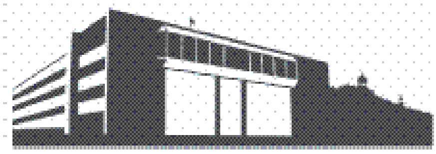

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The possibility of using probe methods for measuring the absolute values of electrode potentials

Abstract. *In this paper, we consider the possibility of a fundamental measurement of the absolute values of electrode potentials using probes - small electrodes, is positioned within the electrolyte through which electric current flows. Getting the probe characteristics in the case of electrolyte solutions is a promising method for direct measurement of both equilibrium and non-equilibrium characteristics of double layers formed at the metal-electrolyte interface. The theoretical and experimental problems to be solved in the sequential development of methods of measuring probe of the absolute values of electrode potentials.*

Keywords: *probe methods, electrode potential, potentials.*

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Introduction

In classical electrochemistry widely used concept of electrode potentials [1]. Based on the predicted direction of the flow of electrochemical reactions, electrochemical cells and calculations are based, etc. However, up to now still in use relative values of electrode potentials measured from the hydrogen electrode, whose potential is taken as zero. The elaboration of ways of experimental determination of the absolute value of the potential difference between the electrode and the solution is still open [2]–[5].

Consideration of this possibility it is advisable to start with an analogy with the problems of plasma physics because this field of knowledge use probe methods developed quite completely [6]–[8]. It should be emphasized that the central issue of the physics of plasma using the probes is not the measurement principle (remaining unchanged around 100 years old), and the interpretation of experimental data [9]. That is why the authors considered it appropriate to devote a separate publication discussing the possibilities offered by the use of probes in physical chemistry.

Theory

In plasma physics developed several theories, allowing communication between the experimentally measured electrical characteristics of the probes and the main plasma parameters. The mention of these theories to the subject matter of this article is for the following reason. In all the probe measurements, one way or another can be measured by only one relationship - the so-called probe characteristic (dependence of the probe current on the probe potential [7], [10], [11]). It carries a maximum amount of information that can give probe methods. All existing probe methods are repelled by this measurement, or characteristics, or derivatives thereof. However, depending on the conditions (mainly depending on the gas pressure range) to obtain the same information (the electron energy distribution function), various theoretical constructs.

Before proceeding to the consideration of the experimental results, we emphasize that, as in plasma physics, there is an important difference between the potential of an isolated probe and space potential (potential, which would be implemented at the point of the probe in his absence) [10]. In plasma physics, this difference was primarily due to the unequal value of the mass of the electron and ion. Namely, the light electrons have high mobility (as well as the diffusion coefficient), and massive ions - low. Therefore, the current condition on the balance of positive and negative probe carriers leads to the fact that the probe assumes an excess negative charge which attracts the heavy ions and, respectively, for light locking is electrons. By a similar mechanism also charged gas-discharge tubes wall [6].

We emphasize that this mechanism determines the appearance of an excess of negative charge in the isolated probe, i.e., the potential of such a probe is different from the potential of space. Similarly, the potential of the wire probe placed in the electrolyte space is different from the space potential. However, the reasons are electrochemical phenomena one of them may be the contact potential difference occurring at the interface between the metal and the electrolyte. This potential difference is the cause of the EMF in Galvano-chemical (electrochemical) current sources [1].

Therefore, the measurement of the difference between the value of the space and the potential of the isolated probe determines the absolute value of the contact potential difference. However, confirmation of this requires a study of the behavior of the probe characteristics.

It is known that the classical theory of Langmuir and Druyvesteyn's probe measurements [10], [12] applies only at sufficiently low pressures, where the mean free path of electrons in the plasma is much greater than the characteristic dimensions of the probe. In this case, the flow of electrons to the probe takes place in free flight mode, which allows a probe to establish a link between the current and the electron energy distribution function.

Currently, developed several approaches that allow much to extend the scope of the use of probe methods in plasma. For example, [13] proposed a theory that allows linking the results of the first derivative of the probe current concerning the potential of the probe with the electron energy distribution function. In [14], [15] proposed a general theory that allows determining the distribution function, knowing the dependence of the probe current on the potential applied to the probe. In [16]–[18] the possibility of probe measurements extended to the atmospheric pressure in difficult conditions.

In general, now we can say that the theory of probe measurements of plasma has gone from a situation where the probe dimensions are much smaller than the main parameter the characterizing collisions in the environment, that is mean free path (Langmuir method) [10] to the opposite case. Namely, methods of V.I. Demidov and L.D. Tsendin [13], [15] allows measurements in a very dense environment where the electron mean free path concerning the elastic collisions with neutral particles is much smaller than the characteristic dimensions of the probe.

About the problems of electrochemistry, this conclusion indicates, first, that there is a basis for borrowing approaches developed in plasma physics. Indeed, the original formulation of the question contained in the works of Langmuir did such borrow meaningless. It is impossible to make such a probe size, which would allow speaking about the drain on his charge carriers that carry current in electrolytes in free flight mode. The method of V.I. Demidov [19] and L.D. Tsendin [20] originally developed for the pressurization mode research when charge carriers' flow to the probe occurs in a diffusion mode. Therefore, at the present stage of borrowing, which was mentioned above, it is quite justified.

Determination of the electron energy distribution function is one of the most difficult problems to be solved with the help of probe methods. For the measurement of the absolute values of electrode potentials so thin measurement is not mandatory. It is well known[6], [11], [13], [19] that the probe characteristic (dependence of the probe current on the potential applied to the probe) allows reliable detection of the two values of the potential: the potential of the insulated probe and the potential of space. The simplest scheme of probe measurements is shown in Figure 1.

