to the large released energy.

The mechanism of the reaction inside the nanobubbles is not clear. Bulk mixtures of gases do not react at room temperature and the pressure is equivalent to the Laplace pressure $P_c = 4\gamma/d \approx 30$ bar for $d = 100$ nm. Of course, we cannot apply the classical combustion theory [46] to a strongly confined system such as a nanobubble. To all appearances fast microsecond dynamics plays an important role for the combustion of a mixture of gases. The detailed mechanism of the reaction is an important point that needs further attention.

The transient nanobubbles considered in this paper cannot help with our understanding of the stability of surface or bulk nanobubbles. The stabilization mechanism can work in these bubbles too but they cease to exist due to external reasons such as aggregation or combustion. The transient nanobubbles exist in a very thin diffusive layer above the surface, but we cannot say for sure whether they are attached to the surface or not. The relation between the transient and surface/bulk nanobubbles is an additional point that has to be understood.

5.2. Possible applications

We anticipate that the transient nanobubbles will have a wide application potential because of their unique properties. For example, dense coverage with homogeneously produced nanobubbles can be used for surface cleaning in
the electronics industry and other applications. Figure 12 demonstrates the proof of concept, where the original clean electrodes have been fouled with nanoparticles. The following homogeneous production of nanobubbles cleans the surface. The cleaning occurs as the result of aggregation of nanobubbles that pull the nanoparticles out of the surface. The cleaning effect has already been stressed for surface nanobubbles produced electrochemically [47] or with other methods [31, 48, 49]. However, homogeneous bubble production is better designed for local cleaning and has a pronounced dragging effect on nanoparticles.

Especially interesting applications are expected for the exploding nanobubble phenomenon. Combustion inside a nanobubble results in significant energy deposition that is localized in a nanovolume. It can be applied, for example, to delete strongly adhered nanoparticles from masks or wafers in the electronics industry. One can easily change the bubble size by electrical means (pulse frequency), significantly varying the energy of explosion.

Combustion in microscopic volumes is considered as difficult or impossible due to fast heat escape via the volume boundary [50]. The situation becomes different for nanovolumes. Exploding nanobubbles are the smallest combustion chambers realized in Nature [51]. They open up the principal possibility to fabricate an internal combustion engine microscopic in all three dimensions.

6. Conclusions

In this paper we described a special type of nanobubble, which we call a transient nanobubble. These bubbles exist for a very short time, \(<100 \mu s\), before aggregating with other nanobubbles to form microbubbles or before explosive disintegration due to reaction between hydrogen and oxygen. The most distinctive feature for all transient nanobubbles is their homogeneous production in the electrochemical process. In contrast with normal heterogeneous bubbling these bubbles nucleate due to fluctuations of the liquid density.

Homogeneous nucleation is possible only for extremely high supersaturations that are related to very high current densities. These conditions can be met on a short-time scale, \(\sim 10 \mu s\), when the diffusion of charged particles in the electrolyte does not restrict the current. On the short-time scale the gas produced on the electrode surface has no time to diffuse far away from this surface. For this reason high supersaturation can be realized only in a diffusion layer of thickness \(\sim 100 \text{ nm}\). In this thin layer only nanobubbles can be formed.

Short voltage pulses of fixed polarity repeated with a frequency \(f\) can densely cover the electrode surface with nanobubbles containing hydrogen or oxygen. These nanobubbles aggregate and form microbubbles on the time scale \(\sim 100 \mu s\). The following dynamics of the microbubbles becomes very slow.

Short voltage pulses of alternating polarity produce nanobubbles containing a mixture of hydrogen and oxygen. If these bubbles are smaller than 150 nm the gases inside them react spontaneously. As a result of this reaction significant energy is released in the close proximity of the electrode surface. The precise mechanism of the spontaneous reaction inside nanobubbles is still not clear and needs clarification.

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