

# On the dynamics of hydrogen bubbles during water electrolysis

## Motivation

The evolution of electrogenerated gas bubbles, such as those formed during water electrolysis, significantly hampers the overall efficiency of the process. These gas bubbles act as almost perfect insulators, increasing the Ohmic resistance both close to the electrode surface and in the electrolyte bulk [1] (see Figure 1). Additionally, they block the surface of the electrode, which leads to additional losses [2]. A better understanding and control of the bubble dynamics [3] is crucial to optimize the cell design and operating parameters.

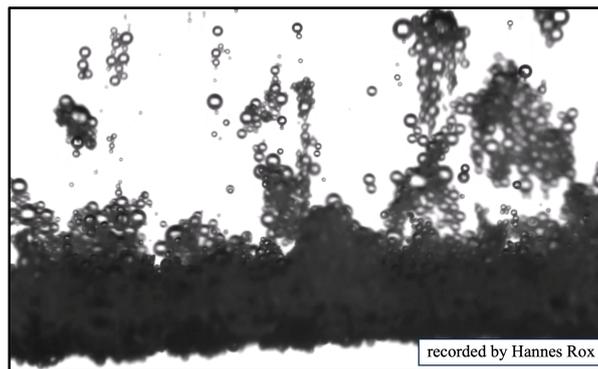


Figure 1: Evolution of the hydrogen bubbles on mesh electrode. Adapted from Rox et al.[1].

The evolution of electrogenerated  $H_2$  bubbles is a multifaceted problem at the intersection of fluid mechanics and electrochemistry. The growth and detachment stages of the evolution are for example interconnected with the gradients of chemical species and/or temperature close to the electrode surface causing Marangoni convection, electrostatic interactions, composition of the electrolyte, wettability of the surface, coalescence events between neighboring bubbles leading to earlier departure, motion reversals as well as to the injection of electrolyte fractions inside the gas phase, etc.

## Assignments

The micro-electrode fabrication provides a platform to study more fundamentally the evolution of electrochemically generated gas bubbles by focusing on single (or few) gas bubble events by spatially constraining nucleation sites. In this context, the dynamics of a pair of  $H_2$  bubbles produced during water electrolysis in acidic (or alkaline) electrolytes at a dual microelectrode are being systematically studied by varying the cathodic potential and electrolyte composition. By combining high-speed imaging and electrochemical methods, you will have the opportunity to explore **the coalescence driven dynamics of pair of hydrogen bubbles** (Section 1) or **Marangoni convection** (Section 2), depending on your preference. During preliminary experiments, the bubble-bubble coalescence events were shown to on one hand lead to a significantly earlier departure than that defined by the buoyancy (see Figure 3). On the other hand, repeated coalescence events may also reverse the motion direction of the once-departed bubble. The latter leads to a growth resumption near the electrode surface until buoyancy-driven detachment. Upon return to the electrode, the increase in the current density leads to noticeable Marangoni convection at the foot of the bubble consecutively imposing additional Marangoni force which substantially alters the undergoing force balance. Depending on the electrolyte composition and magnitude of the electric current, the Marangoni convection can be dominated by either soluto- or thermocapillary effects. The resulting force will act either in a downward or upward direction, hence hindering or assisting the departure process of the bubble from the electrode[4].

# 1 Coalescence-driven dynamics

Soon after the hydrogen evolution reaction begins, a single bubble forms and grows at each of the two electrodes. This process continues until the two bubbles touch and coalesce, which is followed by the departure of the merged bubble (see Figure 2). Figure 3c details this coalescence process, which happens on the order of micro-seconds, and the emerging deformations of the bubble shape. However, as the corresponding shadowgraphs show, even though the bubble jumps off after the coalescence event, it is eventually brought back to the surface through repeated coalescence with newly formed bubbles at both electrodes (see the period between  $t = 3.6$  ms and  $t = 18.8$  ms). Following this return, the bubble rests between the two electrodes just above the surface. There, it continues to grow for a longer time until a buoyancy-driven departure at a much larger size. This will potentially increase the ohmic resistance in the system and lower the electric current, hence the  $H_2$  production rate.

