

Sub-millivolt amplitude potential oscillations observed in the noise of hydrogen evolution on Ag and Cu microelectrodes

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Abstract: A strange effect was observed while using the method of quasi-simultaneous determination of electrochemical voltage noise and impedance to obtain information on the kinetics of the hydrogen evolution reaction on Ag and Cu microelectrodes. Beyond a certain polarizing current density we found microvolt-amplitude potential oscillations on both electrodes with a frequency in the 5 Hz - 5 kHz range. The oscillations were observed in every single experiment with Ag and Cu, while no oscillatory behavior was observed during the control experiments with the Pt microelectrode. The presence of the oscillations indicates that the mechanism of hydrogen evolution is more complex compared to the original assumption. © Versita Warsaw and Springer-Verlag Berlin Heidelberg. All rights reserved.

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1 Introduction

Noise and impedance are strongly correlated phenomena, which are originated from the motion and reactions of the free charge carriers present in the system. The classical treatment of noise, the Langevin method [1] reflects that kind of view, as it applies the same differential equation system from which the impedance is also derived by introducing (white) noise sources in relevant positions. Following that kind of reasoning, recently we established a measuring method and equipment for the quasi-simultaneous determination of electrochemical voltage noise and impedance [2]. We tested it in the determination of the symmetry factor of a single electron transfer electrochemical process. The study was

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based on the ratio of the power spectral density of the voltage noise and the real part of the impedance. Based on that ratio we defined the “relative power spectral density” or simply “relative noise spectrum”:

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} \equiv \frac{S_I(\omega)}{4kTY'(\omega)} \quad (1)$$

where S_U and S_I are the measured power spectral densities, the formal power spectral density of the voltage and current noise, respectively, ω is the angular frequency, k the Boltzmann constant, T the absolute temperature, Z' and Y' are the real parts of the impedance and admittance. The above equation is based on the fact that in thermodynamic equilibrium every electric two-pole exhibits the following noise spectra, called thermal noise:

$$S_U(\omega) = 4kTZ'(\omega) \quad (2)$$

and

$$S_I(\omega) = 4kTY'(\omega) \quad (3)$$

One can calculate noise spectra based on the above equations out of equilibrium; we call those spectra “formal power spectral density” or “formal noise spectra”. The formal noise spectra can be different to the actual noise spectra, and the relative noise spectra express exactly that difference. Since in equilibrium the noise does not provide any additional information with respect to impedance, we propose to investigate noise together with impedance and consider the relative noise spectra as the relevant measure of noise. Here we would like to stress that the actual noise spectra, depending on the kinetic parameters, can be smaller or higher than the formal noise spectra. We showed in our previous work, that in the case of a single electron charge transfer process the value of the relative noise spectra depends on the β symmetry factor of the reaction. Particularly, at such overpotentials where the reaction takes place only in one direction (irreversible reaction), following from Equation 10 in [2] considering the limiting case with $\eta \rightarrow \infty$:

$$\beta = \frac{1}{2S_{rel}(\omega)} \quad (4)$$

Even if the reaction is a complex one or at the actual potential the reaction cannot be considered to be irreversible, one can apply Equation 4 to define an apparent charge transfer coefficient (α_n) calculated from noise. This reasoning is similar to what is supported by Parsons [3] or Kirowa-Eisner, Schmidt and Gileadi [4], namely one can derive an apparent charge transfer coefficient α_T by applying the Tafel-formalism to a polarization curve:

$$\alpha_T = \frac{d(\ln i)}{d\eta} \frac{kT}{e} = \frac{1}{i} \frac{di}{d\eta} \frac{kT}{e} \quad (5)$$

in spite of the fact that the above expression will yield the symmetry factor of a (partial) electrochemical process only under certain circumstances.

The hydrogen evolution process is the most extensively studied electrochemical phenomenon with an enormous amount of available information, making it an ideal test system.

