Supporting Information

Local visualization of catalytic activity at gas evolving electrodes using frequency-dependent scanning electrochemical microscopy

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Contents:

Experimental

1. Chemicals and solutions

Ruthenium (IV) oxide (99.9%) was obtained from Aldrich (Taufkirchen, Germany). NaOH, HCl (37~38%) and H_2SO_4 (95~97%) were purchased from J.T. Baker (Deventer, Netherlands). Electrolyte (0.1 M NaOH, 0.5 M H_2SO_4 and 6 M HCl) were prepared using water purified and deionized with a Milli-Q system (Millipore, Bedford, USA).

2. Materials

Gold wires (purity: 99.99%, diameter 100 µm) were obtained from Goodfellow (Bad Nauheim, Germany). Borosilicate capillaries (outer diameter 1.5 mm, wall thickness of 0.375 mm for fabrication of SECM tips) and glass capillaries (outer diameter 1.5 mm, wall thickness of 0.375 mm for fabrication of cavity electrodes) were obtained from Hilgenberg (Malsfeld, Germany).

3. Preparation of model samples

A 100 µm Au-disk electrode was firstly pretreated in a similar way as the Pt-disk electrode described in the manuscript text. Then the electrode was further electrochemically polished by running 10 cyclic voltammograms in 0.5 M H_2SO_4 between 0 and 1.7 V vs. Ag/AgCl/3M KCl with a scan rate of 200 mV/s. In order to create a cavity, electrochemical etching of gold was performed in 0.6 M HCl by cycling the potential between 0 and 1.3 V vs. Ag/AgCl/3M KCl at 500 mV/s for 10 cycles to obtain ~10 µm deep cavities. A second electrochemical polishing was performed in H_2SO_4 before using the cavity electrode. Ruthenium (IV) oxide (99.9%) powder was then filled into the cavity of the electrode by slightly pressing the electrode tip onto a glass slide on which the powder was placed.

4. SECM measurements

A four-electrode system controlled by a bipotentiostat (Jaissle PG100, IPS, Münster, Germany) has been used. A homemade glass insulated 25 µm Pt-disk microelectrode has been used as WE1. Either a cavity electrode filled with RuO_2 or an industrial O_2-evolving electrode has been used as the sample (WE2). The reason to exchange the connection of the working electrodes in contrast to the traditional SECM set-up, in which the sample and the SECM tip are typically connected as WE1 and WE2, respectively, is to exclude unnecessarily instant potential fluctuation at the small tip, whose potential is generally modulated by the big sample. A homemade agar-based Ag/AgCl/3M KCl electrode (0.209 V vs. NHE) and a Pt-wire (Goodfellow, Bad Nauheim, Germany) with a high surface area shaped to form a coil around the RE and WE1, have been utilized as reference electrode and counter electrode, respectively. The schematic drawing of the SECM set-up is presented in Figure S1A; both WE1 and RE were individually fixed at the SECM holder, and the distance between these two electrodes was kept to 2 mm horizontally (Figure S1B). An optical video microscope has been used to preposition the tip above the active sample surface. An approach curve at E_{tip} = -0.400 V in the feedback mode of SECM in presence of 5 mM $[Ru(NH_3)_6]Cl_3$ in 0.1 M KCl as supporting electrolyte was used to adjust the distance between the tip and the sample surface to 10 µm or 20 µm during the area scan of the model and industrial samples, respectively. A distance of 50 µm was chosen for studying of the sample potential influence on the bubble detachment.

Figure S1. (A) Schematic drawing of the SECM setup, (B) a photographic image of the tip and RE in a close proximity to the sample surface at the gas evolving spot, (C) scheme of the experiments including FFT-data acquisition obtained from the tip current.