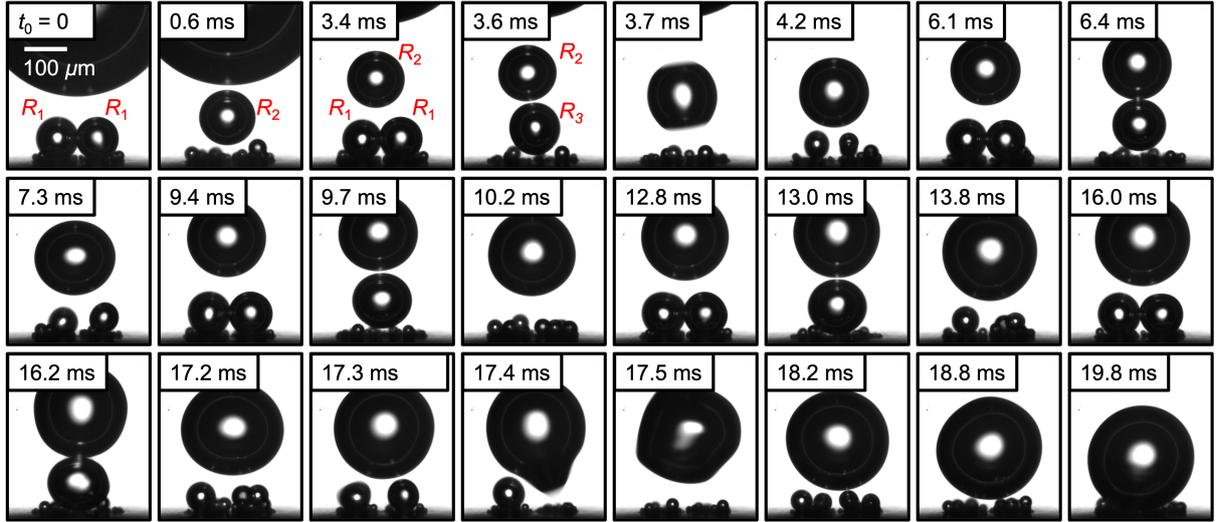


Figure 2: Bubble evolution at -1.3 V (vs RHE) and  $H = 117 \mu\text{m}$ .  $t_0 = 0$  corresponds to an instant of time one frame before coalescence. Recording carried out at 10 kHz.

## 1.1 Coalescence-driven departure

Upon coalescence of two bubbles, there is a release of surface energy ( $\Delta G_s$ ) given as

$$\Delta G_s = 4\pi\gamma(R_l^2 + R_r^2 - R_I^2), \quad (1)$$

where  $R_l$ ,  $R_r$ , and  $R_I$  are the left, right, and merged bubbles, respectively.  $\gamma$  is the surface tension of the electrolyte. The released energy partly dissipates by the bubble oscillations, working against viscous drag ( $W_\mu$ ). When in proximity to the surface, the remaining energy is converted to the kinetic energy ( $E_k$ ) driving the resultant (merged) bubble to jump off the electrode.

In detail, when two bubbles approach each other, the thin film of electrolyte separating them gradually drains (on the order of  $\mu\text{s}$ ) and eventually ruptures. This leads to the formation of a neck, i.e. an open cavity, and a series of capillary waves of varying strengths that propagate along the electrolyte-gas interface. These waves move away from the neck region until they meet at the opposite apex of the coalescence point (see Fig. 3). The strength of these waves decreases as they travel along the interface due to continuous viscous dissipation. Meanwhile, the surface tension  $\gamma$  drives the retraction of the remaining capillary waves towards a spherical shape, deforming the bubble shape. Once the excess surface energy overcomes the work done by the bubble against viscous drag during the expansion and retraction processes, the resultant net component of momentum perpendicular to the surface causes the bubble to jump off the electrode. As neither of the bubbles is attached to the electrode, the adhesion energy  $W_a$  is neglected. Therefore, the process is controlled by surface tension and viscosity. The influence of gravity during the coalescence, before lift-off, is negligible. While the process is considered