The hydrogen evolution experiments on polycrystalline Ag and Cu electrodes in acidic media [5–8] showed a high variety in the exchange current density and Tafel slopes. In addition, the reaction rate was found to be sensitive to the surface state of the electrode in the cases of Au, Ag and Cu [9]. Eberhardt, Santos and Schmickler [10] found a different behavior for Ag single crystals with different orientations. The hydrogen evolution in acidic media is usually considered to take place via the Volmer- Heyrovský mechanism [11]. Alternatively, Kristhallik explained the low value of the apparent Tafel constants obtained from Ag electrodes at low overpotentials with the presence of barrierless charge transfer process [7]. Szabó and Sulyok [8] came to the same conclusions. Though careful electrochemical impedance studies have been published concerning the hydrogen evolution [12, 13], the distinction between the potential reaction schemes was made mainly on the basis of charge transfer coefficients obtained from *dc* polarization curves. However, significant differences from 0.5 in the symmetry factor should also show up in the relative noise spectra. We intended to investigate those differences with our noise-impedance setup.

For the measuring technique, the hydrogen evolution is an attractive choice for the combined noise/impedance study. The relative noise spectra can show difference from unity far from equilibrium, i.e. at overpotentials where the reaction behaves in an irreversible or at least quasi-reversible way. In order to avoid the shunting effect of the double layer capacity a relatively high reaction rate is required. The preferred cell arrangement is a two electrode one with a microelectrode as the working electrode and with a counter/reference electrode having a much larger area than that of the working electrode so that the noise of the counter electrode is neglected.

The above requirements can easily be fulfilled in the study of the hydrogen evolution process. A relatively large area hydrogen filled Pd electrode can serve as an ideal counter/reference electrode. The exchange current density of the hydrogen evolution process is rather low on many electrode materials; therefore, it can behave as a quasi-reversible electrode process.

In addition to the results with Ag and Cu microelectrodes as a reference we show the noise of hydrogen evolution on the Pt microelectrode as well.

2 Features of the relative power spectral density

In order to study the noise of the charge transfer process, the conditions in the cell should be chosen in such a way that there be a frequency region where the charge transfer is the main noise generation process that determines, dominantly, the real part of the admittance.

In a stochastically behaving electrochemical cell with a charge transfer process four kinds of noise generation should be considered, namely: (i) the resistance noise of the solution, (ii) the shot noise of the charge transfer process, (iii) noise of diffusion control, and (iv) the (usually of unknown origin) flicker noise. Considering the high diffusion coefficient of H^+ in the present work we disregarded the diffusion control and thus the

diffusion contribution to noise.

In equilibrium due to thermodynamic reasons the relative noise spectrum must be equal to unity regardless of the actual noise generating process. (Here we emphasize that the noise provides additional information with respect to impedance data only relatively far from thermodynamic equilibrium.) In the case when the noise is originated from the solution resistance the relative noise spectrum is again equal to unity, as in this case:

$$S_U(\omega) = 4kTR_s \quad (6)$$

where R_s means the solution resistance.

If the only (or dominant) noise generation process is the charge transfer process the relative noise spectra will be again constant but its value, denote here with ζ , can be also higher or lower than 1 depending on the charge transfer coefficient (α). The actual charge transfer overpotential (η_{ct}), derived from Equation 9 of Ref. [2]:

$$\zeta = \frac{1}{2} \frac{1 + e^{-\frac{n_e}{kT}\eta_{ct}}}{\alpha + (1 - \alpha)e^{-\frac{n_e}{kT}\eta_{ct}}} \quad (7)$$

where n means the number of electrons involved in the elementary charge transfer step, and e is the elementary charge. Due to thermodynamic requirements ζ is always 1, but at high overpotentials ζ is equal to $1/(2\alpha)$. The value $\alpha = 0.5$ will yield $\zeta = 1$ at every potential.

The noise of the solution resistance and the charge transfer noise are obviously independent from each other therefore their voltage noise spectra are additive:

$$S_U(\omega) = 4kT (\zeta (Z'(\omega) - R_s) + R_s) \quad (8)$$

and

$$S_{rel}(\omega) = \frac{\zeta (Z'(\omega) - R_s) + R_s}{Z'(\omega)} \quad (9)$$

where $Z'(\omega)$ means real part of the total impedance including the solution resistance.

