

# DYNAMICS OF SINGLE H<sub>2</sub> BUBBLES DURING WATER ELECTROLYSIS

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*Abstract: The dynamics of hydrogen gas bubbles growing during electrolysis in H<sub>2</sub>SO<sub>4</sub> on a Pt microelectrode are studied in detail by electrochemical, shadowgraphy and PIV methods. The bubble evolution under potentiostatic conditions is presented in terms of electric current, images and radius of the growing bubble, and the velocity profiles. It allowed to resolve the carpet of microbubbles underneath the growing bubble, the transition to a new oscillatory growth regime and a Marangoni convection around the bubble foot. To substantiate the effect of coalescence and of the electrostatic effect on the bubble departure diameter, a salt (sodium sulfate) was added to regulate the pH and the ionic strength of the electrolyte.*

*KEYWORDS: bubble dynamics, water electrolysis, hydrogen, force balance*

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## 1. INTRODUCTION

The economic large-scale production of hydrogen is of high interest for both hydrogen-based energy storage systems and mobility systems employing fuel cells. One important piece of technology to produce the required high-purity hydrogen consists of water electrolysis. Commercially, the technique has been used for a long time in alkaline electrolyzers, although its percentage of world hydrogen production currently is only around 4%.

One of the key issue to be solved towards large-scale hydrogen production by water electrolysis is to lift the efficiency of the process. In conventional alkaline and Proton Exchange Membrane (PEM) electrolyzers a considerable part of the losses is related to the dynamics of the electrogenerated hydrogen and oxygen bubbles which increase the overpotentials by covering the effective electrocatalytic sites, and by the raising the Ohmic resistance.

One precondition for efficient bubble management is a detailed understanding of the key mechanisms of hydrogen bubble formation, growth, and detachment. However, despite extensive efforts in the past, important aspects of bubble dynamics, such as the interaction and coalescence of bubbles or the different growth modes of the bubbles themselves, are not yet fully answered. Thus, a better understanding of the processes affecting the hydrogen bubble evolution might reveal the key aspects on how to remove them from catalytic sites efficiently i.e. fast and at small sizes. It furthermore has important implications for many catalytic reactions that include gas formation [Lv2017].

The present contribution is focused on our studies on single hydrogen bubble dynamics, including the formation, growth, and detachment at a platinum microelectrode during the water electrolysis of an acidic electrolyte.

## 2. MATERIAL AND METHODS

To produce hydrogen bubbles, the water electrolysis was performed in a three-electrode electrochemical cell that is shown in Fig.1 (a). The experimental setup is similar to the one described in our previous works [Yang2015, Bashkatov2021]. The cell consists of three electrodes inserted into the glass cuvette of 10×10×40 mm<sup>3</sup> filled with H<sub>2</sub>SO<sub>4</sub> of various

concentrations. Single H<sub>2</sub> bubbles are generated on a horizontally installed  $\varnothing 100 \mu\text{m}$  Pt microelectrode, faced upward, see Fig. 1(a). Two Pt wires (0.5 mm) inserted from the top served as anode and pseudo reference electrode, if not otherwise mentioned. The electrodes are connected to the workstation (Zahner-Elektric GmbH) operating in potentiostatic mode.

The bubbles were visualized through a microscope by a high-speed camera providing a spatial resolution of 1000 pix/mm. The flow field around the growing bubble was measured by microscopic Particle Image Velocimetry (PIV) technique with a spatial resolution of 307 pix/mm. To resolve the velocity around the bubble, monodisperse fluorescent polystyrene particles of 5  $\mu\text{m}$  diameter (microParticles GmbH, PS-FluoRed, 530 nm/607 nm) were seeded into the flow. Electrochemical experiments (sampling rate of 1 kHz) yielded the electric current while optical measurements simultaneously performed at 1000...2000 frames per second gave access to the bubble shape. The combination of a microelectrode and a sulfuric acid electrolyte allows to produce single hydrogen bubbles with periodic detachment at very similar bubble sizes (Fig. 1b). Thus it helps to study various phenomena such as the position oscillations or Marangoni convection systematically.