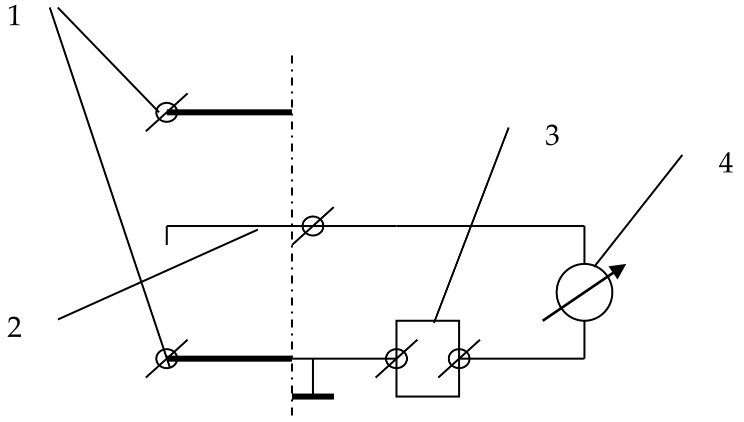

Figure 1. The simplest scheme of probe measurements. 1 - defining electrodes 2 - probe, 3 - generator confining potential, 4 - current meter

Probe characteristics are obtained by changing the potential of the probe (typically of the wire) by an additional power source and measuring the current in the probe circuit. A typical view of the probe characteristic is shown in Fig. 2.

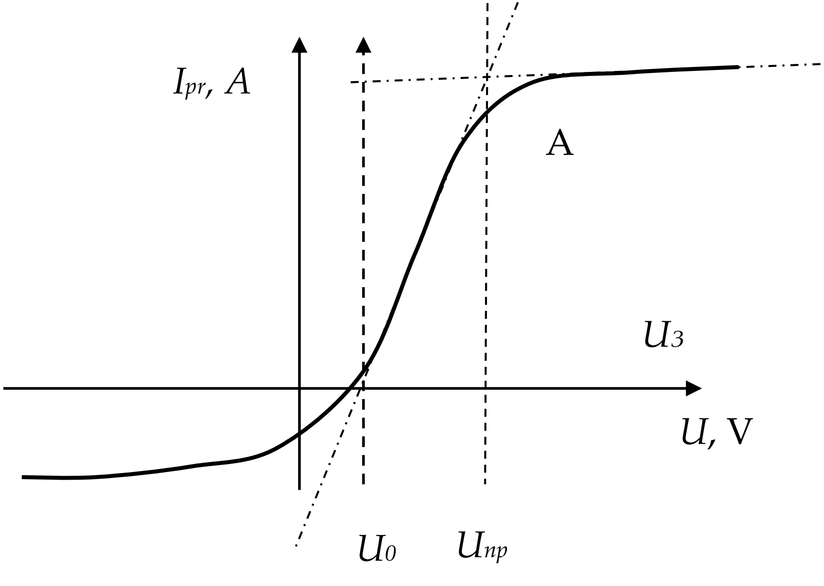

Figure 2. Schematic representation of the probe characteristic

The potential of an isolated probe on this curve corresponds to the point of intersection with the axis of ordinates (the probe current is zero), the potential of the space - the point A, in which the sign of the second derivative of the probe characteristic.

Therefore, having received the probe characteristics, you can define both potentials. We emphasize that the potential of the space is the amount of capacity that would be realized at the point of the probe if the probe is absent. Therefore, by calculating the difference between these potentials is possible to find the absolute value of the potential difference between the conductor and the surrounding conductive medium. This problem is completely solved in plasma physics, however, it remains weak demand in the physics of electrolytes. We show that the definition of space and the capacity of an isolated probe potential fully comply with the decision of this problem, including, in the physical chemistry of electrolytes.

We will build on the existing theory of the formation of the electrode electrochemical potentials that remain unchanged for a long time [1]. According to existing ideas, electrode potentials are generated because of these phenomena. The probe is ionized and enters the solution under the influence of the environment of the molecules located near the surface of the electrode. The theory of Nernst (osmotic theory of electromotive forces, 1889) describes the effect of the value of the dissolution of elasticity [21]. According to this theory, the interaction of the fluid and the latter is surrounded by an electrode ionic atmosphere within the voltage drop which depends on the properties of the medium and the nature of the metal. According to the theory of Nernst, the potential difference between the thickness of the conductor and the surrounding solution is an electrochemical electrode potential. When two electrodes are made of different metals, the outer chain starts to flow through it an electric current.

We note that under conventional theory Nernst potential difference determines the galvanic phenomenon is a voltage drop across the double layer formed near the surface of any metal sample immersed in the solution. Thus, the sample and probe may be made of a suitable material.

A similar interpretation is adopted in plasma physics when considering the capacity of an isolated probe [6], [7]. It is known [6], [7], the potential of the isolated probe differs essentially from the capacity of the space. In plasma, the potential of an isolated probe is formed by the difference between the electron temperature and ion temperature. The more mobile electrons form a more intense flux of negative charge on the surface of a body brought into contact with the plasma. At a steady state, the flow must be balanced by the flow of positive charge formed by heavy ions. Balance can only be realized when the surface acquires a negative charge excess, which limits the flow of electrons, and conversely, positive ions accelerate. As a result of establishing a flow balance insulated probe becomes a non-zero charge, or in other words between the probe material and the environment is assigned a potential difference. Electrochemistry analogy to challenges is that in both cases there are physical and chemical phenomena that lead to the appearance of a potential difference.

Combining the treatment of forming the electrode potential and the capacity of the insulated probe, it can be said that the potential of conductive objects in the conducting medium is determined by the characteristics of the electric double layer formed at the interface.

The community of interpretations allows speak about common methods to measure the potential analog insulated probe - in electrochemistry, this quantity is precisely the electrochemical potential. It should be appreciated that an electrochemical potential is defined as electrochemical factors (environment interaction with the metal), and the voltage drop that occurs due to the non-uniform distribution of metal ions near the surface. However, whatever the mechanism of formation of the double layer at the interface, to measure it remains a suitable scheme shown in Figure 1. Creating a potential difference between the probe and the environment and performing scanning, you can determine the potential at which the current on the probe will be zero. This value is just an isolated probe potential, i.e., electrochemical potential if measurements are made in the electrolyte solution. However, we must bear in mind that the physical meaning has only the potential difference and therefore is required, in general also determine the value of the potential, which should be done the counting.

The direct value of the absolute potential difference can be obtained by measuring (or calculating) the potential of a space, i.e., the potential that would be created at the point where the probe is located if it was not there.