The flicker noise is normally described with the following expression:

$$S(\omega) \propto \frac{1}{\omega^m} \quad (10)$$

where m is usually considered to be 1 [1]. The origin of the flicker noise is generally not clarified. Thus, the exact mathematical expression of its contribution to the total noise spectrum in the presence of the previously described solution resistance and charge transfer noise is also unknown. Although the discussion of the flicker noise is out of the scope of the present paper, we propose two possible models, i.e.: **i.** the flicker noise is a voltage noise the spectrum of which is simply an additive term in the total expression of the voltage noise spectra; **ii.** the flicker noise is an additive term to the relative noise spectra of the electrode process, corrected for the noise of the solution resistance. In the former case from Equation 8:

$$S_U(\omega) = 4kT \frac{C}{\omega^m} + 4kT (\zeta (Z'(\omega) - R_s) + R_s) \quad (11)$$

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} = \frac{\frac{C}{\omega^m} + \varsigma(Z'(\omega) - R_s) + R_s}{Z'(\omega)} \quad (12)$$

and in the latter case:

$$S_U(\omega) = \left(\frac{C}{\omega^m} + \varsigma \right) 4kT(Z'(\omega) - R_s) + 4kTR_s \quad (13)$$

$$S_{rel}(\omega) = \frac{S_U(\omega)}{4kTZ'(\omega)} = \frac{\left(1 + \frac{C'}{\omega^m}\right) \varsigma(Z'(\omega) - R_s) + R_s}{Z'(\omega)} \quad (14)$$

where C and C' are constants, $C' = \frac{C}{\varsigma}$.

Figure 1 shows the expected relative noise spectra for different values of the charge transfer coefficient assuming that the charge transfer process is fairly far from the equilibrium state. (The two models above qualitatively do not yield considerably different relative spectra.) The charge transfer process dominates frequency region II indicated in the figure therefore the charge transfer coefficient can be calculated only from this frequency region. However, selecting inappropriate circumstances (too high or too low polarizing current, too high solution resistance as compared to the total impedance) frequency region I and III (due to flicker noise and solution resistance noise, respectively) can overlap and completely mask the contribution of the charge transfer process to the overall noise.

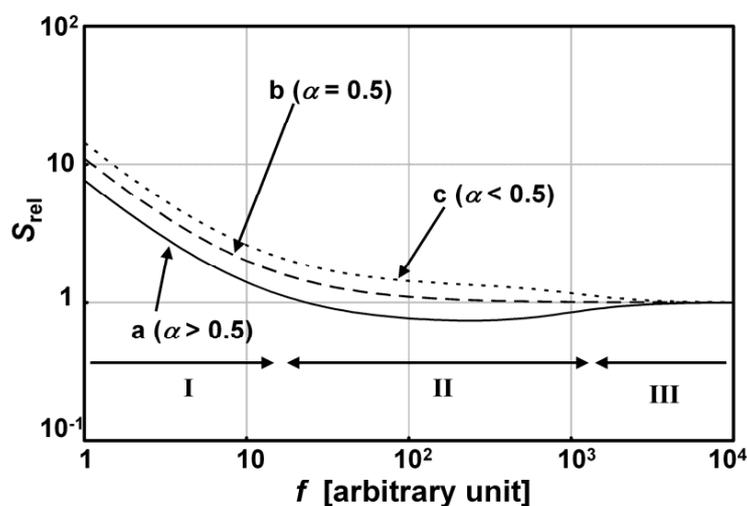


Fig. 1 Calculated relative noise spectra for illustration in the case when the electrode is polarized far away from equilibrium (the charge transfer process practically takes place only in one direction). Curve a, b, c show three different possibilities according to the value of the charge transfer coefficient, namely $\alpha > 0.5$ (curve a), $\alpha = 0.5$ (curve b), $\alpha < 0.5$ (curve c). In frequency region I the flicker noise dominates the relative noise spectra, in frequency region II the charge transfer process, while in region III the solution resistance.