The subsequent studies were carried out in an air-saturated 0.1 M NaOH by applying the sample generation-tip collection (SG-TC) mode of SECM with the SECM tip polarized at -0.400 V vs. Ag/AgCl/3M KCl-Agar RE. For monitoring the bubble-detachment frequency at different sample potentials, the tip was positioned as shown in Figure S1B so that the gas evolving spot was located between the WE1 and RE, however, much closer to the WE1. Figure S1C shows a scheme of the experiment including FFT-data acquisition obtained from the tip current. To evaluate the influence of sample potential on the bubble detachment frequency, the sample was polarized from 0.200 V to 0.690 V. The area scanning of the model sample and the industrial gas diffusion electrode sample has been carried out at E_{sample}

= 0.700 V with an increment of 25 µm in both x- and y-direction. To accurately localize the model sample, a SECM feedback mode study in 5 mM $[Ru(NH_3)_6]Cl_3$ with 0.1 M KCl has been carried out at E_{tip} = -0.400 V while the sample (WE2) was kept at open circuit potential prior to the study in alkaline solution.

A special software has been designed and integrated into the normal SECM software (Sensolytics, Bochum, Germany) so that fast data acquisition and processing could be achieved. A Krohn-Hite (model 3202) low pass filter was put at 20 Hz to cut the high frequency noise. Instead of only one current value being finally read out at each location using the sample SG-TC mode of SECM, the current at the tip was monitored with a sampling frequency of either 1000 Hz for 240 s for evaluating the sample potential influence on the frequency of bubble-detachment or 100 Hz for 30 s at each scanning grid point during an area scan. Data processing was carried out using Origin Pro9, in the study of sample potential influence on the frequency of bubble-detachment, and a home-made software employing the library Exocortex.DSP for FFT, for area scans. MIRA (G. Wittstock, Software and Consulting, Oldenburg, Germany) was used to produce SECM images. The highest peak between 1 to 4 Hz in the FFT-spectra was automatically chosen for plotting amplitude-by-frequency $\rho(x;y)$, amplitude $\alpha(x;y)$, and frequency $v(x;y)$ images. This frequency range was chosen knowing that the detaching frequencies of the bubbles were in this range. If there were no peaks in the FFT, this algorithm would automatically take a frequency of 1 Hz and amplitude equal to the noise level. Whenever this happened, a frequency of 0 Hz was taken instead, meaning the absence of characteristic frequency in that point.

Figure S2A shows a photographic image of the model sample surface where active RuO_2 is located in approximately the middle of the image. Figure S2B represents a feedback mode of SECM image taken over the active RuO_2 catalyst. This image confirms that the active material forms a circular structure with a diameter of ~100 µm and is placed in the center of the scanned area. Figure S2C shows a SECM images taken in the sample generation/tip collection mode (SG-TC).

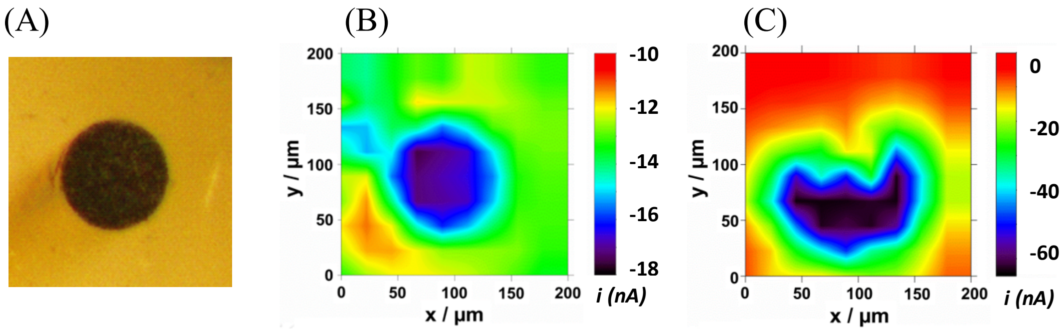

Figure S2. (A) Photographic image, (B) feedback mode image and (C) SG-TC mode image of the model RuO_2 sample surface.

