Supporting information

Relationship between bubble generation behavior and hydrogen evolution reaction performance at high current densities during alkaline water electrolysis

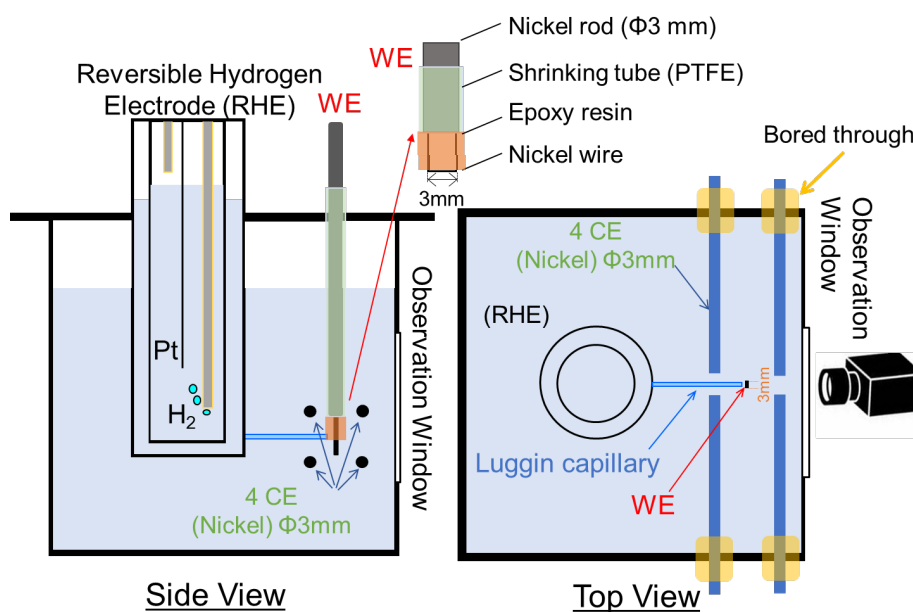D. Kitajima, R. Misumi, Y. Kuroda, S. Mitsushima

Fig. S1 Schematic diagrams of three-electrode cell (side and top view); WE: Working electrode, CE: Counter electrode.
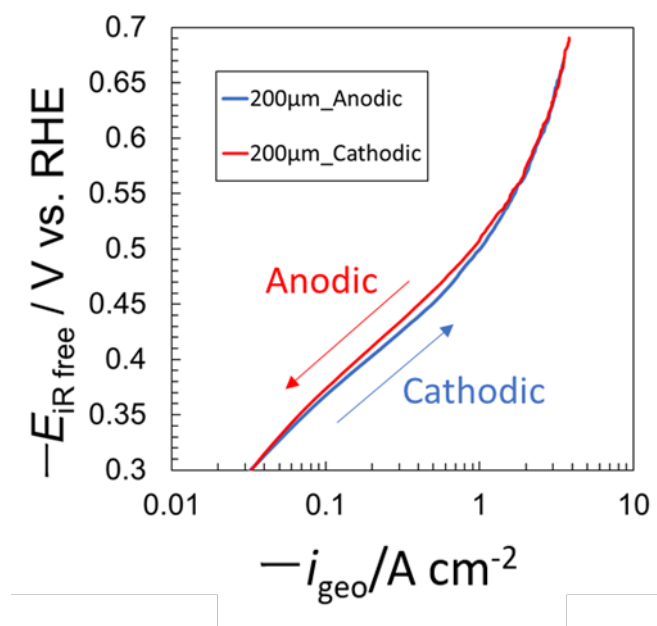
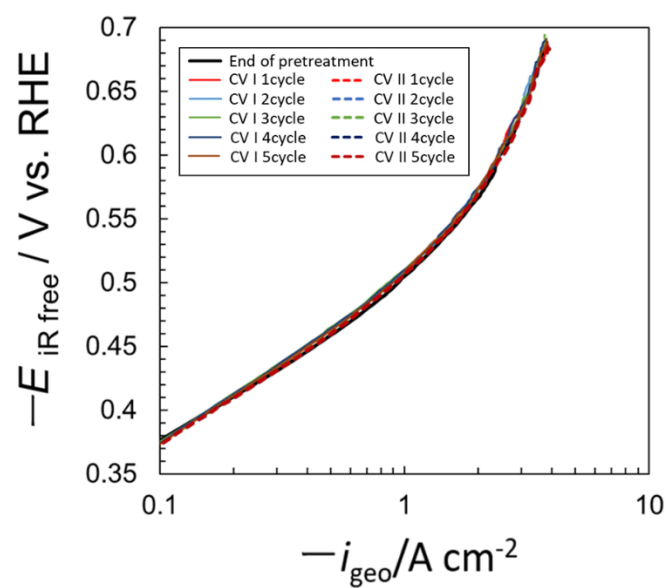**Fig. S2** Polarization curves during anodic and cathodic scans.