Once the frequency region II is dominated by more than one charge transfer processes (with a number m), the calculated apparent charge transfer coefficient will depend on the

parameters of the individual processes. Assuming that the real part of the admittance can be expressed at an η_0 overpotential as

$$Y' = \left(\frac{d}{d\eta} \sum_m i_{0,m} e^{\frac{\alpha_m n_m e(\eta - \eta_0)}{kT}} \right)_{\eta = \eta_0} = \sum_m i_{0,m} \frac{\alpha_m n_m e}{kT} \quad (15)$$

(where $i_{0,m}$, α_m and n_m denote to the partial current at η_0 , the charge transfer coefficient and the electron number involved in the m^{th} partial charge transfer process), the relative noise spectra in that frequency region will be

$$S_{rel} = \frac{S_I}{4kTY'} = \frac{\sum_m 2n_m e i_{0,m}}{4kT \sum_m i_{0,m} \frac{\alpha_m n_m e}{kT}} = \frac{\sum_m n_m i_{0,m}}{2 \sum_m \alpha_m n_m i_{0,m}} \quad (16)$$

Particularly, at such high overpotentials, where only cathodic or only anodic charge transfer partial processes are dominant, Equation 7 and 16 will yield the following apparent charge transfer coefficient:

$$\alpha = \frac{\sum_m \alpha_m n_m i_{0,m}}{\sum_m n_m i_{0,m}} \quad (17)$$

An obvious consequence of the above expression is that if all the charge transfer coefficients are equal to 0.5 the apparent one obtained from the noise/impedance method will be 0.5 as well.

3 Experimental

The experiments were carried out in two electrode cells applying a $d=50 \mu\text{m}$ embedded disk microelectrode as the working electrode, and a large surface area ($\sim 4 \text{ cm}^2$) Pd foil as counter/reference electrode. The Cu and Ag microelectrode were prepared by electrochemical deposition to the surface of a Pt microelectrode, using a $0.5 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4 + 10^{-2} \text{ mol/dm}^3 \text{ CuSO}_4$ solution for Cu, and a $28 \text{ g/dm}^3 \text{ Ag}_2\text{CO}_3 + 370 \text{ g/dm}^3 \text{ Na}_2\text{S}_2\text{O}_3 \times 5\text{H}_2\text{O}$ solution for the Ag deposition. The Cu was deposited by cycling the electrode with a 100 mV/s sweep rate between -160 mV and $+30 \text{ mV}$ with respect to a large Cu counterelectrode. For the Ag deposition, a -25 mV deposition potential superimposed with a 1 kHz , 0.1 V amplitude sinusoidal signal with respect to an Ag counter electrode. The Pd counter electrode was gently flame annealed; then, it was filled with hydrogen by applying -2.3 V with respect to a Pt counterelectrode in a 0.5 M sulfuric acid solution. The polarization was stopped upon the appearance of the first bubbles at the edges of the foil; the oversaturated Pd electrodes proved to exhibit too much noise during the experiment. The electrode was left in the sulfuric acid for 12 hours in order to reduce (or dissolve) the potential oxide layer that may have formed during the flame annealing process. The obtained Pd electrode showed a stable potential (within 10 mV) for a few days.

The metal depositions and recording of cycling voltammograms were carried out by a laboratory made potentiostat. The combined impedance/noise measurements were carried out with the setup described in our previous communication [2].

All the experiments have been carried out at room temperature around 25 °C. The temperature for each experiment was separately measured and recorded.

4 Results and discussion

The polarization curves obtained with 5 mV/s sweep rate are shown on Figure 2 for both electrode materials. In the case of the Ag electrode in accordance to literature data [7, 8] two regions can be distinguished. At small current densities (up to 1 mA/cm²) the estimated Tafel slope is about 60 mV, but for higher current densities it is around 120 mV. With Cu electrode, in contrast to the Ag electrode, we found only one Tafel region exhibiting a slope of about 200 mV.

The two Tafel-slopes observed on Ag can be rationalized with the Volmer-Heyrovský mechanism [11], which is usually assumed to be valid in strongly acidic media. The alternative explanation of Krishtalik [7] attributes the low value of the Tafel slope at low overpotentials to a barrierless charge transfer process.