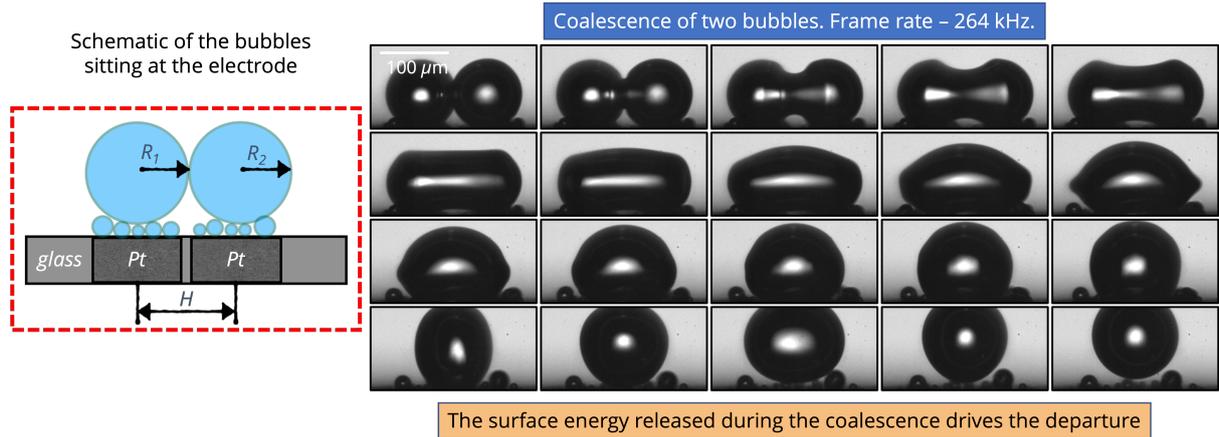


Figure 3: Schematic of two bubbles sitting at Pt microelectrodes and experimental snapshots of coalescence-driven departure process recorded at a frame rate of 264 kHz.

highly inefficient, with only a small portion of surface energy translating into kinetic energy, it is sufficient for a resultant bubble to jump off the electrode.

One way to estimate the translated kinetic energy of the jumping bubble is by tracking the maximal distance the bubble would jump over the electrode or by measuring the initial jumping velocity of the bubble. While the latter is associated with measurement difficulties, the measurement of the maximal distance can be realized by using an upside-down configuration of the dual-electrode setup, presented in Figure. 4. The left snapshots demonstrate that the maximal jumping position of the merged bubble, hence the magnitude of the translated kinetic energy, will depend on the initial size of both bubbles, in this case given by the distance between two electrodes ( $H$ ).

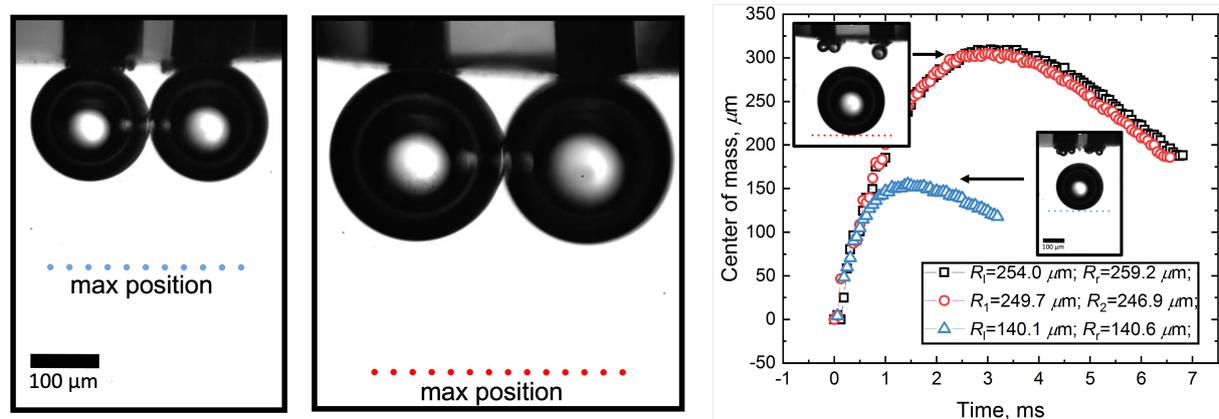


Figure 4: On the left: the snapshots of two gas bubbles prior their coalescence for two different electrodes; On the right: the bubble position over time following coalescence-driven jump off of the electrode surface.

In that context, this study focuses on the systematic characterization of the ratio between the translated kinetic energy ( $E_k$ ) and the released surface energy ( $\Delta G_s$ ) as a function of the distance between two electrodes ( $H$ ), parent size ratio and possibly the electrolyte viscosity. The bubble position over time (including its maximal position) is to be predicted by the model based on the force balance and compared with the experimental results.