Fig. S3 Variation in polarization curves with cycle number (CV I = before EIS, CV II = after EIS).
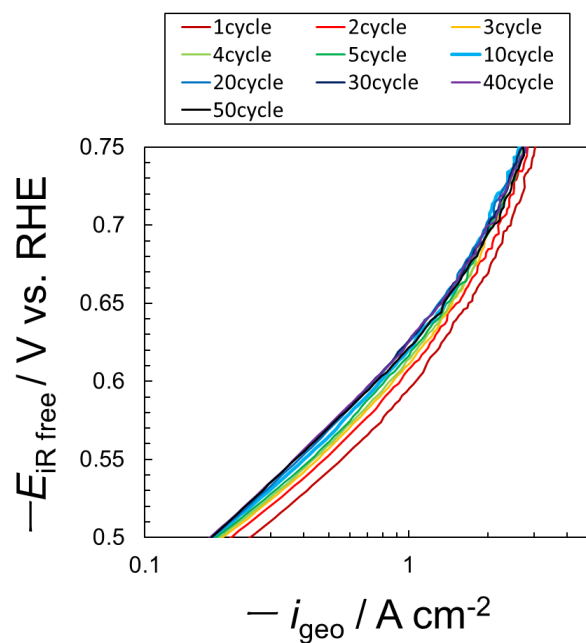
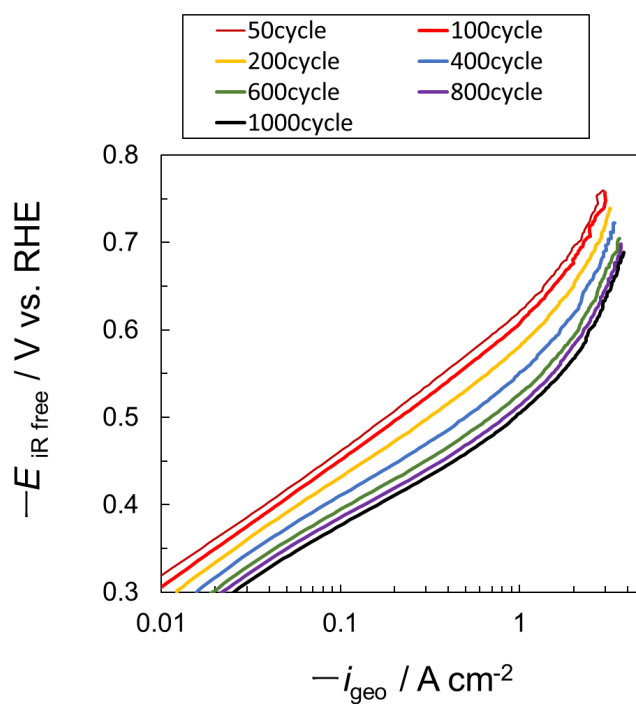**Fig. S4** Polarization curves during pretreatment (1–50 cycles).