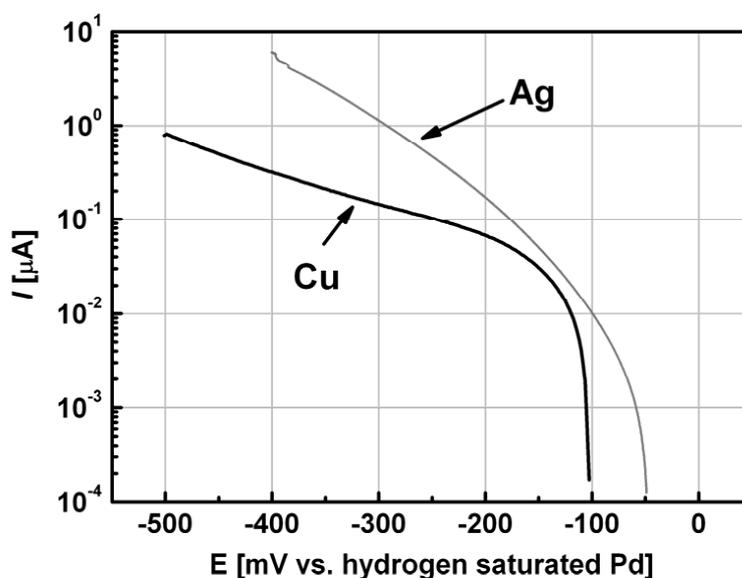


Fig. 2 Polarization curves of Ag (grey line) and Cu (black line) microelectrodes, carried out with 5 mV/s sweep rate.

The Ag electrode (Figure 3) and the Cu electrode (Figure 4) show the relative noise spectra and the real part of the impedance for three different polarizing currents. Up to 20 kHz the solution resistance and the impedance in all cases shows minor contribution (see Figure 3b and Figure 4b). The upper limit of frequency region II (dominated by the charge transfer process both in impedance and in noise generation) can be considered a value 20 kHz or higher. The dominance of the flicker noise (which determines the lower frequency limit of region II) starts at various frequencies depending on the electrode material and the applied polarization current. In the case of the Ag electrode, the frequencies are approximately 400 Hz, 1 kHz and 2 kHz when $I_{ext} = -9.5$ nA, -20 nA and

-50 nA, respectively. However, in the case of Cu the frequencies were about 5 kHz and 6 kHz for $I_{ext} = -50$ nA and 100 nA. With the Cu electrode having $I_{ext} = -200$ nA, the total frequency range was dominated by the flicker noise; thus, the charge transfer coefficient could not be calculated. In all of those regions (except the latter case) the relative noise spectra do not differ significantly from unity, which means an apparent charge transfer coefficient with a value of 0.5 in each case.