For quite rough estimates is acceptable to use the straight-line portion of the dependence potential between the two electrodes. As is known [22], near the cathode and anode holds significant potential heterogeneity of distribution. This heterogeneity, as in the case of the formation of an isolated probe potential is due to the non-uniform distribution of charge carriers near the interface. However, there is a portion in which the field remains approximately constant, which is used during the method four electrodes by measuring conductivity. Introducing into the inter-electrode gap, two additional electrodes and measuring the potential difference can be made dependent on interpolation and determining the potential of space at the point where the probe is located. The required calculations can be performed when the distance between the auxiliary electrodes 2 and 1, and the distance between one of these electrodes and the probe.

Inaccuracies arising from the use of this approach may be considered negligible only when the distortions introduced by the probe into the potential distribution between the cathode and the anode should be relatively small. In other words, the potential of the probe in the vicinity of the space to be formed only specify the electrodes, wherein the characteristic dimensions of the region in which the distortions are spot insertion probe should be much smaller than the characteristic dimension of the field variation produced No electrodes. This factor justifies the use of the probes as small as possible dimensions: in this case, the potential distribution in the vicinity of the probe can be considered approximately constant (more precisely, its gradient is negligibly small in comparison with its field produced by the probe, and to be measured).

However, for a more accurate determination of the absolute electrochemical potentials is desirable to define the potential of the space directly from the probe characteristic, as is done in plasma physics. Consequently, in the first step of constructing a coherent theory probe measurements of the absolute values of electrochemical potentials are necessary to develop consistent theory forming double layers in conditions when the surface perpendicular to the electrode an electrical current flow. This will calculate the electrochemical probe characteristics.

Currently, there is a basis for such a theory. In this paper, the authors [23] showed that a consistent theory of the formation of non-equilibrium double layers can be developed based on the concepts of thermodynamic frequencies defined in [24]. In [25] it is shown that the differential equations describing the formation of double layers under the above conditions, allow an analytical solution. The next natural step is to direct payment of the electrochemical characteristics of the probe based on previous results.

Experimental

The starting materials and solvents

Sodium nitrate mark "chemically pure" is used without further purification.

Distilled water

The methodology of the measurement probe

The paper experimentally investigated the characteristics (the dependence of the probe current on the probe potential) of copper and platinum probes [26], [27].

With copper, the probe has used a solution of sodium nitrate concentration of 0.3 g / l. With a block of platinum, the probe has used a concentration of 0.23 sodium nitrate and 0.92 g / l.

Probe characteristics (the dependence of the probe current on the probe potential [6], [7]) were recorded with the help of the experimental setup collected by the scheme shown in Figure 3.

A cylindrical cell was filled with a buffer solution (sodium nitrate was used). Feed electrodes, which are supplied with fixed potential difference 12, are located near the cell walls. Platinum electrodes were fixed diameter of 0.32 mm at the top lid of the cell, made of organic glass. This made it possible to withstand the distances between the electrodes (6 cm). The probe is made of a platinum wire of the same diameter, was mounted strictly to specify the center between the electrodes on the geometrical axis connecting electrodes.

We used the experimental geometry in two versions.

1. Geometry and experimental conditions that meet platinum probe
2. Geometry and experimental conditions corresponding to the copper probe:

Used flat electrodes defining a width of 20 mm and a thickness of 0.95 mm. Electrodes were placed in a cylindrical cell having an inner diameter of 76.5 mm. potential difference value by defining electrodes was 12.06 V at a depth of immersion in a solution of 33.5 mm with 68.2 mm between them. The probe was placed 1.07 mm thick in the center is strictly between the electrodes.

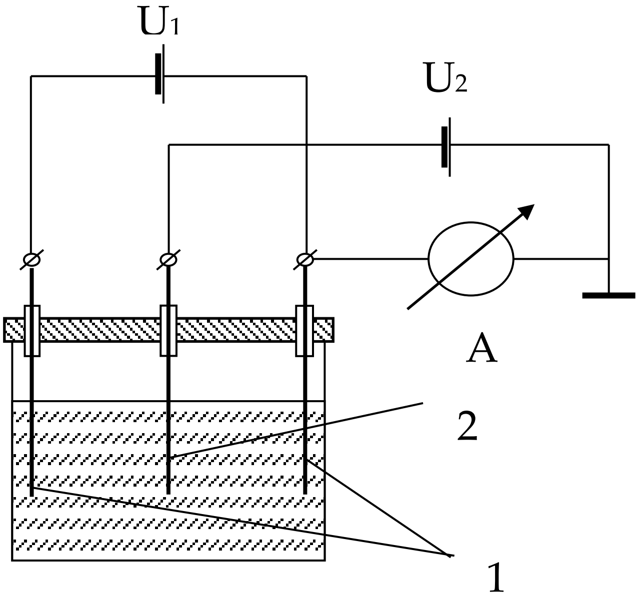

Figure 3. Scheme of the measurement setup
(1 -defining electrodes 2 - probe A – amperemeter, the U1 - given potential, the U2 - the potential of the probe)

Registration of probe characteristics was performed as follows. On the probe from the additional power supplied difference potentials U2 which is a potential barrier. This term is taken from the plasma physics; it points out that there is a range of potential values, in which the probe is relatively small current flows as the electrolyte potential at the point where the probe is counterbalanced by the voltage applied to the probe from an additional source.

Locking potential was varied from 0 to 13, i.e. It was completely blocked by a range of charge voltage on a given electrode. For each given value U2 measured amperage in the probe circuit. The potential difference U1 for all measurements was maintained constant using a stabilized power supply working in potentiostatic mode.

To ensure the permanence conditions of the experiment buffer solution are updated after every five measurements of the probe current. The solution was continuously stirred using a magnetic stirrer.

It should be emphasized that the chosen scheme of probe measurements is simple, with the proper performance of the experimental measurements being time-consuming. Upon receipt of each value of the probe, currently used several measurements of the same type that is shown in Table 1.