Fig. S5 Polarization curves during pretreatment (50–1000 cycles).
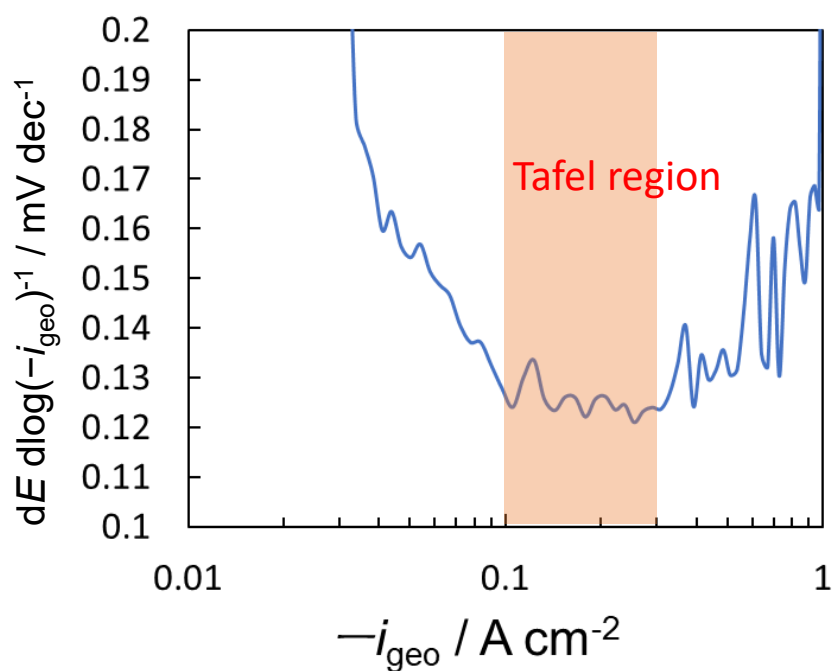
Fig. S6 Relationship between derivative of polarization curve $\mathrm{d}E\,\mathrm{d}(\log(-i_{\mathrm{geo}}))^{-1}$ and current density $-i_{\mathrm{geo}}$.

Movie 1 Slow-motion movies of hydrogen bubble generation starting from potential loading using a 200 μm wire electrode: (a) $i_{\mathrm{geo}} = -0.1$ A cm^{-2}, (b) $i_{\mathrm{geo}} = -0.4$ A cm^{-2}, (c) $i_{\mathrm{geo}} = -1.0$ A cm^{-2}, and (d) $i_{\mathrm{geo}} = -2.0$ A cm^{-2}.

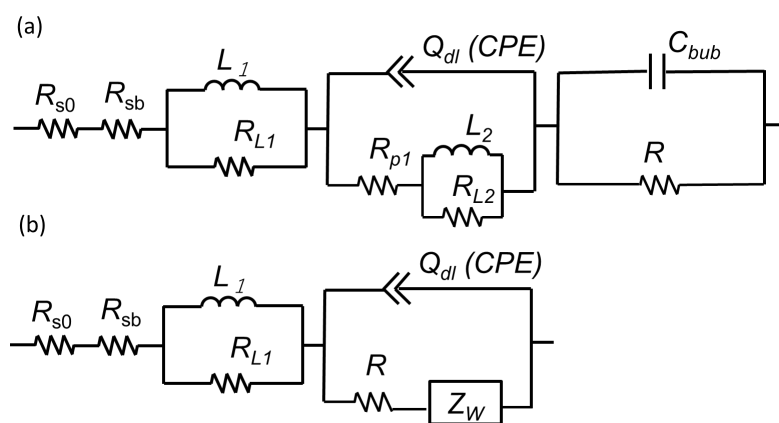**Fig. S7** Equivalent circuits including (a) RC circuit for low frequency range and (b) Warburg impedance for low frequency range.
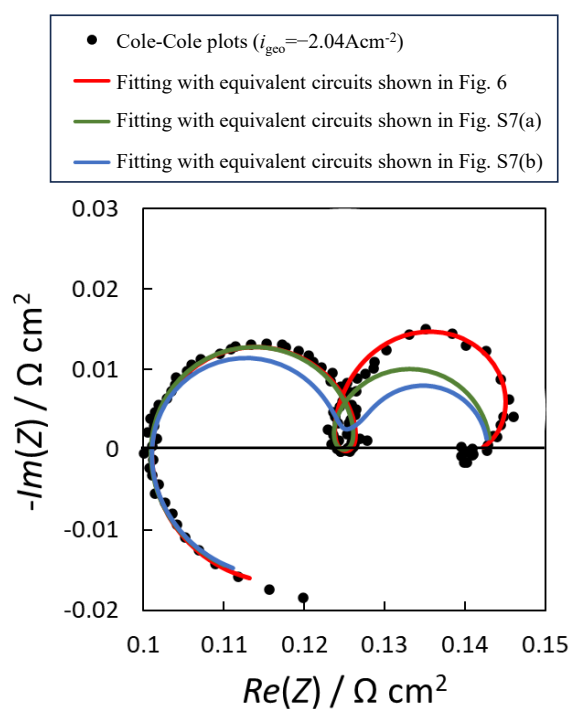