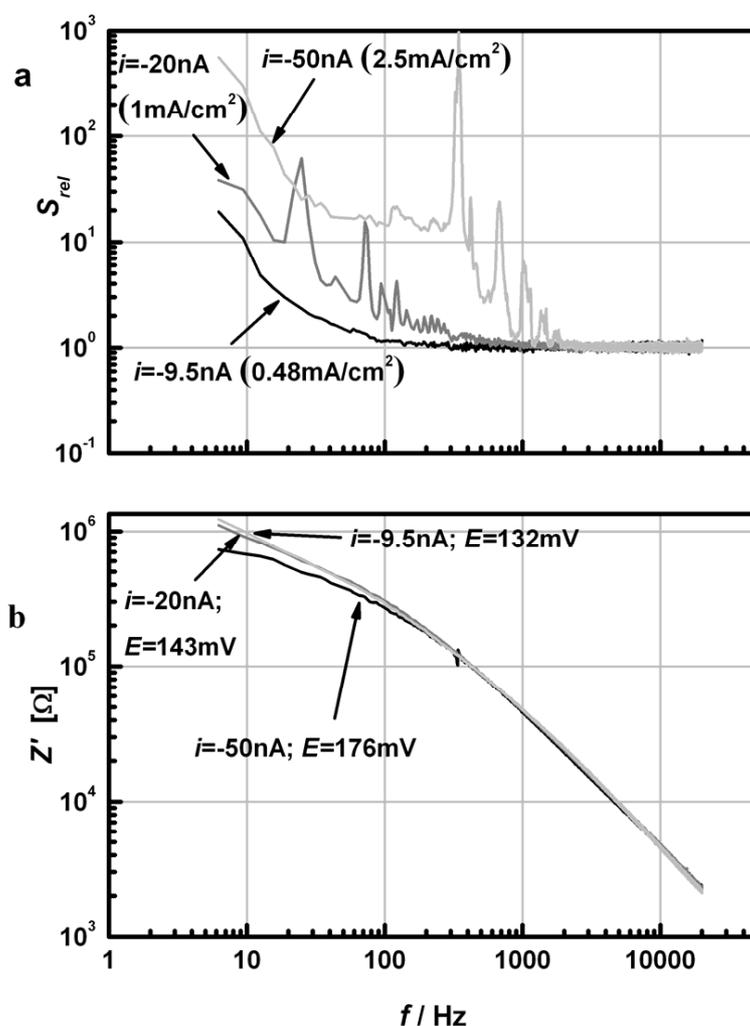


Fig. 3 Relative power spectral density (a) and real part of impedance (b) measured on $d = 50 \mu\text{m}$ Ag microelectrode in a $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution for three different external currents.

In the case of the Ag electrode, the three current densities where the measurements were carried out can be found just around the transient between the two Tafel regions. If each of those Tafel regions were dominated by a single rate determining charge transfer step with different symmetry factors the noise method should also show change in the apparent charge transfer coefficient. The obtained constant values indicates that all the elementary charge transfer processes involved have a charge transfer coefficient equal to 0.5. The existence of two Tafel-regions with slopes 60 mV and 120 mV is in accordance

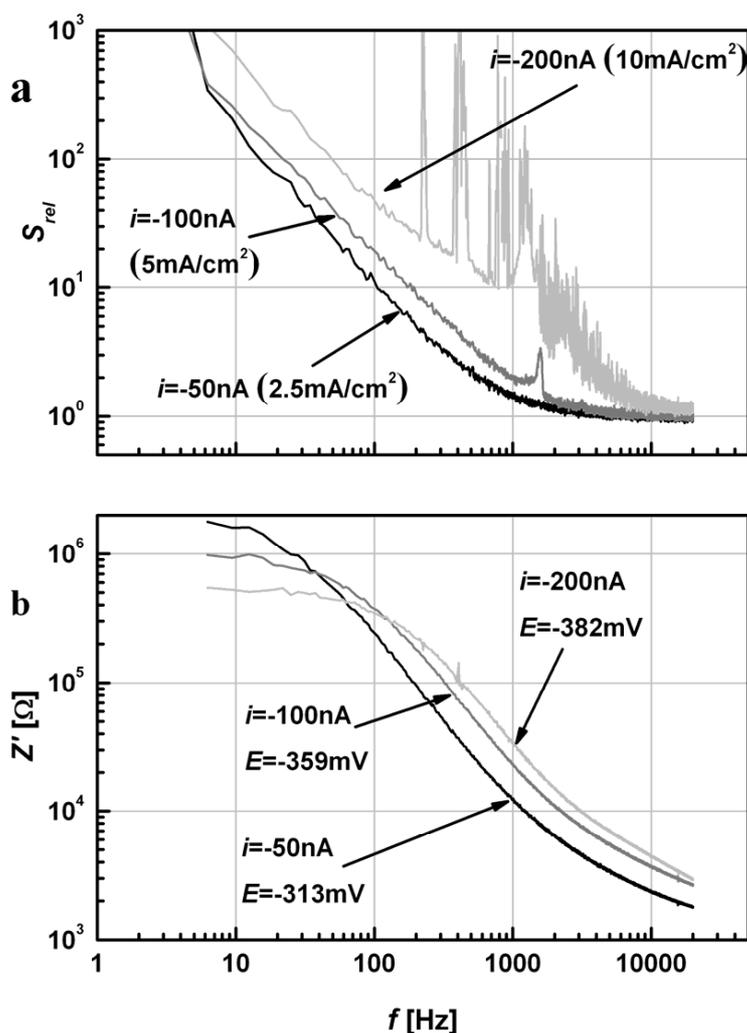


Fig. 4 Relative power spectral density (a) and real part of impedance (b) measured on $d = 50 \mu\text{m}$ Cu microelectrode in a $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution for three different external currents.

with the Volmer-Heyrovský mechanism [11]. On the other hand, our results indicate that at low overpotentials the presence of barrierless charge transfer as rate determining process is rather unlikely.