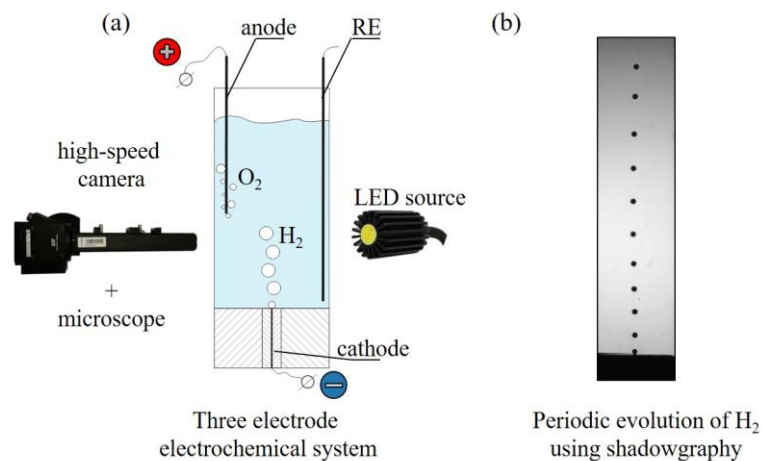


Fig. 1: (a) Schematic of three-electrode electrochemical system and (b) an example of periodic H<sub>2</sub> bubbles evolution

### 3. RESULTS

In Figure 2, a detailed insight into the bubble evolution in 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> at -4 V is documented. In Fig. 2(a) bubble images at different periods of the evolution, from nucleation toward detachment are shown. The corresponding evolution of bubble radius and electric current over time is plotted in Fig. 2(b) for five bubbles subsequently produced after each other. Each curve starts with the nucleation and ends off when a bubble detach. The first cycle corresponds to the images in (a). The time interval between two neighboring circles, denoting the nucleation and detachment, represents the bubble lifetime  $T$ .  $R(t)$  from Fig. 2(b) is calculated from the charge  $Q = I \times t$  transported via Faraday's law. When the diffusion into bulk

is only a minor contribution and the whole hydrogen produced form a single bubble, its volume, respectively its radius, can be calculated at each instant of time [Yang 2015].

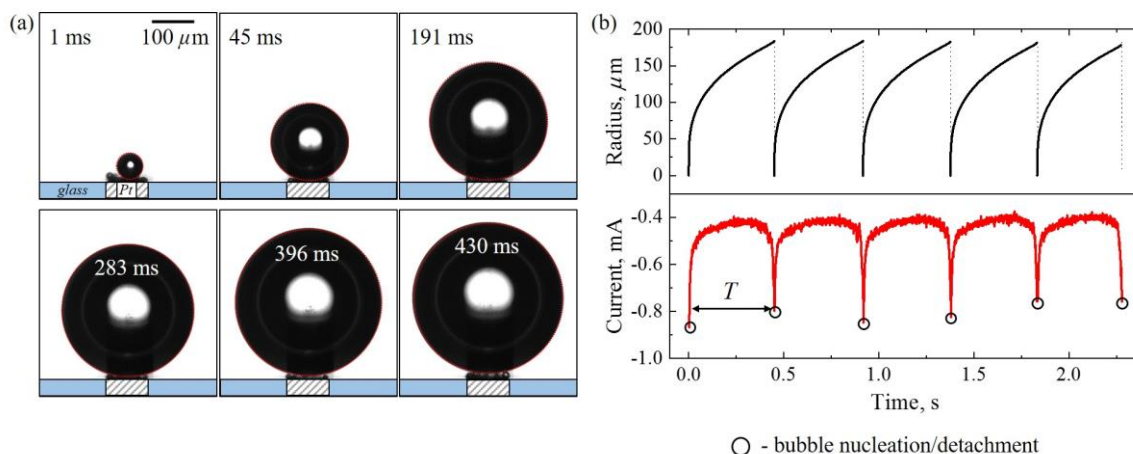


Fig. 2: (a) Snapshots representing the bubble evolution and (b) radius of the bubble and electric current over time in 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> at -4 V (vs pseudo RE).

The bubble starts to nucleate and grow when the potential is applied. Multiple nano- and micro-bubbles form and populate the electrode surface immediately. These micro-bubbles coalesce rapidly and form a single bubble sitting at the center of microelectrode with  $R \approx 30 \mu\text{m}$  already after 1 ms. The bubble continues to grow by both coalescence with microbubbles at the foot of the electrode and direct gas diffusion from the electrolyte in the vicinity to the electrode which is oversaturated with H<sup>+</sup> ions. The microbubbles mentioned above form a so-called bubble carpet [Bashkatov2017]. The bubble detaches, in Fig. 2(a) at  $t \approx 430$  ms, when buoyancy exceeds the downward forces that keep the bubble close to/at the electrode. The peaks in electric current are due to the low Ohmic resistance shortly before bubble formation and after its detachment, when the electroactive electrode area is released for the reaction. The growth rate of the bubble, reflected by the slope of the  $R(t)$  curve, varies along with time  $t$  as a result of electric current  $I$  which is affected by the bubble size and position. The detachment of the bubble is immediately followed by the nucleation of a new bubble at the microelectrode. The hydrogen bubble evolution on the Pt microelectrode follows a  $R(t) \propto t^{1/3}$  law [Yang2015] and was found to depend on the cathodic potential and the electrolyte concentration [Bashkatov2019].