Fig. S8 Comparison of fitting results obtained using different equivalent circuits.

Text S1. Validation of EIS and CV measurements

Fig. S9 shows the integrated and summed values of R_{p1}, R_{p2}, and R_{sb} obtained from the Cole–Cole plots versus the current density, in comparison to the CV polarization curve. The integrated value of the apparent polarization resistance due to the electrical double layer, R_{p1}, was calculated by subtracting the integrated value of the negative resistance, R_{L2}, from the integrated value of the charge-transfer resistance, R_{ct} (Eq. (7)). The integration constants for Eq. (7) were calculated based on the exchange current density obtained from CV measurements. For R_{L2}, R_{sb}, and R_{p2}, the potential change ΔE_j due to resistance component R_j over any current density interval ($a < -i_{geo} < b$) can be calculated using the following formulae:

$$\Delta E_j = \int_a^b R_j \, di_{geo} \quad \text{(S1)}$$

$$\Delta E_j = \frac{R_{j,a} + R_{j,b}}{2}(b - a) + C \quad \text{(S2)}$$

where C is the integration constant and is equal to zero. For Eq. (S2), the integral was calculated by linear interpolation of the discrete current–potential values obtained from EIS measurements.

Fig. S9 shows that the sum of the potentials calculated based on R_{p1}, R_{p2}, and R_{sb} was in good agreement with the actual CV polarization curve. This confirms the reliability of the CV measurements, EIS measurements, and equivalent circuit analysis. It was also confirmed that the deviation of the polarization curve from the Tafel slope at a high current density was caused by the resistance components R_{sb} and R_{p2} owing to the effect of bubbles.
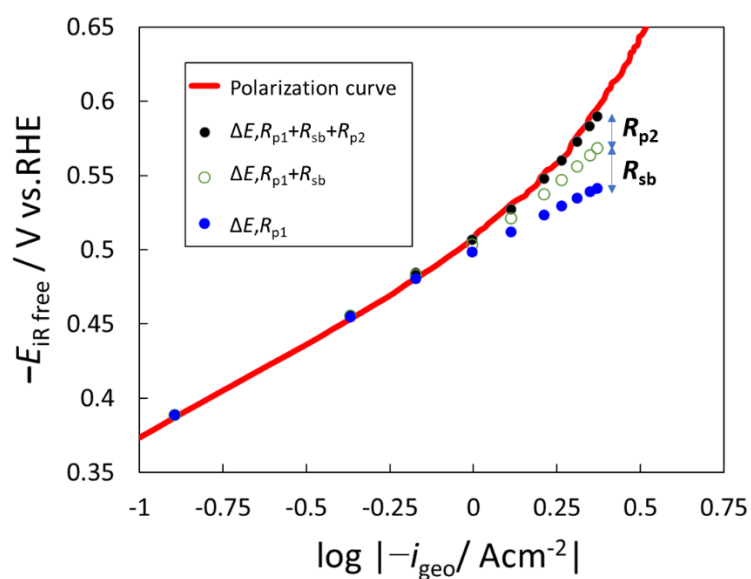
Fig. S9 Relationship between current density $-i_{geo}$ and potential $-E_{iR\ free}$, as determined by integrating the resistance values obtained from the Cole–Cole plots.
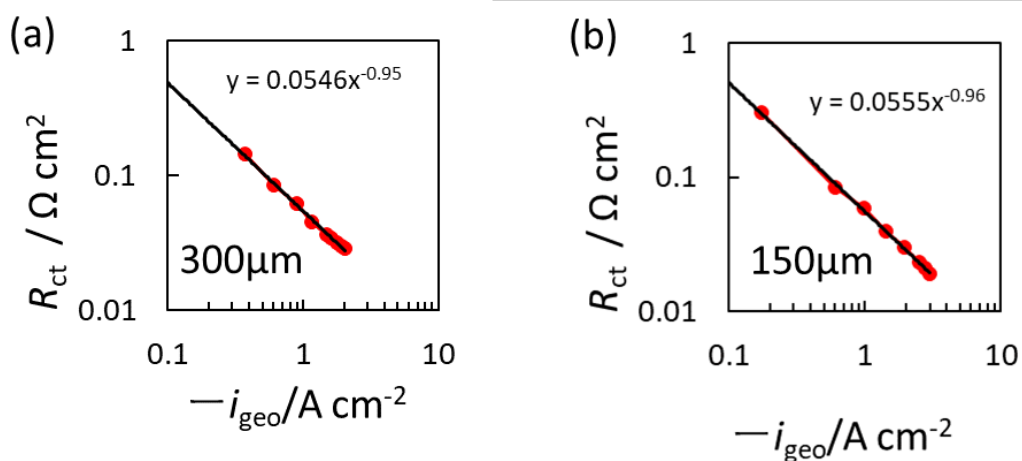