## 1.2 Coalescence-driven motion reversals: mass center

Figure 2 demonstrates that once departed bubble might be eventually brought back to the surface through repeated coalescence with newly formed bubbles at both electrodes. Although the probability

of such an event depends on how fast the primary bubble is moving away from the electrode (previous part of the project) and on  $H_2$  production rate (given by the electric current), it is interesting to track the mass center of the merged bubble, since the coalescence prior the motion reversals occur between the bubbles having a large size ratio and in the vicinity of the wall (electrode). Such configuration could cause additional hydrodynamic effects around the merging bubble during and after the coalescence.

The sketch in figure 5 illustrates the relevant mechanism for the bubble return. A newly formed bubble (with radius  $R_s$ ) on one of the electrodes catches up and coalesces with the departed bubble with radius  $R_l$ . Due to momentum conservation, the resulting bubble is then located at the joint center of mass of the two coalescing bubbles, which implies a downward shift by  $d_l$  and  $d_s$  compared to the location of the bubble with radius  $R_l$  and  $R_r$ , respectively.

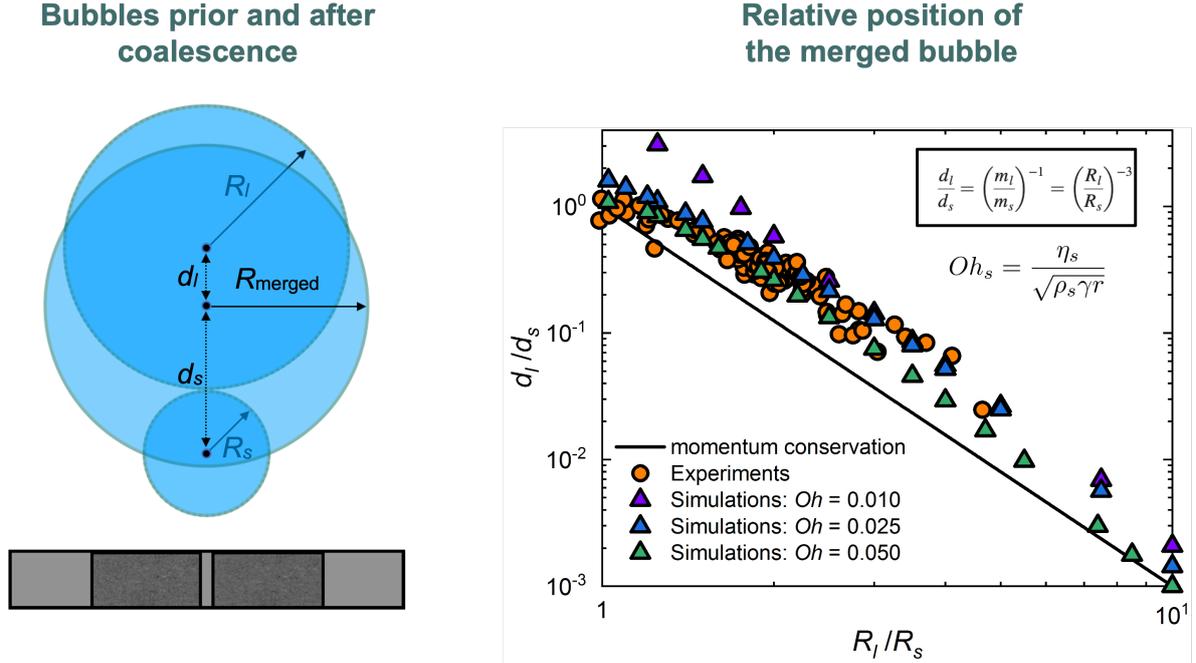


Figure 5: Left: schematic of the bubble prior and after coalescence; Right: the relative position of the merged bubble as a function of parents size ratio. The black line is based on the momentum conservation. The circles are experimental data. The triangles are product of numerical simulations, carried out by Vatsal Sanjay. The results are preliminary and given only for reference.

Figure 5 on the right documents the relative position of the merged bubble as a function of the parents' size ratio. The black line is based on the momentum conservation. The circles are the experimental results. Each point is extracted from a single and independent coalescence event. The triangles are the results from numerical simulations carried out by Vatsal Sanjay for different Ohnesorge numbers ( $Oh$ ). From these preliminary results, one can conclude that the merged bubble is moving for a larger distance toward the electrode as a result of each coalescence event than one would anticipate from the momentum conservation.

