Supplementary information

Marangoni convection at electrogenerated hydrogen bubbles

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1. Electrochemical cell setup[1]

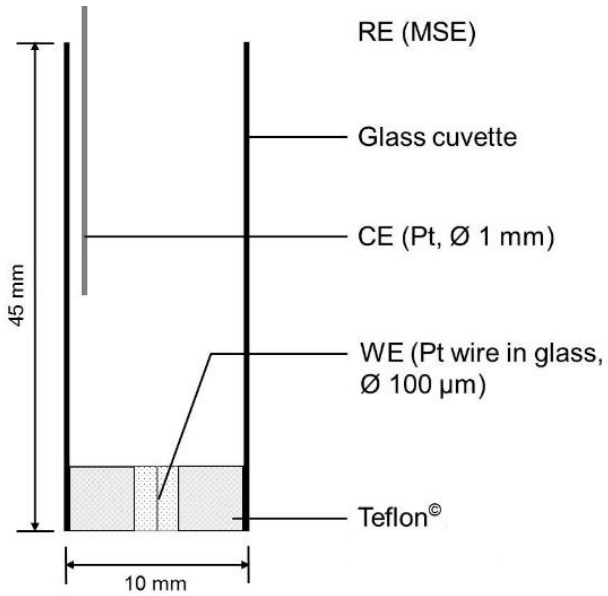

Fig. S1 Sketch of the 3-electrode electrochemical cell. RE - reference electrode; MSE - Mercury/mercurous sulphate electrode; CE – counter electrode; WE – working electrode.

As shown in Fig. S1, the electrolysis was carried out in a glass cell at 3-electrode setup. The cell was made from a cuboid glass cuvette (Hellma) with the dimension of height × width × depth = 45 × 10 × 10 mm^3. The working electrode was a 100 µm thick Pt wire with a purity of 99.99 % and was burned into a glass capillary (diameter 6 mm). This capillary was then inserted into a Teflon® plate. The Pt electrode surface was polished with SiC paper, ending with #4000. The bottom of the glass cuboid cell was cut to mount the Teflon® 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. Electrolysis was carried out in 1 M H_2SO_4 electrolyte at potentiostatic conditions with a Zahner Zennium electrochemical workstation with a sampling rate of 1000 Hz. The glass cell and Teflon® plate were cleaned with Caro's acid and rinsed carefully with deionized water before performing the first measurement. The cell and electrode were cleaned three times with distilled water and fresh electrolyte before every further series of experiments. After the experiments, the glass cell was filled with distilled water so that the Pt electrode was preserved under wet conditions. Before the next series of experiments, the glass cell was treated with the same rinsing procedure as detailed above.

2. Bubble growth dynamics[1]

The hydrogen gas inside the bubble can be treated as an ideal gas according to

$$pV = nR_gT \quad (1)$$

where p is the pressure in the bubble, n is number of moles, R_g is the gas constant of 8.314 J/mol K, and T denotes the operating temperature in the unit of K.

According to Faraday equation, the electric charge Q is given by

$$Q = znF = \int I \, dt \quad (2)$$

in which z =2 is the charge number for hydrogen, F = 96500 C/mol is the Faraday constant and I is the current.

As shown in previous studies, almost the entire amount of hydrogen produced at the microelectrode diffuses into the bubble. Under these conditions, Eq. (2) and (3) can be combined.

$$n = \frac{Q}{2F} = \frac{pV}{R_g T} \tag{3}$$

For a spherical bubble shape, the bubble Volume V is given by

$$V = \frac{4}{3}\,\pi\,R^3 = \frac{QR_gT}{2pF} \tag{4}$$

with R being the radius of the bubble.

Accordingly, the growth of the bubble radius can be written as

$$R = \left(\frac{3R_gT}{8\pi pF}\right)^{\frac{1}{3}} Q^{\frac{1}{3}} \tag{5}$$

when the current is constant (e.g. at galvano-static conditions), Eq. 5 can be further written as $R = \beta t^{1/3}$. In the presented experiments, the current remained almost constant at a plateau during most of the time of the bubble growth, as indicated in Fig. (3), because of a high surface coverage of the electrode. Hence, the bubble also follows the 1/3 law during this growth phase. As the bubble approaches its detachment, it slowly begins to lift, resulting in a lower surface coverage and an increase of the current. This is also the reason that the bubble grows faster and deviates from the 1/3 law before detachment.

The evolution of a single bubble radius at E = -8V is shown in Fig. S2. The black curve shows the bubble radius obtained by the bubble images and the blue curve shows the bubble radius calculated by Eq.(5). A very good overlapping of the black and blue curve indicates that the bubble size could be well predicted by the measured current transient. The red dotted line in Fig. S2 presents the calculated bubble radius based on the 1/3 law. It fits only to one part of the bubble growth period when the plateau current was measured. An increased

cathodic current before bubble detachment will result in an increase of the charge through the electrode, which was indicated in the deviation of the 1/3 law in the figures after t > 4s.

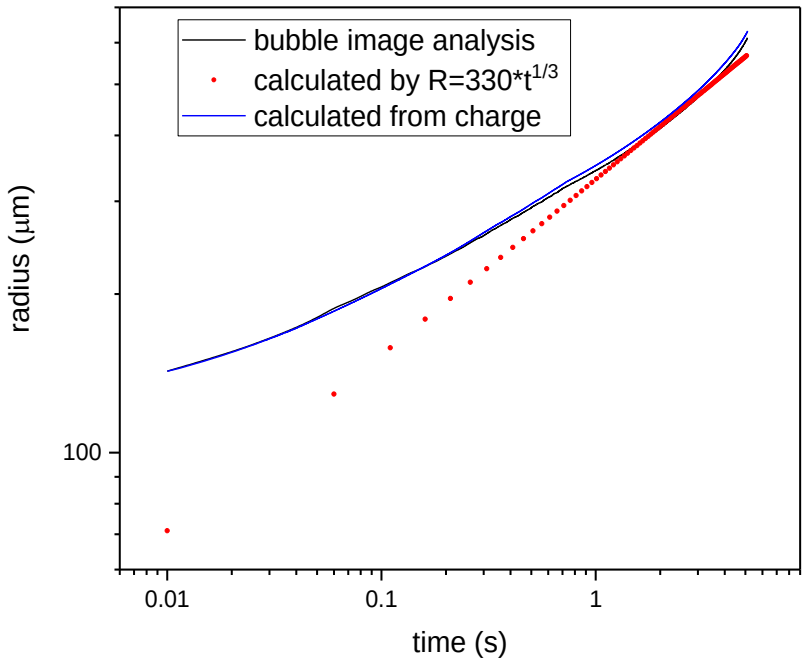

Fig. S2 The growth of a large H_2 bubble at E = -8V as a function of time. The red dotted line corresponds to a growth $R(t) \propto t^{1/3}$, in detail $R = 330\mu m \times t^{1/3}$ (t is time in second). The blue curve shows the bubble radius calculated by the charge according to Eq. (5).

Reference:

1. X. Yang, F. Karnbach, M. Uhlemann, S. Odenbach and K. Eckert, *Langmuir*, 2015, **31**, 8184–8193.