Fig. S10 Relationship between charge-transfer resistance R_{ct} and current density $-i_{geo}$ using (a) 300 μm and (b) 150 μm wire electrodes.
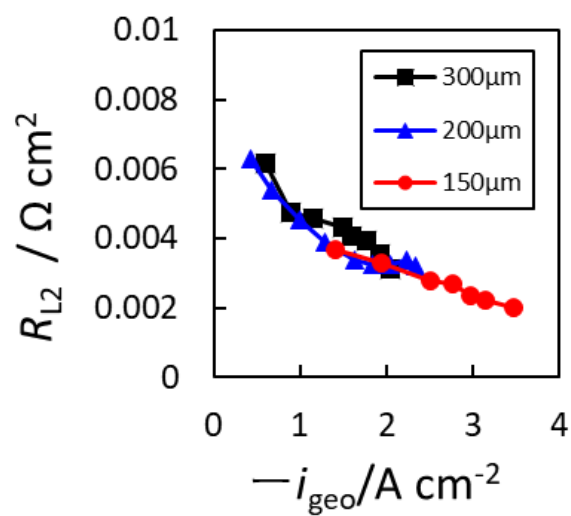
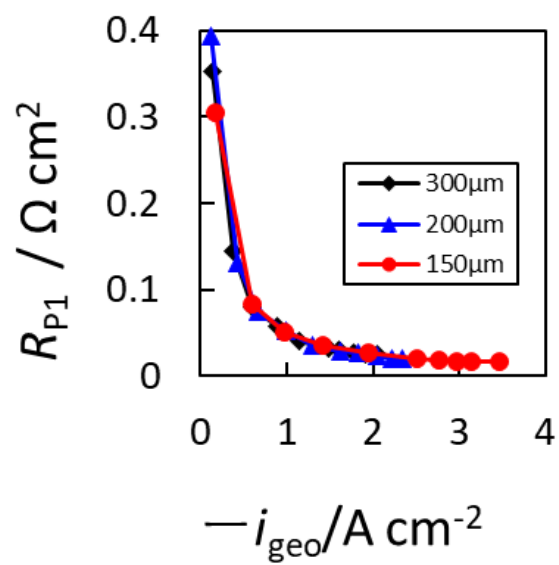**Fig. S11** Relationship between R_{L2} and current density $-i_{geo}$.