In that context, this study focuses on (i) the systematic characterization of the mass center of the merged bubble following the coalescence event as a function of parent size ratio and possibly of electrolyte viscosity; (ii) on the research of existing literature on the given topic and finally (iii) building up the model explaining the observed phenomenon.

## 2 Marangoni convection around $H_2$ bubbles

The surface tension for a given liquid-gas pair is known to depend on the physical properties of the interface, namely the temperature, chemical composition, and electric potential in the presence of interfacial charge. Thus, interfacial gradients of these physical properties cause the surface tension to vary along

the interface and are known as thermal-, solutal- and electrocapillary effects [5]. As a result, due to unbalanced forces at the interface, fluid elements there experience a net shear stress and move towards interface regions of higher interfacial tension. The resulting capillary flow is commonly called Marangoni flow [6].

In the case of electrogenerated gas bubbles, in this particular case  $H_2$  bubbles, the variation of the surface tension along the bubble-electrolyte interface reads as

$$\frac{\partial \sigma}{\partial S} = \gamma_1 \frac{\partial T}{\partial S} + \sum \gamma_2^{(i)} \frac{\partial c^{(i)}}{\partial S} + \gamma_3 \frac{\partial \phi}{\partial S} \quad (2)$$

for the thermal-, solutal- and electrocapillary effects. Here,  $S$ ,  $\gamma_1$ ,  $\gamma_2^{(i)}$  and  $\gamma_3$  denote the tangential coordinate along the interface and the partial derivatives of the surface tension with respect to temperature  $T$ , species concentration  $c^{(i)}$  and electric potential  $\phi$ .

It has been found that the electrolyte flow at the bubble-electrolyte interface, shown in Figure 6, primarily originates from either soluto- or thermocapillary effects imposing electrode-normal force components altering the bubble departure depending on the applied electric current or potential, and electrolyte composition [7, 4]. The temperature gradient was found to be largely caused by the highly concentrated

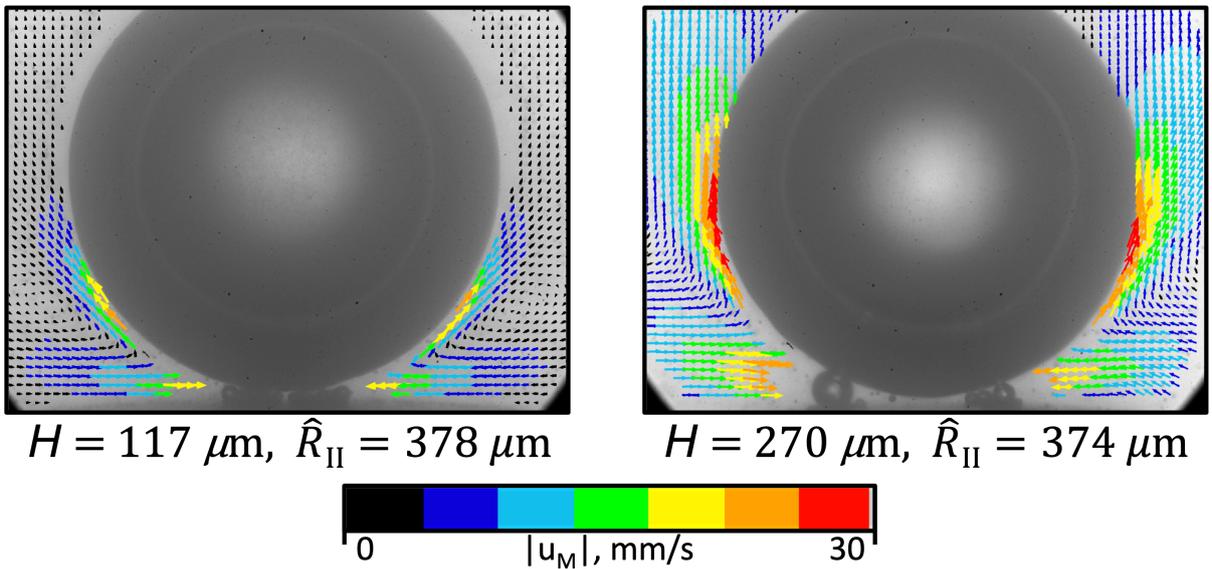


Figure 6: Velocity fields,  $|u_M|$ , representing Marangoni convection at dual microelectrode at  $-2.8$  V (vs. RHE) and  $H = 117 \mu\text{m}$  and  $H = 270 \mu\text{m}$ .  $H$  is the interelectrode distance. The velocity is measured in a period of 25 ms before the bubble departure.