In the case of the Cu electrode all the measurements were taken at the Tafel-region with a 200 mV slope. If the Tafel-slope is due to a single rate determining charge transfer step the noise/impedance method should yield an apparent transfer coefficient that is considerably less than 0.5. Our result clearly indicates that the mechanism of hydrogen evolution, even in that region, follows a complex mechanism.

The most noticeable feature of the measured noise spectra is that beyond a certain d.c. current density ($\sim -5 \text{ mA/cm}^2$ for Cu and $\sim -1 \text{ mA/cm}^2$ for Ag electrodes) the spectra showed explicit peaks indicating periodic oscillation. As an example, Figure 5 shows a typical oscillating voltage *vs* time curve in the case of Ag electrode with $i = -50 \text{ nA}$. Oscillation under galvanostatic conditions has been reported several times in the case of

anodic oxidation of hydrogen [14, 15]; however, we found only one paper commenting on oscillation during hydrogen evolution [16]. The main difference is that during oscillation under anodic polarization the amplitude is several hundred mV while in the case of cathodic polarization it is only a few or less than 1 mV. In our experiments the highest observed amplitude was about 0.25 mV. The peak in the dark grey curve of Figure 4a at 1.5 kHz corresponds to an oscillation with amplitude less than $0.1 \mu\text{V}$. The whole measurement took place approximately 20 minutes; the sharpness of the peak indicates that the oscillation was fairly stable during that time. The frequency of the recorded oscillations varied more or less between 5 kHz and 5 Hz. The amplitude and the frequency were not completely reproducible but the effect was observed in every measurement. Qualitatively, we found that the frequency of the oscillation decreased while the amplitude increased with increasing d.c. current. The spectra always showed a considerable higher harmonic content even with such low amplitude that is also unusual for such low amplitude oscillations. Figure 6 shows a typical oscillating potential-time function in the case of Ag electrode with $i = 20 \text{ nA}$ external current.

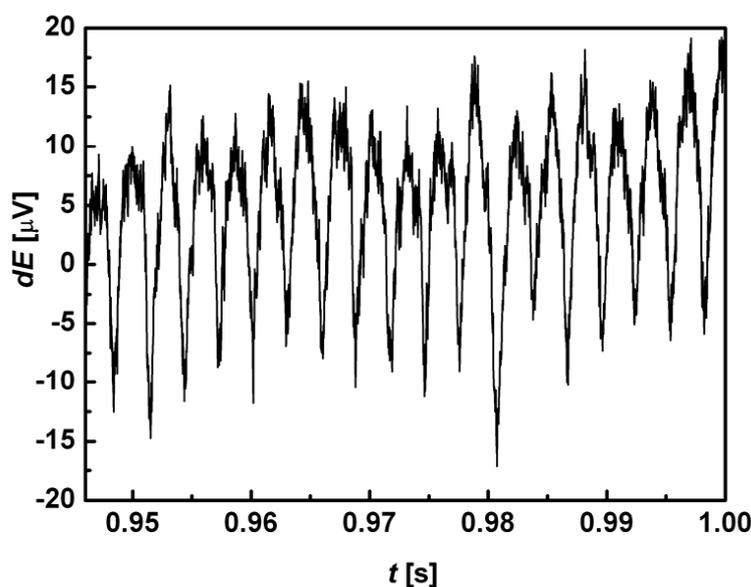


Fig. 5 Relative power spectral density measured on $d = 50 \mu\text{m}$ Pt microelectrode in a $0.5 \text{ M H}_2\text{SO}_4$ aqueous solution for three different external currents.