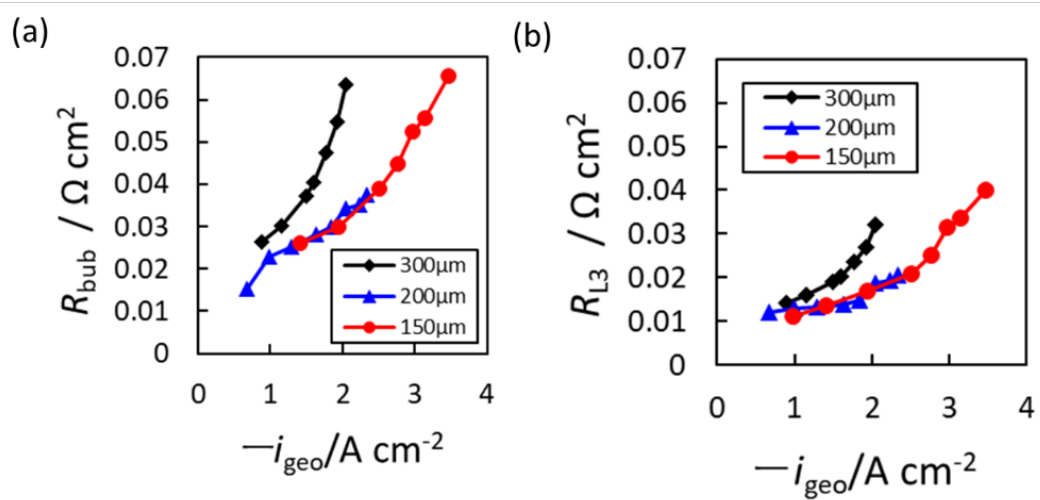**Fig. S12** Relationship between R_{p1} and current density $-i_{geo}$.

Fig. S13 Relationship between resistance components (a) R_{bub} and (b) R_{L3} and current density $-i_{geo}$ at different electrode diameters.

Text S2. Relationship between adsorbent and equivalent circuit

In general, the adsorption-based impedance $Z_{F,\text{ads}}$ is given by Eq. (S3) [21,30,36].

$$Z_{F,\text{ads}} = \frac{1}{A + \frac{B}{j\omega + C}} \qquad \text{(S3)}$$

where $A = \frac{\partial i}{\partial E}$, $B = \frac{\partial r}{\partial E}\frac{\partial i}{\partial \theta}$, $C = -\frac{\partial r}{\partial \theta}$, j is imaginary unit, and ω is frequency. Here, $r = \frac{d\theta}{dt}$ and θ is the adsorption coverage. For A, $\frac{\partial i}{\partial E}$ is the charge-transfer resistance; therefore, $A > 0$. For C, if a steady state is assumed, the change rate of coverage r with respect to the change in coverage θ must be negative; therefore, $\frac{\partial r}{\partial \theta}$ is negative, so $C > 0$. Consequently, if $B > 0$, an inductive semicircle (negative resistance) would emerge, whereas if $B < 0$, a capacitive semicircle would emerge. Thus, the sign of B relates to the impedance behavior. Two differential terms were considered to constitute B: $\frac{\partial r}{\partial E}$ and $\frac{\partial i}{\partial \theta}$. Based on a report by Shiroma et al. [36], since $\frac{\partial i}{\partial \theta}$ is the change in current i relative to the change in coverage θ, it is positive for adsorbates that promote reactions (e.g., reaction intermediates and catalysts) and negative for adsorbates that poison the reaction sites.

