Theses of Ph.D. Dissertation

Study of the shot noise of electrochemical charge transfer processes

Ildikó SZENES

ELTE* Ph.D. School for Chemistry
Analytical colloid- and environment-chemistry, electrochemistry programme

School leader: György INZELT, Doctor of Chemical Sciences
Programme leader: Gyula ZÁRAY, Doctor of Chemical Sciences
Theme leaders: Béla LENGYEL, Doctor of Chemical Sciences
              Gábor MÉSZÁROS, PhD

MTA** Research Laboratory of Material- and Environmental Chemistry
Chemical Research Centre

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Objectives of the work

* Eötvös Loránd University of Sciences
** Hungarian Academy of Sciences
The classical theory of electrochemical noise based on independent elementary events has been elaborated in the early 1970s. According to that view noise and impedance are strongly correlated phenomena, both of them being originated from the motion and reactions of the free charge carriers present in the system. The noise corresponds to the deviation from the expected potential or current values while the impedance corresponds to those expected values themselves. In thermodynamic equilibrium noise and impedance unequivocally determine each other in the following way:

\[
S_U(\omega) = 4kTZ'
\]

\[
S_I(\omega) = 4kTY'
\]

where \( S_U \) and \( S_I \) refer to the power spectral densities of potential and current, respectively, \( Z' \) and \( Y' \) stand for the real part of impedance and admittance, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Based on the above equations Bezegh and Janata, also Mareček et al. proposed the measurement of noise spectra instead of impedance itself. However, very few attempts have been made for the contemporary measurement of noise and impedance, first of all due to technical difficulties.

The above considerations indicate that noise does not provide any additional information with respect to impedance. Out of equilibrium the noise spectra can differ from the formally calculated noise spectra using the above two equations and that deviation provide the really important information. Thus noise measurements should be carried out always in combination of impedance measurement, and only fairly far from equilibrium.

During my work I intended to fill up the gap caused by the lack of basic electrochemical noise experiments, paying special attention to the shot noise of charge transfer processes.

The Erdey-Grúz-Volmer theory considers the charge transfer coefficient potential independent. Conversely, the absolute rate theory assumes – in accordance with the parabolic potential energy curve – the change of the charge
transfer coefficient with changing potential. The Marcus-Hush theory also predicts the dependence of the charge transfer coefficient on the potential, which dependence is, in accordance with the theory, in close connection with the reorganization energy. Along with the difference of the measurement results in the theories and literature, different problems arise in connection with the measurement of the charge transfer coefficient as well.

The conventional determination of the charge transfer coefficient is usually performed with the Tafel-extrapolation. In this case the potential has to be swept very slowly over a several 100 mV range, during which the surface state of the electrode may change and contaminating substances may be absorbed on the surface, etc. Therefore, the precise measurement needs special procedures and attention.

For the explanation and examination of the above phenomena, we planned and later constructed and tested a new measuring instrument. With the help of this equipment, the objective of the dissertation was the determination of the relative noise spectrum and drawing conclusions concerning the kinetics of the electrochemical processes.

Attempts have already been made for the quasi contemporary determination of the shot noise and impedance of charge transfer processes in our Laboratory earlier. The results have been published in previous Ph.D. theses. The experimental setup consisted of two separate units, one for the impedance and one for the noise measurement. Switching between the two type of experiment was carried out manually, it took too much time and also resulted the significant disturbance of the cell. Thus we could not ensure the equal state of the electrode during noise and impedance measurement. Although the obtained results showed far the best correlation between noise and impedance among those published in the literature the setup was not suitable for carrying out series of experiments. The first problem to solve was the composition of a setup which switches between impedance and noise automatically. The determination of an impedance-noise spectra pair takes place within the shortest possible time (within 1 minute), and keeps recording those data pairs periodically. I needed to
solve the calibration of the experimental setup and the way of processing the obtained raw data series as well.

From the recorded data series pairs one can basically calculate two important parameters. The first parameter is the symmetry factor in the case of a single charge transfer process or the apparent charge transfer coefficient in the case of a complex electrode reaction. The second parameter stands for the electron number change in the case of a simple, or for the apparent electron number change in the case of a complex reaction, provided that one can extract the current noise corresponding to the charge transfer process from the overall noise.

The precise determination of the symmetry factor (charge transfer coefficient) is important as for the experimental verification of modern charge transfer theories, being one kind of evidence the potential dependence of the symmetry factor. The Erdey-Grúz-Volmer theory considers the charge transfer coefficient to be potential independent. Conversely, the absolute rate theory assumes – in accordance with the parabolic potential energy curve – the change of the charge transfer coefficient with changing potential. The Marcus-Hush theory also predicts the dependence of the charge transfer coefficient on the potential, which dependence is, in accordance with the theory, in close connection with the reorganization energy. Along with the difference of the measurement results in the theories and literature, different problems arise in connection with the measurement of the charge transfer coefficient as well.

The conventional determination of the charge transfer coefficient is usually performed with the Tafel-extrapolation. In this case the potential has to be swept very slowly over a several 100 mV range, during which the surface state of the electrode may change and contaminating substances may be absorbed on the surface, etc. Therefore, the precise measurement needs special procedures and attention.