In our opinion, the oscillation could not be due to the instability of the electronic circuitry because: (i) a passive electronic circuit consisting of a battery, a condenser and two resistors provides the polarizing current [2]; (ii) we tested the system with dummy cells having similar impedance to what was measured in the electrochemical cell. As a comparison we also carried out noise/impedance measurements with a Pt microelectrode. The results presented in Figure 5 did not show any oscillating behavior. This is in contrast to the findings of Hull and Lewis [16]. The reason may be that we applied polished electrode while they used platinized Pt. We also tested whether the Pt under the deposited Cu and Ag layer (due to potential incomplete coverage) can play role in

the oscillation. We could exclude this possibility by carrying out measurements on a (bulk) Au embedded disk electrode ($d = 0.3$ mm), in this situation again the same type of potential oscillation was observed in every case.

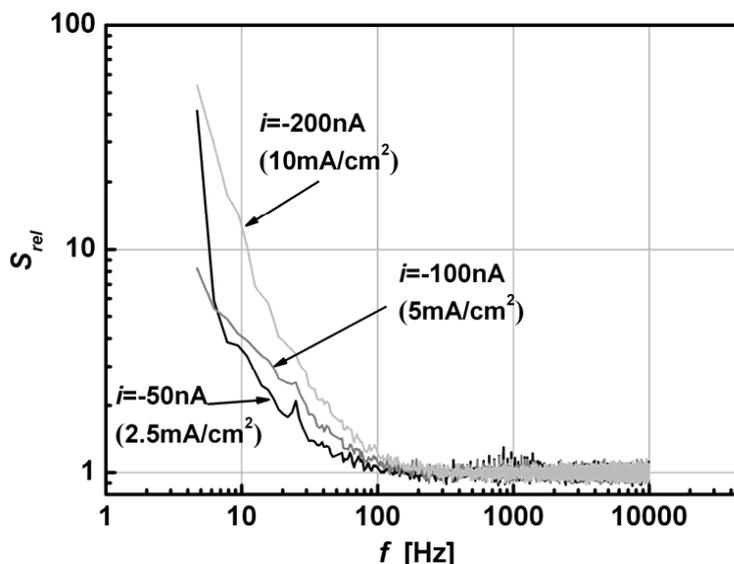


Fig. 6 Typical oscillating potential-time function in the case of Ag electrode, $i = -50$ nA.

We also considered the role of gas bubble formation in the electrode in the oscillations. By visual observation with all the applied current densities the formation of one bubble could be seen, which adhered to the surface of the electrode and did not leave during the measurement. However, the formation of micro size bubbles cannot be excluded. On the other hand the finding that the frequency of the oscillation decreased with increasing current – what is just the opposite that one would expect for bubble formation – suggests that the reason for the μV oscillation is not the periodic formation of gas bubbles. Though we cannot really specify the reason of the oscillation we think that it can be the indication that the mechanism of hydrogen evolution on Ag and Cu may be more complex than the current accepted mechanisms.

5 Summary and conclusions

We determined the relative noise spectra of the hydrogen evolution process in the frequency range where the charge transfer is the dominant noise generating process. Our goal was to see whether or not significant deviation from unity arises in the relative noise spectra since that difference – considerably far from equilibrium – indicates the deviation in the symmetry factor of the charge transfer process(es) from the 0.5 value. Though the polarization curves on Ag and Cu microelectrodes showed various Tafel-slopes we obtained relative noise spectra equal to unity in each case. The results suggest that either the symmetry factors of all the partial processes equal to 0.5 or one of the processes is still close to equilibrium with a high exchange current density.

To our surprise, beyond a certain polarizing current density we observed a reproducible sub-millivolt non-sinusoidal potential oscillation. The frequency of the oscillation varied between 5 Hz and 5 kHz while the amplitude varied between 0.1 μV and 200 μV . We also carried out experiments with dummy cells having similar impedance to that of the investigated systems and with Pt microelectrode. In these control experiments we never detected oscillation thus we could exclude that the phenomena be due to an artifact. Although we could not give an explanation of the oscillation in our opinion it indicates that the mechanism of the hydrogen evolution process is more complex than it is usually assumed to be.

Acknowledgment

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