A new bubble growth regime recently reported in [Bashkatov2019] is exemplarily shown in Figure 3 in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> at -6 V. The evolution of the bubble in this case is characterized by the transition from monotonic to oscillatory growth due to distinct oscillations in the bubble position leading to electric current oscillations. In Fig. 3, (a) represents the electric current along the whole growth cycle and (b) zooms in (a) to reflect a part of the oscillations shortly before detachment. Fig. 3(c) shows two snapshots representing the bubble at two different moments during the oscillations: (i) – bubble is at highest position and (ii) – is at lowest, marked correspondingly in (b).

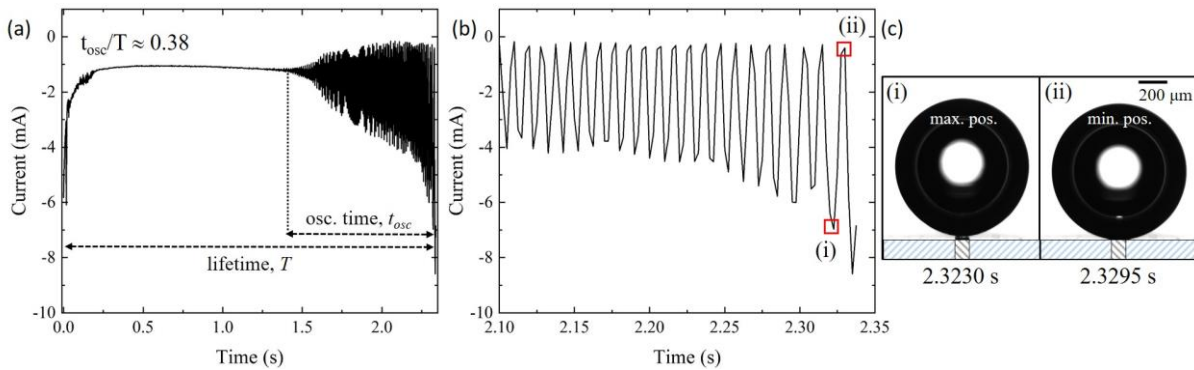


Fig. 3: An example of bubble oscillations in 0.5 mol/L at -6 V: (a) The electric current over time. The oscillations take about 40 % of bubble lifetime; (b) Zoom into (a), representing the current oscillations shortly before detachment; (c) Two snapshots representing the bubble at a selected maximum and minimum of the current oscillations: (i) – bubble is at highest position and (ii) – is at lowest. Potential is applied vs pseudo RE.

The oscillatory phenomenon consists in periodic upward and downward movements of the bubble accompanied with the carpet formation, also oscillating in time. Similarly, to conventional bubble evolution represented in Fig. 2, the bubble grows by the coalescence with the microbubbles and the diffusion of  $H^+$  ions and slowly moves upward. Once the bubble trying to leave the electrode, thereby going up, it returns to the electrode, initiating by that the successive long-lasting position oscillations. As the bubble goes up, the Ohmic resistance drops, which increases the electric current. When the bubble goes down, the opposite situation happens. It reshapes the geometry of the current lines  $j$  directed from anode to cathode which in turn affects the electric force. In [Bashkatov2019] it was shown numerically that the electric force, that brings the bubble back to the electrode, increases together with the carpet thickness until its critical value of around  $\delta_{crit} = 20...30 \mu m$  at which the bubble detaches. The oscillation amplitude (and carpet thickness) rises during the oscillations until this critical value  $\delta_{crit}$ .

In Figure 4, the velocity field  $|V|$  is shown around the hydrogen bubble produced in 1 mol/L  $H_2SO_4$  at -6 V. The velocity is averaged over 0.4 s shortly before detachment.