Table 1

An example of the experimental data obtained in the measurement of the probe characteristic

Voltage, V	The strength of current, mA					
	Experiment №1	Experiment №2	Experiment №3	Experiment №4	Experiment №5	average value
12	-2,16	-2,15	-2,14	-2,17	-2,18	-2,16
11,8	-2,03	-2,04	-2,05	-2,042	-2,038	-2,04
11,6	-1,97	-1,99	-1,98	-1,96	-2	-1,98
11,4	-1,95	-1,88	-1,92	-1,9	-1,85	-1,9

11,2	1,8	1,82	1,79	1,83	1,81	-1,81
11	1,66	1,67	1,68	1,69	1,7	-1,68
10,8	1,61	1,59	1,6	1,62	1,63	-1,61
10,6	1,53	1,54	1,53	1,55	1,55	-1,54
10,4	1,49	1,48	1,47	1,47	1,47	-1,47
10,2	1,38	1,4	1,39	1,4	1,38	-1,39
10	1,32	1,33	1,31	1,32	1,32	-1,32
9,8	1,245	1,24	1,25	1,25	1,24	-1,245
9,6	1,15	1,16	1,17	1,19	1,18	-1,17
9,4	1	1,1	1,2	1,1	1,1	-1,1
9,2	1,01	1,02	1,03	1,02	1,02	-1,02
9	0,95	0,955	0,945	0,95	0,95	-0,95
8,8	0,89	0,89	0,89	0,89	0,89	-0,89
8,6	0,81	0,8	0,82	0,81	0,81	-0,81
8,4	0,73	0,74	0,75	0,739	0,741	-0,74
8,2	0,67	0,68	0,67	0,68	0,68	-0,676
8	0,6	0,62	0,61	0,62	0,6	-0,61
7,8	0,531	0,529	0,528	0,532	0,53	-0,53
7,6	0,459	0,461	0,47	0,46	0,45	-0,46
7,4	0,39	0,397	0,4	0,4	0,4	-0,397
7,2	0,33	0,32	0,31	0,34	0,35	-0,33
7	0,25	0,26	0,25	0,25	0,25	-0,252
6,8	0,21	0,21	0,21	0,22	0,2	-0,21
6,6	0,13	0,14	0,14	0,14	0,135	-0,137
6,4	0,08	0,09	0,09	0,08	0,075	-0,083
6,2	0,02	0,02	0,02	0,01	0,01	-0,016
6	0	0,01	0,01	0	0	0
5,8	0,09	0,05	0,7	0,8	0,06	0,07
5,6	0,03	0,04	0,04	0,03	0,04	0,036
5,4	0,08	0,08	0,08	0,08	0,085	0,081
5,2	0,11	0,12	0,13	0,14	0,15	0,13
5	0,16	0,17	0,15	0,16	0,16	0,16
4,8	0,17	0,16	0,18	0,17	0,17	0,17
4,6	0,17	0,18	0,19	0,18	0,18	0,18
4,4	0,2	0,22	0,21	0,21	0,21	0,21

4,2	0,22	0,23	0,21	0,22	0,22	0,22
4	0,24	0,24	0,24	0,25	0,23	0,24
3,8	0,25	0,26	0,26	0,26	0,27	0,26
3,6	0,29	0,29	0,28	0,29	0,3	0,29
3,4	0,37	0,38	0,36	0,39	0,35	0,37
3,2	0,43	0,43	0,43	0,42	0,44	0,43
3	0,45	0,44	0,46	0,45	0,45	0,45
2,8	0,5	0,5	0,5	0,51	0,49	0,5
2,6	0,58	0,57	0,59	0,58	0,58	0,58
2,4	0,6	0,64	0,62	0,62	0,62	0,62
2,2	0,72	0,71	0,73	0,74	0,7	0,72
2	0,8	0,8	0,8	0,81	0,79	0,8
1,8	0,87	0,87	0,87	0,88	0,86	0,87
1,6	0,93	0,92	0,94	0,93	0,93	0,93
1,4	1,02	1,02	1,01	1,03	1,02	1,02
1,2	1,09	1,1	1,09	1,08	1,09	1,09
1	1,14	1,15	1,16	1,15	1,15	1,15
0,8	1,25	1,21	1,24	1,22	1,23	1,23
0,6	1,28	1,3	1,27	1,31	1,29	1,29
0,4	1,36	1,35	1,35	1,35	1,34	1,35
0,2	1,43	1,42	1,44	1,43	1,43	1,43
0,13	1,5	1,48	1,49	1,49	1,49	1,49

Results and discussion

The results of probe measurements

Example experimentally obtained probe characteristic is shown in Figure 4. The resulting probe characteristic has two distinct features. First, near the value equal to half the capacity of the master there is a transition region in which there is an inflexion point of the probe characteristic. Second, the probe characteristic becomes a straight line when the probe is different from the potential substantially. The latter fact has a clear explanation: if the probe potential is significantly different from the potential of space is due to geometrical factors, namely the probe begins to perform the function of the electrode. In this case, conventional registers curve electrolytes. Note that straight, which is asymptotically approaching probe characteristics are close to parallel, and their equations are characterized by the coefficients shown in Table 2. (Numeric codes correspond to the numbers of lines shown in Figures 4 and 5).

Table 2

The numerical values of the coefficients of the approximating straight

Number of straight	1	2	3	4
k	1,55	1,63	1,04	1,71
b	- 8,82	- 10,82	- 6,64	- 11,39

From the perspective of the probe measurement portion, the main interest is the section of specifications corresponding to the vicinity of the inflexion point. This plot is shown in Figure 4 on an enlarged scale.

Figure 5 shows that the transition portion of the probe characteristic has a pronounced asymmetry. Furthermore, in this area, there are also areas in which the probe characteristic can be approximated by straight lines with a confidence value of greater than 0.99 (lines 3 and 4 in Figure 5). In addition, the resulting differentiation depending upon the application of numerical filtering procedure [28] allows up to 0.05 V to determine the value of the potential of the isolated probe. This value is $Uisolat.probe = 6.55 \pm 0.05\ V$.