Joule heating, given by  $|\vec{j}|^2/\kappa_{el}$ , at the foot of the bubble.  $\vec{j}$  is the local current density vector in the electrolyte and  $\kappa_{el}$  is the electric conductivity of the electrolyte. The solutocapillary effects arise from the ion concentration gradient. — The region near the platinum electrode has a lower ion concentration than the bulk region due to the fast proton consumption which leads to a corresponding anion concentration gradient along the bubble/ electrolyte interface to satisfy electroneutrality. For example, in the case of  $H_2SO_4$ , a lowered ion concentration near the platinum surface region lowers the local surface tension. Consequently, the solutal Marangoni flow along the bubble surface steers away from the platinum surface, and therefore the solutal Marangoni force would act towards the electrode. However, the sign of the resulting solutal Marangoni force will depend on the electrolyte composition, namely on whether the surface tension is decreasing or increasing with ion concentration [4].

In that context, this study focuses on the systematic characterization of the Marangoni convection (both soluto- and thermocapillary driven) around  $H_2$  bubbles produced at single or dual microelectrode systems as a function of electric current or potential, and electrolyte composition.

## What to expect? What will you learn?

We are looking for enthusiastic students with an interest in experimental work. You can expect a readily available setup, state-of-the-art measurement equipment, comprehensive support, interesting discussions, and supervision of the work.

### You will learn

- About the dynamics of electrogenerated gas bubbles produced during water electrolysis
- How to perform electrochemical and high-speed optical measurements
- Image processing in Matlab/Python (by your choice)
- Basic and advanced scientific data analysis

Please, feel free to contact Aleksandr in case of any related questions. Contacts below:

Supervision	E-mail	Office
Dr. Aleksandr Bashkatov	<a href="mailto:a.bashkatov@utwente.nl">a.bashkatov@utwente.nl</a>	Meander 114c
Assoc. Prof. Dr. Dominik Krug	<a href="mailto:d.j.krug@utwente.nl">d.j.krug@utwente.nl</a>	Meander 251
Prof. Dr. Detlef Lohse	<a href="mailto:d.lohse@utwente.nl">d.lohse@utwente.nl</a>	Meander 261

## References

- [1] Hannes Rox, Aleksandr Bashkatov, Xuegeng Yang, Stefan Loos, Gerd Mutschke, Gunter Gerbeth, and Kerstin Eckert. Bubble size distribution and electrode coverage at porous nickel electrodes in a novel 3-electrode flow-through cell. *International Journal of Hydrogen Energy*, 48(8):2892–2905, 2023.
- [2] Andrea Angulo, Peter van der Linde, Han Gardeniers, Miguel Modestino, and David Fernández Rivas. Influence of bubbles on the energy conversion efficiency of electrochemical reactors. *Joule*, 4(3):555–579, 2020.
- [3] Aleksandr Bashkatov, Syed Sahil Hossain, Gerd Mutschke, Xuegeng Yang, Hannes Rox, Inez M Weidinger, and Kerstin Eckert. On the growth regimes of hydrogen bubbles at microelectrodes. *Physical Chemistry Chemical Physics*, 24(43):26738–26752, 2022.
- [4] Sunghak Park, Luhao Liu, Çayan Demirkır, Onno van der Heijden, Detlef Lohse, Dominik Krug, and Marc TM Koper. Solutal marangoni effect determines bubble dynamics during electrocatalytic hydrogen evolution. *Nature Chemistry*, 15(11):1532–1540, 2023.
- [5] Steven Lubetkin. The motion of electrolytic gas bubbles near electrodes. *Electrochimica acta*, 48(4):357–375, 2002.
- [6] Syed Sahil Hossain, Gerd Mutschke, Aleksandr Bashkatov, and Kerstin Eckert. The thermocapillary effect on gas bubbles growing on electrodes of different sizes. *Electrochimica Acta*, 353:136461, 2020.
- [7] Julian Massing, Gerd Mutschke, Dominik Baczyzmalski, Syed Sahil Hossain, Xuegeng Yang, Kerstin Eckert, and Christian Cierpka. Thermocapillary convection during hydrogen evolution at microelectrodes. *Electrochimica Acta*, 297:929–940, 2019.