To further support the explanation of Figure 3 in the manuscript, one possible extreme case is explained in Figure S3. Considering an electrolyte volume close to the sample surface, which is partially saturated with oxygen. The tip positioned away from the active area will detect a quasi-stable cathodic current due to electrochemical reduction of the dissolved oxygen (Figure S3A). However, if the tip is positioned close to the gas evolving area, the current would fluctuate quasi-periodically. Three factors would contribute to the amplitude and the average value of the current in this case. The first one considers convection effects due to the bubble departure leading to the increase of the surface concentration of oxygen at the surface of the tip. In this case, the average current value would be more negative as compared to those related to the position of the tip away from the active spot. The second one considers a situation when the departing gas bubbles locally increase the effective electrolyte resistance. Under potentiostatic conditions, this will periodically decrease the tip current and, in some cases, lower the average current values close to the active area. The third one considers an already existing bubble which will grow up by removing the oxygen from the supersaturated solution in close proximity to the tip, thus reducing the supersaturation of the electrolyte and the reductive current detected at the tip, as schematically explained in Figure S3B. The resulting SG-TC SECM image would therefore depend on the relative contribution of these three main factors.

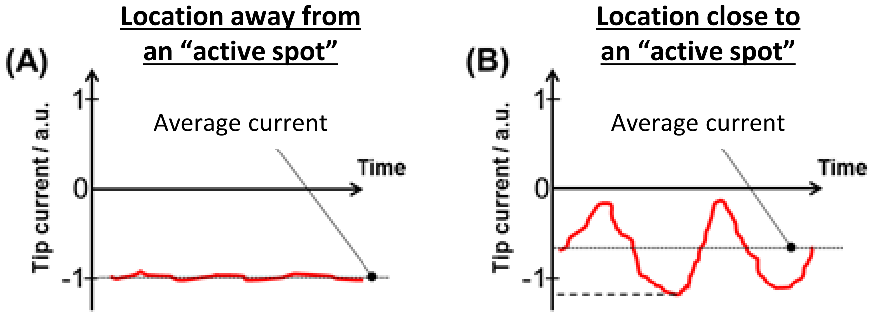

Figure S3. Schematics illustrating the importance of frequency analysis of current transients in SECM investigations of gas evolving electrodes. Under potentiostatic conditions, departing gas bubbles locally increase the effective electrolyte resistance and can lower the average current values close to the "hotspots".

Figure S4 shows the individual amplitude *α*(*x*;*y*) and frequency *ν*(*x*;*y*) images, which correspond to the amplitude-by-frequency *ρ*(*x*;*y*) images in Figure 3 of the main text.