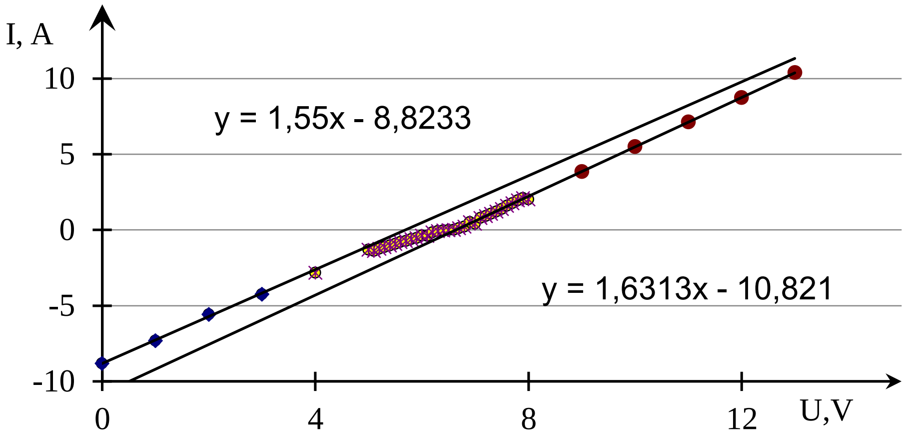

Figure 4. Example of the probe characteristic (copper wire probe in a solution of sodium nitrate)

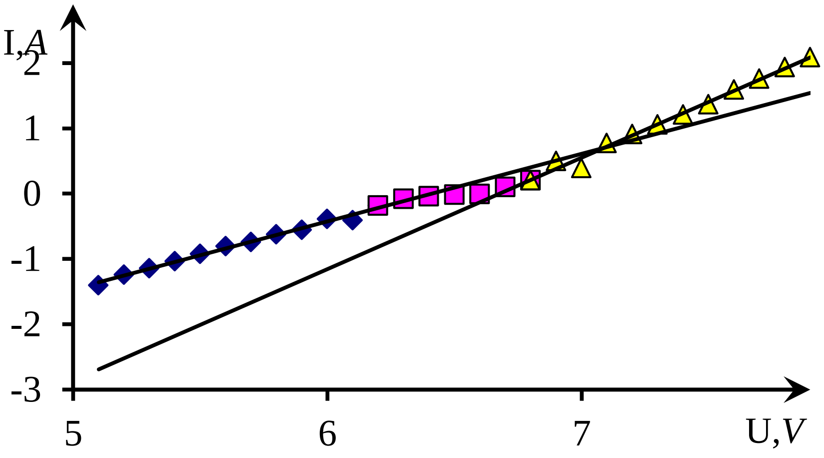

Figure 5. Transition portion of the probe characteristic

We emphasize that the chosen scheme of the experimental measurements of the potential of the space can be determined from symmetry considerations. Namely, when the location of the probe is strictly at the center of the cell having symmetrical electrodes, the potential of the point where the probe is located, obviously would be half of the voltage at the predetermined electrodes. This value is $Uspace = 6.03 \pm 0.01\ V$. The difference in these potentials is illustrated in Figure 5 (vertical lines).

Methods of numerical processing of measurement results

The experimental points for the probe characteristics obtained as described above have a definite spread, which is particularly significant when obtaining numerical differentiation dependencies.

In plasma physics to overcome this difficulty, as a rule, applies radio-technical differentiation method associated with the modulation of the probe potential at a certain frequency, and the subsequent allocation of the corresponding harmonic bandpass filter. This method is the need to use sophisticated equipment.

In this study, we used the method of numerical filtering of experimental dependencies. This method was tested in [29] on the experimental results obtained in the various physical and chemical nature of the system, and its accuracy can be considered satisfactory for the present study, in which only proved in principle the possibility of changing the absolute value of the contact potential difference between the electrode and solution.

The numerical filtering method used in the work is as follows.

Performing any linear filtering can be reduced to a convolution integral [16].

$$f(t) = \int_{-\infty}^{\infty} f(t - t^{/}) g(t^{/}) dt^{/} \, . \tag{1}$$

Applying the method of rectangles to the convolution integral (1), we have:

$$\widetilde{f}(t) = \sum_{i=-\infty}^{+\infty} f(t - t_i^{/}) g(t_i^{/}) \Delta T \, . \tag{2}$$

It is assumed here that the values of the function in question asked at the time points spaced at regular intervals are equal ΔT. Formally, the resulting formula (2) gives the value of the filtered function at arbitrary times (continuous function). Considering the size, defined at discrete points in time, as a rule, it makes sense to limit ourselves to finding the values of the filtered function for the same values of the argument, in which the initial function is given.

In other words, the formula (2) $t = k\Delta T$ can be put. Then,

$$\widetilde{f}(t_k) = \sum_{i=-\infty}^{+\infty} f(t_k - t_i) g(t_i) \Delta T \, . \tag{3}$$

For equidistant nodes is the relation:

$$t_k - t_i = k\Delta T - i\Delta T = (k - i)\Delta T = t_{k-i} \, . \tag{4}$$

Therefore, the formula (3) can be rewritten as:

$$\widetilde{f}_k = \sum_{i=-\infty}^{+\infty} f_{k-i} g_i \Delta T \, . \tag{5}$$

Replacing limits on finite (selected based on the requirements specified accuracy of calculations)

$$\widetilde{f}_k = \sum_{i=-M_2}^{+M_1} f_{k-i} g_i \Delta T . \tag{6}$$

The weights g_i must meet the requirement

$$\sum_{i=-M_2}^{+M_1} g_i \Delta T = 1 . \tag{7}$$

Where

$$\widetilde{f}_k = \frac{\sum_{i=M_2}^{M_1} f_{k-i}\, g_i}{\sum_{i=M_2}^{M_1} g_i} . \tag{8}$$

The Fourier transform of a rectangular function defined in the frequency plane, expressed by the formula

$$g_{rect}(t) = \int_{-\nu_0}^{\nu_0} \exp(2\pi i \nu t) d\nu = \frac{\sin(2\pi \nu_0 t)}{\pi t} = \frac{\sin(2\pi t / T_0)}{\pi t} . \tag{9}$$

This formula was proved in numerous courses of lectures on optics, radar theory, the theory of communication. Its meaning lies precisely in the fact that all of the frequencies that exceed a given modulus are not included in the integral (1), which provides a frequency cutoff.

The schedule filter function for the value of $T_0 = 12$ is shown in Figure 6.