The noise-impedance method provides a promising alternative to the Tafel-
extrapolation. An advantage of the method is that – in contrast to any other technique – it provides the charge transfer coefficient from a noise-impedance measurement pair at a single potential thus making the charge transfer coefficient to be a local character of the polarization curve. On the other hand it permits a view into a higher frequency range in comparison with the d.c. conditions of the Tafel-extrapolation.

The electron number change of charge transfer processes is an important aspect of electrochemical kinetics. Though one can rarely assume a charge transfer step involving several electrons, in the case of a complex mechanism the individual processes can become in strong coupling (e.g. via adsorbed intermediates) therefore, depending on the time scale, due to the strong correlation between the elementary steps the reaction can exhibit the behavior of a several electron charge transfer process. Thus the overpotential and frequency dependence of the apparent electron number change can provide important information on the mechanism and kinetics of complex electrode reactions.

In accordance to the above reasoning the goals of my work were the construction of a setup performing quasi contemporary noise and impedance measurements, the solution of the technical details in conjunction of the setup, then the determination of the symmetry factor (charge transfer coefficient) and apparent electron number change of simple and complex charge transfer reactions.

**The method used for the objectives**

Taking into account that basically the development of a – unique – measuring technique has been carried out, the primary applied method has already explained among the objectives. I also carried out supplementary classical electrochemical experiments like recording polarization curves in a potentiodynamic way.
Scientific results achieved

1. I have developed measurement procedure and measurement equipment for the quasi-contemporary measurement of the electrochemical potential noise and impedance. The method performs impedance- and noise measurements in an alternating way. The advantage of the method is that the measurements closely following each other in time can be considered as “coherent” ones, in the meaning that they belong to the same momentary state of the electrode surface. From the impedance-noise spectrum pairs achieved in this way, the relative noise spectrum is calculated separately, and then these later are averaged. From the relative noise spectrum obtained in this way, kinetic information can be gained. I have worked out the calibration of the measurement instrument and the further processing method of the measured data as well.

2. With the examination of Fe(II)/Fe(III) redox-reaction in sulphuric acid solution, I proved that the equipment is suitable for the simultaneous detection of coherent electrochemical potential noise and impedance spectra. Calculating from the measured relative noise spectra, I obtained 0.63 as the value of the anodic symmetry factor.

3. I have worked out a model for the frequency dependence of the relative spectrum considering the impact of the low frequency flicker noise and the noise of the solution resistance as well.

4. I have shown that in the case of several independent charge transfer reactions taking place simultaneously the apparent charge transfer coefficient appears as the average of each charge transfer coefficient weighted with the value of the stationary partial currents belonging to them:

\[ \alpha = \frac{\sum_m \alpha_m n_{m,0} i_{0,m}}{\sum_m n_{m,0} i_{0,m}}. \]

If the value of all charge transfer coefficients equals to 0.5, the value of the above apparent charge transfer coefficient is 0.5 as well. Similarly, 0.5 is
obtained in the case if any reaction shows reversible behavior (i.e. the partial currents of that process are significantly higher than the current measured in the external circuit).

5. Applying the theory elaborated by Tyagai for the noise of the Volmer-Heyrovský mechanism, I have stated that the apparent electron number calculated from the current noise at high overpotentials is a value between one and two, depending only on the stationary hydrogen coverage at the given potential:

$$n_{app} = 2[(1 - \Theta)^2 + \Theta^2],$$

indication that from the value of the apparent electron number one can conclude on the hydrogen coverage.

6. I have performed measurements to examine the noise of hydrogen reduction at Ag and Cu microelectrodes in a sulphuric acid solution. From the results, I first examined the relative noise spectrum and the apparent charge transfer coefficient calculated from it. I obtained the value 0.5 in the case of both electrodes at all applied overpotentials, indicating that either the symmetry factor of all charge transfer partial processes equals to 0.5 or one of the partial processes behaves reversibly in the investigated cases.

7. Further, I have also calculated the values of the apparent electron number from the measured noise data, and I have shown that after the subtraction of the noise belonging to the constant phase element (CPE) determined from impedance the apparent electron number equals to a value between one and two in a relatively broad frequency range. The resulting values can be explained with the theory of Tyagai on the noise of the Volmer-Heyrovský mechanism.

8. On both the Ag and the Cu electrodes I have observed reproducible potential oscillation with sub-millivolt amplitude beyond a certain d.c. current density. The frequency of the oscillation was between 5 Hz and
5 kHz. The amplitude of the oscillation increased while its frequency decreased with increasing d. c. current.
LIST OF PUBLICATIONS

Ildikó Szenes

Publications concerning the dissertation


Szenes, G. Mészáros, B. Lengyel: Study of the shot noise of electrochemical charge transfer process Central European Journal of Chemistry, accepted for publication

Other publications

Publications published in scientific journals referred to


Independent scientific books, schoolbooks and lecture notes


Conference publications, annuals


Professional lectures at scientific institutes