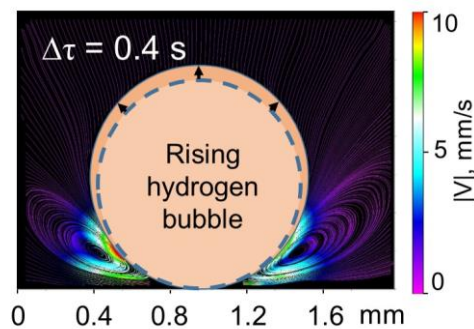


Fig. 4: Velocity field  $|V|$  around the hydrogen bubble, produced in 1 mol/L  $H_2SO_4$  at -6 V, averaged over 0.4 s shortly before detachment. Potential is vs MSE.

The velocity profile has a clear vortex structure close to the bubble bottom. This is a clear fingerprint of the so called Marangoni convection which is driven by a shear stress at the gas-liquid interface caused either by thermal and/or concentration gradients. In previous works [Yang2018, Massing2019, Hossain2020], we found that the Marangoni convection can largely be attributed to the thermocapillary effect caused by Ohmic heating due to the high current density appearing at the microelectrode. Numerical simulation proved that the main features of the convection can be attributed to the thermal Marangoni effect. The effect was shown to

be important at large planar electrodes as well. Furthermore, the convection is known [Yang2018] to enhance together with the electric current, i.e. along with the bubble evolution or when the cathodic potential is increased. Therefore, the velocity is the highest shortly before detachment, when the current attains a maximum value.

To suppress the coalescence and to weaken the downward forces including electrostatic interaction between the bubble and electrode, a salt, sodium sulfate of different concentration was used. In Figure 5, the bubble detachment diameter over cathodic potential is shown for two cases: (a) constant pH at various ionic strength and (b) constant ionic strength at various pH.

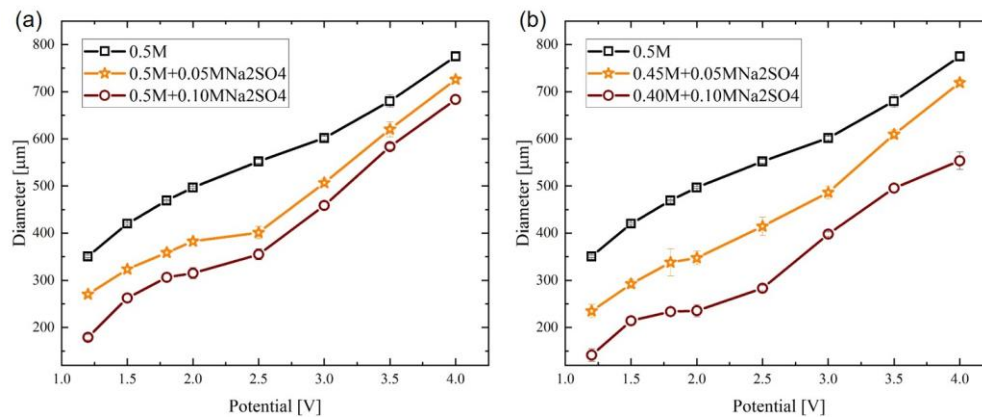


Figure 5: Detachment diameter over potential for: (a) constant pH, with various ionic strength controlled by Na<sub>2</sub>SO<sub>4</sub>; (b) various pH, with constant ionic strength controlled by Na<sub>2</sub>SO<sub>4</sub>. Potential is vs MSE.

The increase of the potential leads to higher downward forces keeping the bubble stronger at the electrode and therefore to higher values of the bubble diameter at the detachment. In both situations, (a) and (b), the addition of the salt inhibits the bubble-bubble coalescence. As a result, the bubble detaches with a smaller diameter.

#### 4. DISCUSSION AND OUTLOOK

In potentiostatic mode, which is the case in this study, the electric current reflects the bubble dynamics. Besides the cathodic potential and the conductivity, given by the electrolyte concentration, the current also depends on the resistance caused by the bubble size, its position and thus the electroactive area available at the electrode. The latter is related to the force pulling the bubble towards the electrode, which are the Marangoni and electric forces as well as with the bubble-carpet coalescence-driven  $F_{g-g}$  force [Hossain et al. 2021].

The Marangoni flow, exerting the Marangoni force  $F_M$ , is attributed to the thermocapillary stress tensor and rises as per current density increase [Yang2018]. The magnitude of the electric field  $E$ , contributing to the electric force  $F_e$ , was recently shown to vary together with the bubble position and therefore with electric current [Bashkatov2019], and to contribute to the oscillation mechanism. It was shown, both the critical carpet thickness at detachment and the oscillation frequencies of the bubble as predicted by the model agree well with the experiment. The rate of gas carpet-bubble coalescence, exerting bubble-carpet coalescence-driven force  $F_{g-g}$ , enhances with current as well. The shift of the center of mass toward the electrode is expected, when two bubbles coalesce, even of different sizes. The situation might become even more delicate when many nucleation sites are available at an increasing hydrogen production rate.