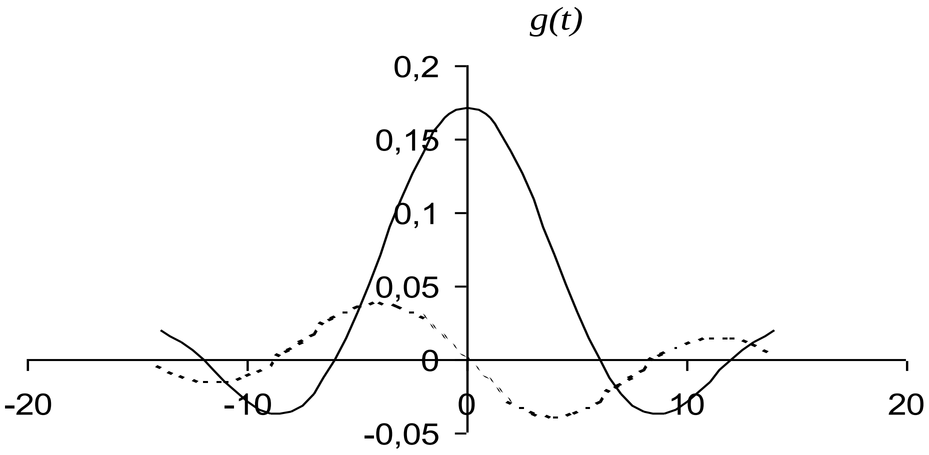

Figure 6. Filter function (solid line) and it is derivative (dotted line)

In the formula (8) was used as the calculated values of weights are calculated using the formula (9), all calculations are carried out using Microsoft Excell application.

The results of the numerical processing of measurement results

Examples of registration probe characteristics results are shown in Figure 7 and Figure 8. The curves differ from each other in the buffer solution concentration (0.023 and 0.092% by weight).

The resulting curves occur to have the following features. First, for those values of the probe potential at which the probe potential approaches the potential of one electrode probe characteristic asymptotically approaches a straight line. Second, the resulting straight for each of the analyzed cases are close to parallel.

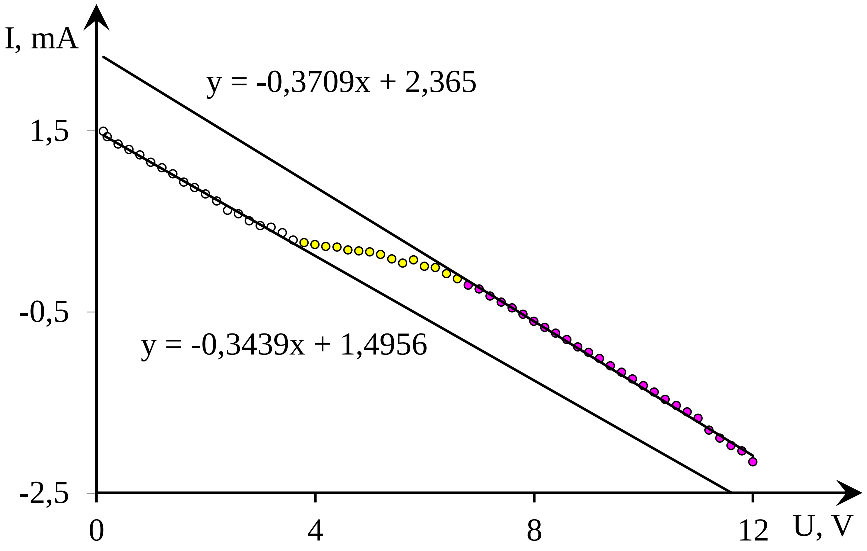

Figure 7. Probe characteristic platinum probe in sodium nitrate solution at a concentration of 0.023% by weight

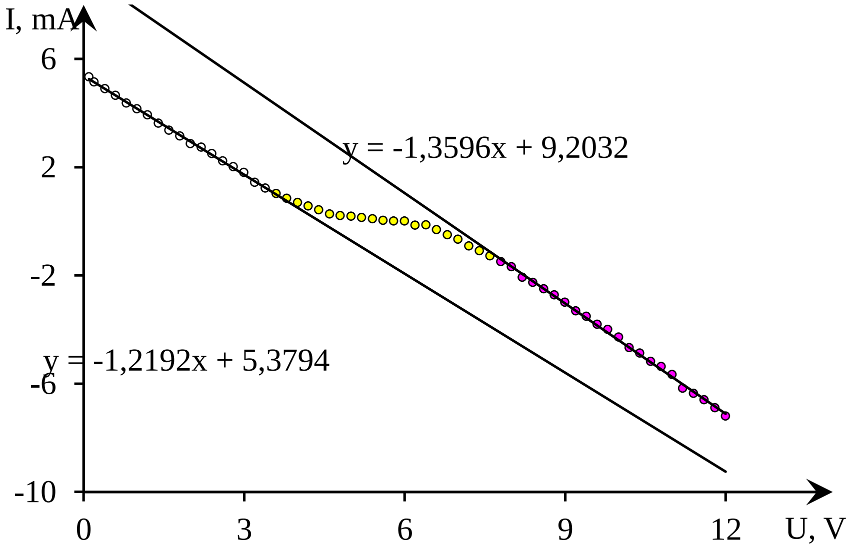

Figure 8. Probe characteristic platinum probe in sodium nitrate solution at a concentration of 0.092% by weight

Based on analogies with the results of plasma physics, it can be argued that the informative part of the probe characteristic accounts for the central region (II), in which it differs significantly from the course straight. Indeed, the area outside the probe, acquiring the potential equal to the potential of one electrode and begins to play a role, not probe and the additional electrode, as confirmed character rectilinear probe characteristics obtained in the areas (I) and (III).

A consistent theory of probe measurements in electrolytes is currently not yet developed, there are only a few works [24], [30], [31], in which it is proved that the system of differential equations describing the concentration distribution and field non-equilibrium double layer, an analytic solution. However, in plasma physics, we know that the informative part of the particle energy distribution function carries not the probe characteristic and its first and second derivatives. Therefore, at this stage of research, it seems appropriate to set the basic properties of symmetry of the probe characteristics in the electrolytes to find their singular points.

The selected point on the probe characteristic is the point corresponding to the potential of the insulated probe, i.e., the point of intersection specified characteristics with the horizontal axis. Provided that the potential is applied to the probe, the insulated probe is equal to the potential at the probe circuit current flows, which corresponds to the statement made above. To experimentally obtain characteristics of this point up to 0.02 V corresponds to 6 V.

This value corresponds to the potential of space at the point of the probe (i.e. the potential that would be realized at the specified point in the absence of the probe). Indeed, consider the equivalent circuit of the electrochemical cell (Figure 9).

