

Electronic Supplementary Information (ESI)

Concentration profile of dissolved gas during the hydrogen gas evolution: an optical approach

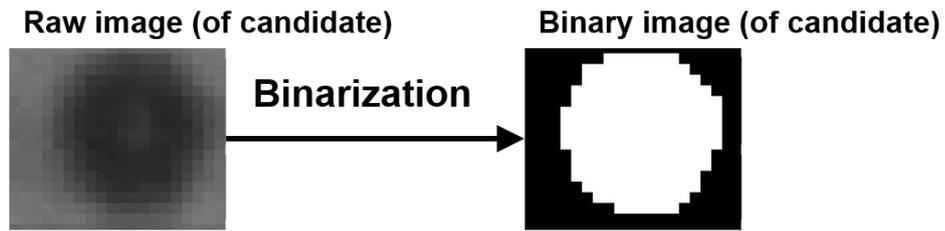
Kota Ando,^a Yoshiharu Uchimoto,^b and Takashi Nakajima^{a*}

^aInstitute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto 611-0011, Japan

^bGraduate School of Human and Environmental Studies, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan

*Corresponding author: nakajima@iae.kyoto-u.ac.jp

Step 1: Binarization



Step 2: Circularity evaluation



Step 3: Tracking & Calculation

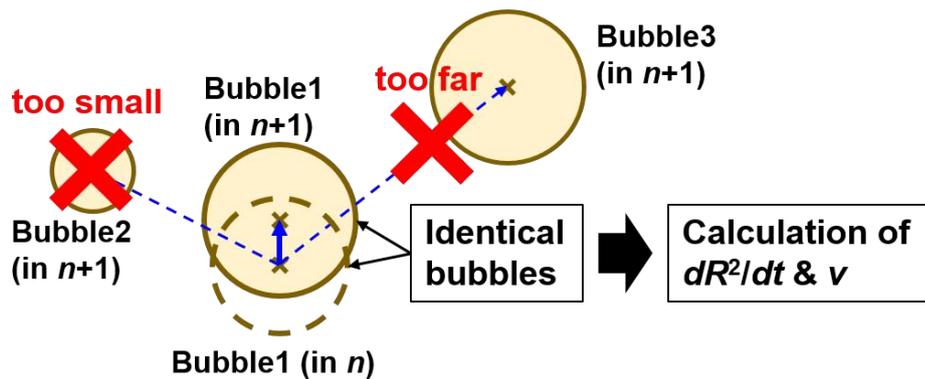


Figure S1 Illustration of optical image analysis (step 1, 2) and *tracking* (step 3) of the bubbles. [Step 1] Binarization of the raw images with an appropriate threshold value to preselect the candidates for bubbles. [Step 2] Evaluation of their Heywood circularity factors (i.e., perimeter of the preselected image divided by the circumference of the circle with a same area) to recognize the preselected candidate image as a bubble only if it is in the range of 1 ± 0.03 . [Step 3] At time t , bubble 1 is located as shown by the dashed circle. In the next frame of the movie at time $t + \Delta t$, three bubbles, for example, are found nearby by image analysis (three solid circles, bubble 1,2, and 3). To judge which bubble at time $t + \Delta t$ is associated with bubble 1 (dashed circle) at time t , the distances between them are estimated (solid and dashed blue arrows) to find that the closest one is associated with the solid blue arrow. This way we can successfully track the motion of bubble 1, and we can continue this process over all frames and all bubbles of interest.

Theoretical background

Epstein-Plesset equation

The time evolution of a *stationary* bubble with a radius, R , in a supersaturated solution with a *uniform* dissolved gas concentration can be described by the well-known Epstein-Plesset (EP) equation [1], which reads

$$\frac{dR}{dt} = D \frac{C - k_H P_B}{n_B} \left[\frac{1}{R} + \frac{1}{\sqrt{\pi D t}} \right], \quad (\text{S1})$$

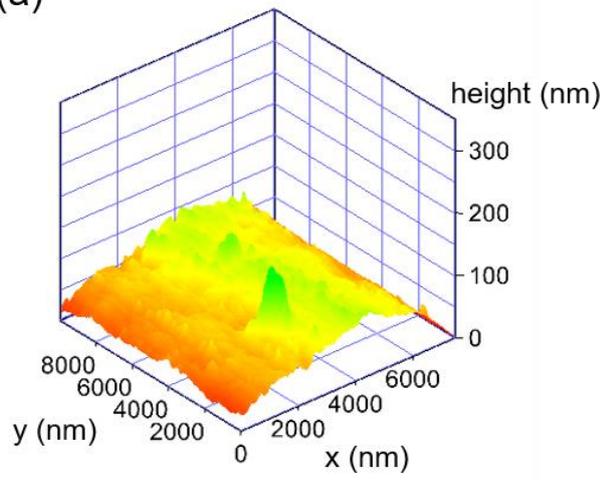
where D and C are the diffusion coefficient and initial dissolved gas concentration, respectively, with k_H being the Henry constant, and P_B and n_B the pressure of the gas and number density of the gas molecules inside the bubble. The right-hand side of the EP equation, Eq. (S1), consists of the time-independent and time-dependent terms, and the latter is negligible if $R^2 \ll \pi D t$ or equivalently $dR^2/dt \ll \pi D$, where $\pi D \approx 12 \mu\text{m}^2/\text{ms}$ since $D=4.2 \mu\text{m}^2/\text{ms}$ for hydrogen molecules in water [2]. In such case, we may discard the time-dependent term on the right-hand side of Eq. (S1), and the simplified EP equation reads,