In recent work [Bashkatov2021], the existence of reversals of the bubble's (lateral) movement was shown in a microgravity environment following coalescence events. These negative forces keeping the bubble at or close to the electrode, and enhance further as per potential and concentration increase.

At each instant of bubble evolution, the force balance is at the nearly equilibrium state. As the bubble grows, the equilibrium breaks and the bubble tends to move upward, increasing gradually the carpet thickness, and seeking by that a new equilibrium. The increase of carpet thickness increases the electrochemical reaction rate, hence the electric current and therefore also the Marangoni and electric forces, and the coalescence rate. The process continues until the increment of these current/distance/geometry-dependent downward forces is smaller than the increment of the buoyancy force, thus overpassing irreversibly the equilibrium state. In such a terminology, the detachment is a lasting process rather than an instant of time.

### *Membraneless electrolyzer*

A current focus of our works is oriented towards the membraneless electrolyzer architecture as a platform to study the coupling between electrochemistry and fluid dynamics in more details. By elimination of membranes or diaphragms from typical electrolyzers, advantages like reducing of the CAPEX, increasing of the lifetime of the device and a higher tolerance to impurities can be achieved. Additionally, due to their simple design, membraneless electrolyzers can be easily produced using additive manufacturing.

Mainly two types of membraneless electrolyzer are studied, distinguished according to the type of electrode: flow-by (FB) and flow-through (FT) electrodes [Esposito2017]. Due to the flow-induced separation of the products, the understanding of the bubble dynamics is important to optimize the efficiency and operating conditions of membraneless electrolyzers [Pang2020]. A new 3D printed electrolyzer cell with good optical access to the working electrode is introduced. This promises the possibility to study the nucleation, growth and detachment of multiple H<sub>2</sub> bubbles depending on the flow rate, applied current density, the type of working electrode (e.g. foam, woven mesh) as well as the type of membraneless electrolyzer (FB or FT).

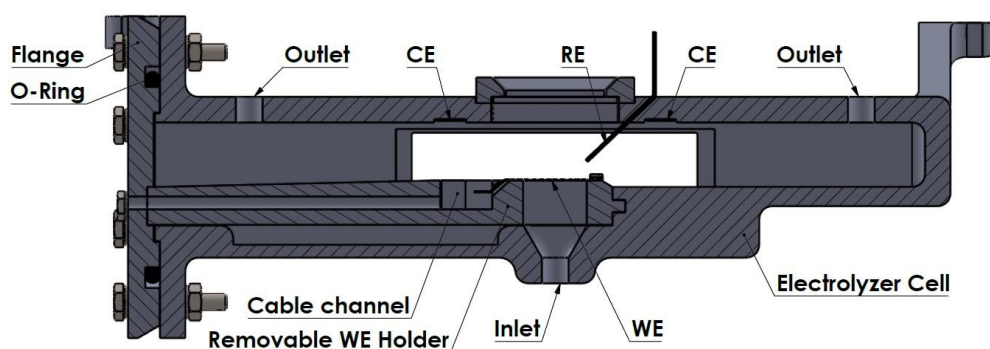


Fig. 6: Sketch of the 3-electrode-system with a flow-through electrode mounted on the removable working electrode (WE) holder

The in-house designed three-electrode system, which is shown in Figure 6, allows studying the bubbles formation process at the macro electrodes by optical measurements in top and side view simultaneously with electrochemical approaches. The electrodes having a modified

structure (i.e. having a mesh or foam pattern) can be placed and tested for their performance. The purity of the hydrogen is of importance and is especially questioned with the absence of membrane, separating the oxygen and hydrogen gases, and therefore is to be measured by gas-chromatography.

## 5. CONCLUSION

The bubble dynamics is an important aspect of electrolysis to be considered. The force balance which the bubble experiences varies very delicately during bubble evolution interrelated with the electric current and experimental parameters. The increase of the downward forces along with the bubble evolution results in the carpet of microbubbles and the transition to oscillatory growth regime. The future works besides projecting the existing knowledge to the macro electrodes are worth to be spent to the study of the bubble-bubble coalescence in more detail. The membraneless electrolyzer architecture is, besides its interesting features a suitable platform for such in-depth studies.

## ACKNOWLEDGEMENTS

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