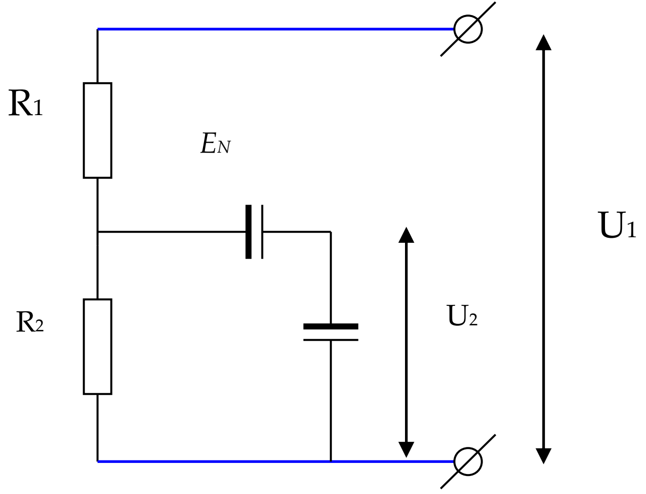

Figure 9. The equivalent circuit diagram of the probe measurements

The selected scheme in which the space in between the probe and each of the electrodes is the same leads to the conclusion that the equivalent resistance of R_1 and R_2 is equal to what would have been the mechanism of formation of potential irregularities in the distribution of the electrode regions. Therefore, shown in Figure 9, the circuit divider generates a voltage at the point of the probe potential equal to half the voltage across the electrodes defining, i.e., 6 V.

From this one can make a preliminary determination that the own EMF E_0 caused the formation of a potential difference between the metal and the electrolyte, in this case, is zero. However, the specified point on the probe characteristic is not its only feature.

We show that the inflexion points of the probe characteristic (the point at which it reaches the derivative extremum) at the same time is also a responsible point, for which the resulting curve is symmetric for the inversion operation.

In Figure 10, curves 1 and 2 shows the initial characteristics of the probe and filtered.

The filtering was performed using a numerical bandpass filter cutoff frequency components all having an oscillation period of more than 4 V. The same figure shows the first derivative of the probe characteristic obtained at baseline (curve 3) and filtered data (curve 4). The use of a filtering procedure allows a smooth dependence of the first derivative of the probe current on the probe potential.

The resulting curve of the first derivative of the probe characteristic is symmetrical relative to the point at which the derivative reaches its maximum. Visually, you can verify this by using the following construct. We carry out a shift on the x-axis value of U = 4,8 V, and then defer the values of experimental points from the absolute value of the obtained values. Provided that the above curve is symmetrical, thus obtained two curves should coincide. The described construction is shown in Figure 11, it is seen that the right and left-wing obtained according to coincide with high precision, at least in the region of interest for the interpretation of measurement results of the probe.

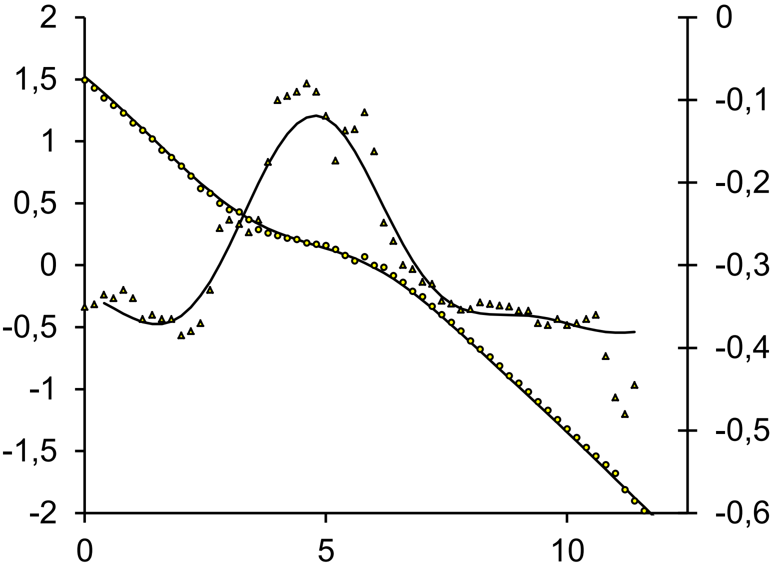

Figure 10. In the initial main axis (1 point) and filtered (2, solid) probe characteristic in the minor - the first derivative of the original characteristics (3 points), and the filtered curve (4, solid)

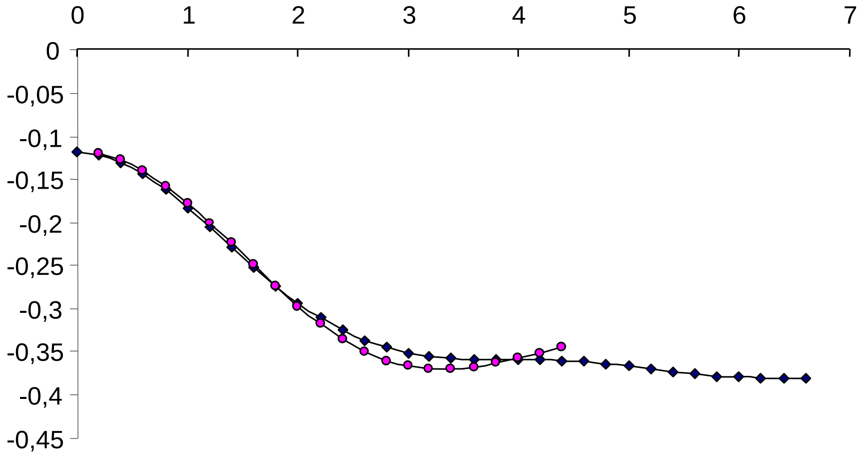

Figure 11. Checking the symmetry of the first derivative of the probe characteristic

Consequently, probe characteristic generally has at least two singular points, one of which (by analogy with the theory of the methods of the probe in plasma) may be associated with the isolated probe and the other with the space potential.