$$\frac{dR^2}{dt} = 2D \frac{C - k_H P_B}{n_B}. \quad (\text{S2})$$

For our purpose, this simplified EP equation have to be read and used in a slightly different way, since in our case, the bubbles are *not* stationary and the dissolved gas concentration of electrolyte is *not* spatially uniform: upon detachment from the electrode, bubbles are moving upward in the electrolyte and the dissolved gas concentration, C , has a spatial gradient as a function of distance from the

electrode. This means that the value of C decreases as the bubble moves away from the electrode. A simple way to overcome this complication to solve Eq. (S2) is to take the iterative procedure to evaluate C : from the two successive frames of the movie, named frame n (at time t_n) and frame $n+1$ (at time $t_n+\Delta t$ with Δt being the interval between the two successive frames), of the optical images of the i^{th} bubble at distance $x_{i,n}$ and $x_{i,n+1}(\sim x_{i,n})$ from the wire electrode, we obtain the bubble radii, $R_i(t_n, x_{i,n})$ and $R_i(t_{n+1}, x_{i,n})$, through the image tracking analysis. Then, by replacing dR^2/dt on the left-hand side of Eq. (S2) with the value of $(R_i^2(t_{n+1}, x_{i,n})-R_i^2(t_n, x_{i,n}))/\Delta t$ which is extracted by the image tracking analysis, we can algebraically solve Eq. (S2) for the concentration of the dissolved gas, C , at distance x_n from the wire electrode, since all other parameters on the right-hand side of Eq. (S2) are known. We repeat this process for all the frames of the movies taken under a certain current, so that we can obtain the entire variation of C as a function of distance from the electrode. Note that carrying out the image tracking analysis for the bubbles is the key to extract the value of $(R_i^2(t_{n+1}, x_{i,n})-R_i^2(t_n, x_{i,n}))/\Delta t$ or equivalently concentration of the dissolved gas using Eq. (S2).

(a)



(b)

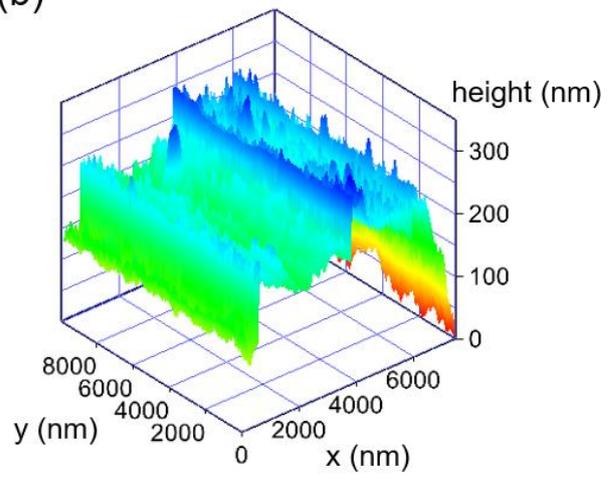


Figure S2 AFM data of the wire electrode. (a) Before and (b) after the electrolysis with 0.1 M KOH at -8 mA for 1 hour.

Reynolds number

The Reynolds number, Re , associated with a bubble in a liquid can be calculated by $Re = \rho v l / \mu$ where ρ , v , l , μ are the density of the liquid, relative velocity between the bubble and flow (which is no more than the upward flow velocity for the case of rising bubble), representative length, and viscosity coefficient, respectively. Employing the bubble diameter, $2R$, for l , we find that Re is no more than 0.06 for the bubble with $2R = 29 \mu\text{m}$ ($= l$) by using the flow velocity itself, $1.87 \mu\text{m/ms}$, for v (Fig. 4), which is the largest possible number for v and hence for Re . Since Re represents the ratio of inertial force to the viscosity force, such a small value of Re means that the dynamics of the bubble in our case are governed by the viscosity.

Reference

- [1] P. S. Epstein and M. S. Plesset, J. Chem. Phys., 1950, **18**, 1505.
- [2] H. Vogt, Electrochim. Acta, 1980, **25**, 527–531.