

THE CONDUCTIVITY OF THE ELECTROLYTE IN POROUS NICKEL ELECTRODES

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The effectiveness of porous electrodes is due to the fact that they possess a large internal surface. This surface constitutes a surface of separation between the solid phase (the material of the electrode) and the volume of the pores. The intensity of heterogeneous electro-chemical processes taking place within the surface of a porous electrode is determined, not only by the properties of the surface itself and the polarization of the electrode, but also by the conditions under which the active substances reach the place where reaction occurs, and the reaction products are removed, as well as by the conditions under which the electrical current passes through the body of the porous electrode and the pores contained within it, these being filled with the electrolyte.

The geometrical configuration of the solid phase of a porous electrode, as well as that of the pores within it, is quite complex, so that in the majority of cases it is impossible to carry out a reliable theoretical calculation of transference phenomena within such an electrode. A considerable number of experimental and theoretical works in this region have been devoted primarily to the flow of liquid through the porous systems. These are all considered in a very detailed review by Sheidegger [1]. The phenomena of electrical conductivity and diffusion in the liquid phase in porous systems has been considerably less investigated. Reference should be made, particularly, however, to the interesting work of Fatt [2], who investigated the conductivity of porous systems on lattice-type models which reproduced to a considerable extent the interlaced structure of the porous space in real porous substances. It is unfortunate that the direct transfer of the results of these investigations into real porous electrodes is incapable of being carried out.

Thus, to determine the effective value of the penetrability of porous electrodes in relation to the diffusion currents of a substance and the passage of an electric current within the pores, it is practically always necessary to have recourse to direct experiment. The problem becomes particularly complex in the case of the so-called gas diffusion electrodes. Within the body of such electrodes are present simultaneously three continuous phases; solid, liquid, and gaseous. Because of the effect of capillary forces within the body of the electrode, close contact is created between the gas and liquid phases in the immediate neighborhood of the surface of the solid phase on which the electro-chemical reaction occurs. Contact between the gas and liquid in the gas diffusion electrode is attained through partial displacement of the liquid from the pores of the electrode by the gas. The conditions of transference in such electrodes, are, of course, very complicated, since they depend, not only on the structure of the solid phase, but also on the ratio of the quantities of liquid and gaseous phases within the porous space of the electrode.

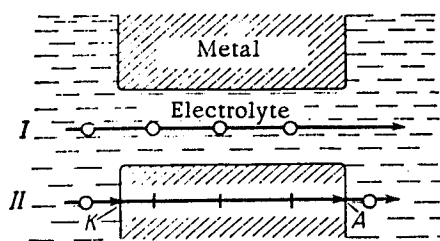


Fig. 1. Two possible paths by which current may pass through a porous electrode filled with electrolyte. Location in which the process arises: K—cathode; A—anode. Current: I) ionic; II) Electronic.

The present communication is devoted to the results of investigating the effective penetrability of the liquid phase within the pores of nickel electrodes of various structures, for different ratios of the liquid and gaseous volumes in the pores. The penetrability of the liquid phase is estimated from the value of its effective electrical conductivity. We shall, in what follows, describe this conductivity in terms of the specific conductivity of the liquid phase in the pores, related to one cubic centimeter of the porous electrode.

Measurement of the electrical conductivity of electrolytes in porous non-conducting materials presents no problems of principle, and have been carried out more than once for various purposes [3-6]. It is somewhat more difficult to measure the conductivity of electrolyte present in the pores of a conducting electrode made of such materials as metals. In this case, conditions should be maintained in which the current passes

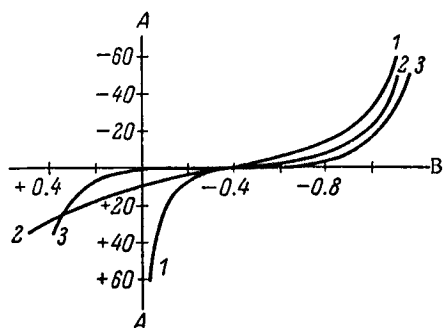


Fig. 2. Polarization curves for a porous nickel electrode with anodic and cathodic polarization. A) Current, I (μ A); B) potential, φ (V). 1) Normal solutions of: 1) potassium chloride; 2) potassium sulfate; 3) sodium hydroxide.