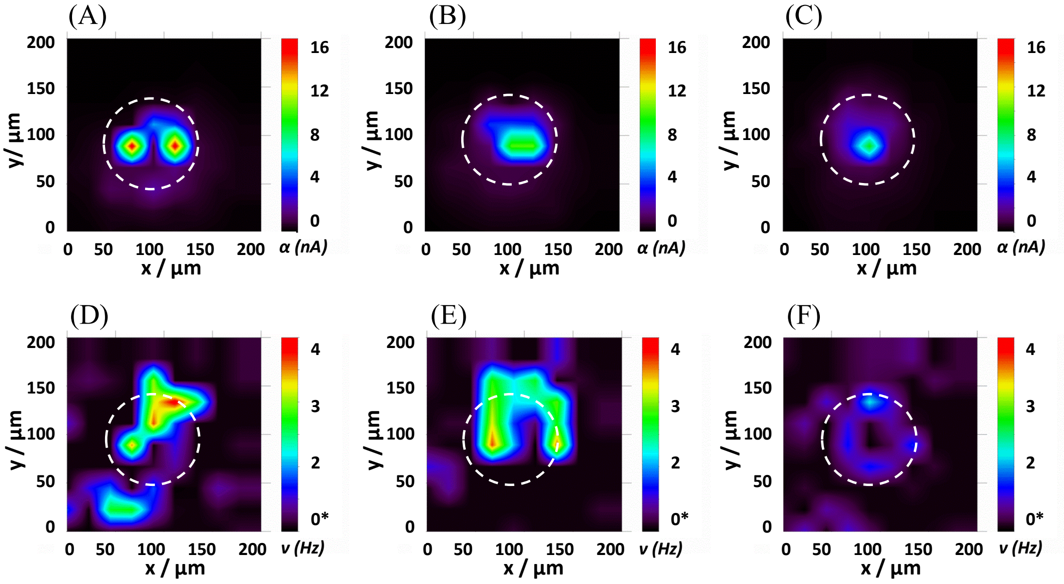

Figure S4. (A-C) amplitude, *α*(*x*;*y*), and (D-F) frequency, *ν*(*x*;*y*), images taken over the RuO_2 surface. White dotted lines indicate the approximate position of the cavity filled with RuO_2 ($E_{sample} = 0.700$ V).

Figure S5 shows the individual amplitude *α*(*x*;*y*) and frequency *ν*(*x*;*y*) images, which correspond to the amplitude-by-frequency *ρ*(*x*;*y*) images in Figure 4 of the main text.

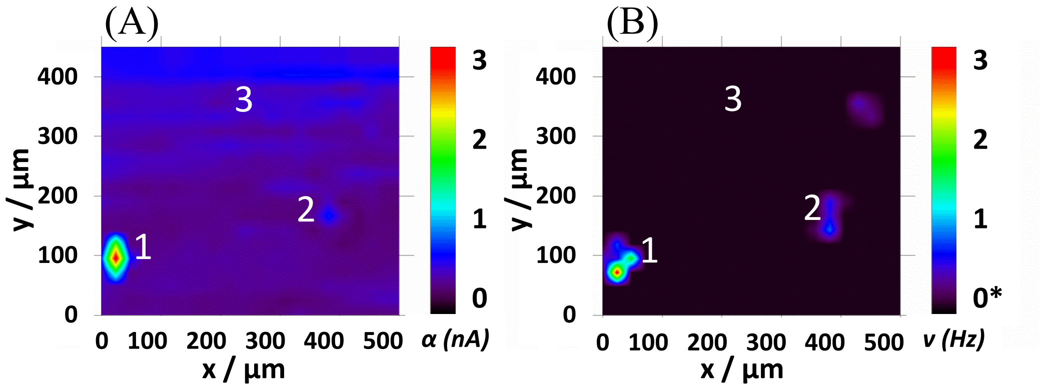

Figure S5. (A) Amplitude, $\alpha(x;y)$, and (B) frequency, $\nu(x;y)$, images taken over a dimensionally stable anode (DSA) surface ($E_{\mathrm{sample}} = 0.700$ V).

5. The parameter ρ

Defining the Fourier transform of the signal *f(t)* as:

$$F(\xi) = \int_{-\infty}^{+\infty} f(t)\exp(2\pi i \xi t)dt \qquad \text{(S.1)}$$

Where ξ is the frequency, i is the complex unit, and capital letters are used to represent the transform of a variable.

The derivative of *f(t)* can be derived in the frequency domain as:

$$\frac{d}{dt} f(t) = (2\pi i \xi)F(\xi) \qquad \text{(S.2)}$$

The parameter α in the main text represents the amplitude of the fundamental wave of the noise in the current transient measured at the SECM tip and v is the frequency of this wave. By multiplying $v\cdot$and α one obtains:

$$v \cdot \alpha \propto (2\pi i v)F(v) \qquad \text{(S.3)}$$

Where the amplitude is defined as $\alpha = |F\ (v)|$. From Equation (S.3) it is clear that the parameter $\rho = v\cdot\alpha$ is related to the derivative of the current transient. When α is the maximal amplitude in the frequency domain and v is the frequency of this wave, ρ is related to the largest and fastest periodic variation of the current transient.