The accuracy of determining the capacity of the space based on geometrical factors (the accuracy of the values given above relate only to the stability of the power supply) this accuracy can be significantly lower due to the possible offsets of the probe concerning the center of symmetry of the system. If we assume that the assessment of the potential varies linearly from one electrode to another master. (It overestimates the potential change of the space when you change the location of the electrode as the real potential between the electrodes is less steep, on which is based, for example, the fourconductometric method). The experimentally obtained difference between the potential of the space and the potential of an isolated probe is ΔU = 0,5 V. When the voltage on the electrodes defining U_0 12.06 V and the distance between them is $l =$ 68.2 mm corresponds to the change in potential displacement:

$$\Delta x = \frac{\Delta U}{U_n} l = 3 \pm 0{,}2 \ mm. \tag{10}$$

which is three times greater than the maximum error in determining the position of the probe equal to its diameter.

Thus, our experimental measurements indicate the presence of a significant difference between the potential of an isolated probe and potential space, especially if we consider that the variation in the voltage of 0.5 V is responded much larger value changes the coordinates of the probe.

We show that the difference between the potential of an isolated probe and potential space under the chosen experimental geometry is a good approximation to the contact potential difference between the metal (in this case - copper) and a solution. Emerging with systematic errors can be considered by calculation.

Figure 12 shows the geometric arrangement of the electrodes in the measuring cell. Selected experimental geometry is characterized by two planes of symmetry (AB) and (CD), which lie at the intersection of the wire probe axis. lines of force distribution in the cell will have the same symmetry planes, with the proviso that the mobility of cations and anions, which dissociates used in experiments 1: 1 salt, the same (and default implicit proviso that electrostatic dissociation model adequately describes the mechanism the electrical conductivity of the electrolyte and the probe is relatively weakly perturbed the structure of the lines of force). In this case, the fact of symmetry is proved by simultaneous measurement of the direction of the electrostatic field (or, concerning the symmetry, the operation is the same, a change in the direction of the coordinate axes) and the ion charge sign appearing in the hydrodynamic equations of motion of the ions. The same value of the contact potential difference between the cathode and the anode solution and the solution is determined and that the electrodes are made of the same metal.

In the case where the probe current is zero (the probe isolated) components of the current vector lying in the AB plane, vanish. From symmetry considerations that unperturbed potential plane AB (potential that would be achieved in this plane without probe) is exactly equal to half the voltage at the predetermined electrodes, and consequently, the potential of the solution at any point of this plane is sufficiently far from the electrode, is known, and equal to the value specified above. Consequently, measured in the above-described potential difference between the isolated probe and potential space (up to fulfill the assumptions set forth above) is equal to the contact potential difference between the solution and the probe material.

Under real conditions, the mobility of anions and cations usually differ. However, the contribution of electrode layers in the potential drop between the metal and the electrolyte, caused by the spatial distribution of the ions may be accounted for by calculation. In addition, it can be shown that the remains balanced even with differing mobilities of the anions and cations in the quasi-stationary field distribution concerning the conditions of the plane AB.

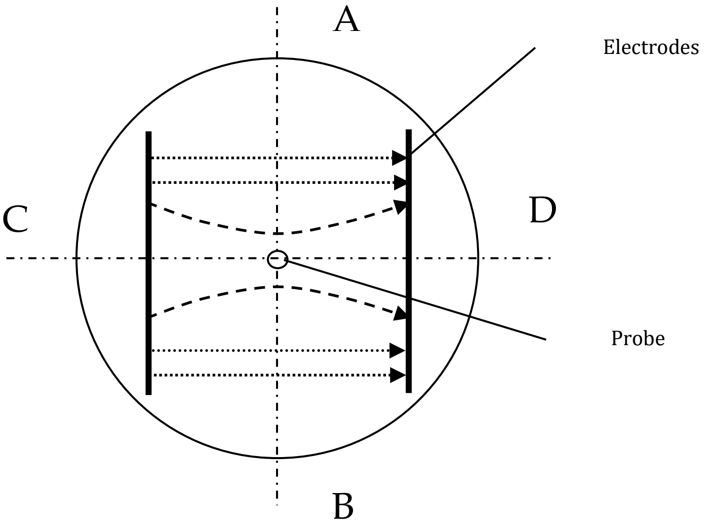

Figure 12. The planes of symmetry (AB) and (CD) of the measuring cell

Conclusion

Thus, the usage of the probe circuit can measure the absolute value of the contact potential difference between the metal and the electrolyte. In the investigated case, the value is 0,5±0,1 V. (up to a systematic error due to the difference in the mobility of cations and anions and the assumption of a stationary nature of the formation of the field distribution).

However, experimental results show that the potential of the space obtained by calculation more closely the potential value of an isolated probe (instead of the abscissa of the inflexion point). Therefore, it is possible to make a preliminary conclusion is that the formation of the EMF, characterizing the transition metal-electrolyte flows in a more complicated mechanism than it follows from the theory of equilibrium.

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Электродтық потенциалдардың абсолюттік мәндерін өлшеу үшін зонд әдістерін қолдану мүмкіндіктері

Аңдатпа. Мақалада зондтар - электр тогы өтетін электролит ішінде орналасқан шағын электродтар көмегімен электродтық потенциалдардың абсолюттік мәндерін өлшеудің іргелі мүмкіндігі қарастырылады. Электролит ерітінділерінде зонд сипаттамаларын алу металл-электролит шекарасында түзілген қос қабаттардың тепе-теңдік және тепе-теңдік емес сипаттамаларын тікелей өлшеудің үздік әдісі болып табылады. Электродтық потенциалдардың абсолюттік мәндерін өлшеудің зондтық әдістерін кезектестілікпен әзірлеу кезінде шешуді қажет ететін теориялық және эксперименттік мәселелер талқыланады.

Түйін сөздер: зондтық әдістер, электродтық потенциал, потенциалдар.

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Возможность использования зондовых методов для измерения абсолютных значений электродных потенциалов

Аннотация. В настоящей работе рассматривается принципиальная возможность проведения измерений абсолютных значений электродных потенциалов при помощи зондов - электродов малого размера, располагаемых внутри электролита, через который протекает электрический ток. Получение зондовых характеристик для случая растворов электролитов представляет собой перспективный метод прямого измерения как равновесных, так и неравновесных характеристик двойных слоев, формирующихся на границе металл-электролит. Обсуждаются теоретические и экспериментальные задачи, которые необходимо решить при последовательной разработке зондовых методов измерения абсолютных значений электродных потенциалов.

Ключевые слова: зондовые методы, электродный потенциал, потенциалы.

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