The small change in adsorbate coverage θ with respect to the potential E in the DC state, $\frac{d\theta^{DC}}{dE^{DC}}$, can be expressed using Eq. (S4):

$$\frac{d\theta^{DC}}{dE^{DC}} = \frac{\frac{\partial r}{\partial E}}{\left(-\frac{\partial r}{\partial \theta}\right)} \qquad \text{(S4)}$$

where $\frac{\partial r}{\partial E}$ represents the ease with which the coverage r changes when the potential E is changed, and $-\frac{\partial r}{\partial \theta}$ ($= C$) acts like a brake that maintains the coverage θ stable relative to the potential E. Since $-\frac{\partial r}{\partial \theta}$ is always positive, $\frac{\partial r}{\partial E}$ and $\frac{d\theta^{DC}}{dE^{DC}}$ have the same sign;

therefore, the sign of $\frac{\partial r}{\partial E}$ corresponds to an increase or decrease in coverage θ relative to the potential E at a DC steady state. Thus, the inductive semicircle, quantified as R_{L2} for the purpose of this study, appears when $B > 0$. In the cathodic reaction, $\frac{\partial i}{\partial \theta} > 0$ and $\frac{\partial r}{\partial E} > 0$ when the reaction intermediates adsorbed on the electrode are considered to promote the reaction. This indicates that the adsorbate coverage increases as the potential becomes lower (more negative). In addition, R_{L3} could be considered a negative resistance component associated with enhanced detachment of reaction-preventing adsorbed bubbles from the negatively charged cathode surface as the cathode potential becomes more negative.
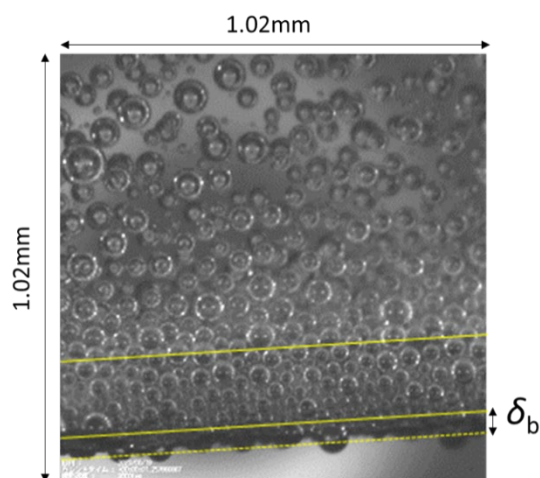
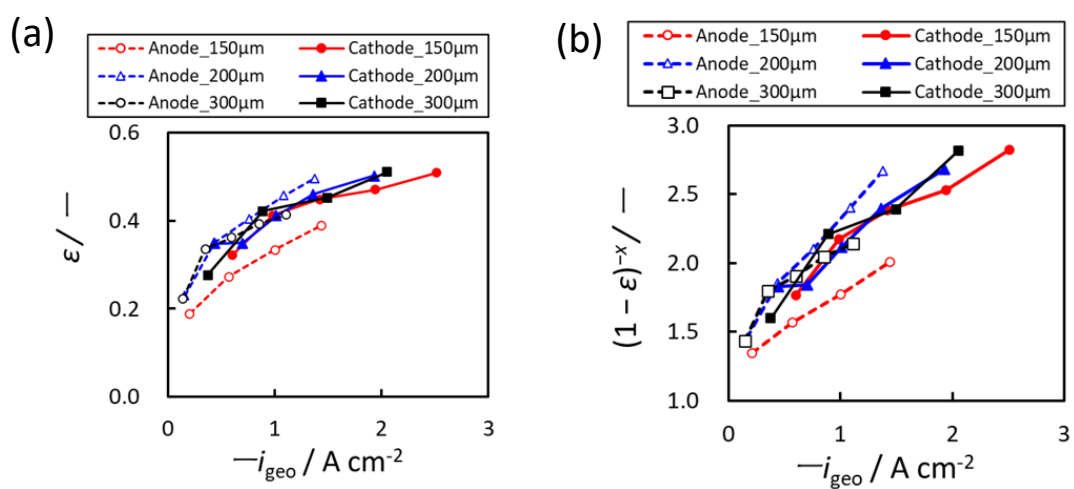**Fig. S14** Schematic definition of δ_b.

Fig. S15 Relationship between (a) ε and (b) $(1 - \varepsilon)^{-x}$ and current density $-i_{geo}$ at the anode and cathode with different electrode diameters.