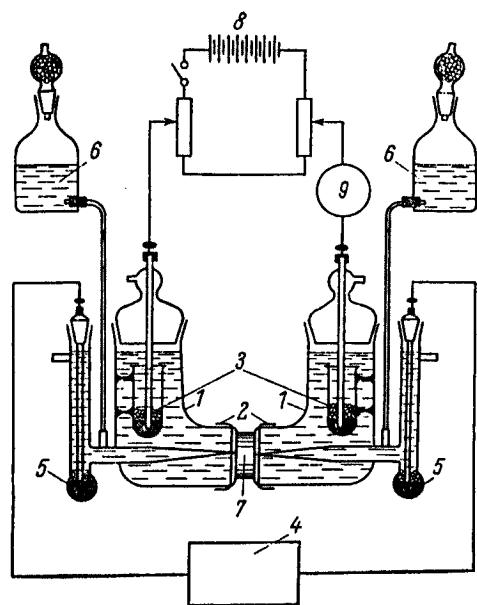


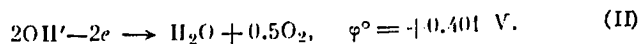
Fig. 3. Apparatus for measuring the conductivity of an electrolyte in porous electrodes.

only through the electrolyte and not through the metal, in direct contact with the electrolyte, even though the metal usually has considerably higher conductivity than the solution. This kind of measurement has been carried out in one of our previous investigations [7].

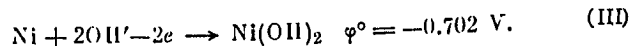
The possibility of independent measurement of the electrical conductivity of the electrolyte within the pores of a metallic electrode arises from the different mechanism of conductivity in the two media. If a current passes through an electrolyte present within a porous electrode, for sufficiently low current values, this current will be due entirely to ionic conductivity, since this method is energetically preferable to conduction through the metal, which, although it is more highly conducting, suffers from the necessity of overcoming the two potential jumps at the points of transition from electrolyte to electrode and from electrode to electrolyte. Figure 1 gives a schematic presentation of the two possible ways in which the current can pass through a porous electrode filled with electrolyte. When the current passes according to the second mechanism, electro-chemical reactions take place at points K and A, resulting in a considerable waste of energy.

To obtain undistorted values of the conductivity of the electrolyte within the electrode pores, it was necessary to choose the electrolyte in such a way that some potential region existed in which the electrode would have an "absolute" polarizability in relation to all potentials possible in this region, though the reaction would only take place in one direction (either cathodic or anodic). Conjugated reactions on the oppositely located side of the electrode would be hindered by the fact that the rate of the mutually conjugated reactions should be the same. From this point of view, we now consider a nickel electrode in a solution of alkali. The possible processes in such a case are the following:

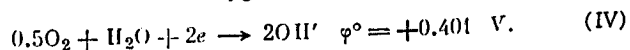
Decomposition of water:



Oxidation of nickel:



Reduction of dissolved oxygen:



Possible combinations in pairs of oxidation and reduction processes, and the minimum potential differences necessary for the occurrence of the processes are:

$$(1)-(II) \quad \varphi^\circ = 1.229 \text{ V},$$

$$(1)-(III) \quad \varphi^\circ = 0.126 \text{ V},$$

$$(II)-(IV) \quad \varphi^\circ = 0.$$

It can be seen from this comparison that the first pair of associated reactions is thermodynamically possible only when considerable potential difference exists within the electrolyte at opposite sides of the porous electrode. In practice, this difference is even greater because of the considerable overpotential of reactions (I) and (II). For the second pair, the "permitted" potential difference is less, but in practice this may be considerably greater than 0.126 V, since nickel in alkaline solution regularly undergoes passivation. The third pair of reactions, the conjugation of evolution and reduction of oxygen is theoretically possible at the same potential, but here also passivation can occur within a quite wide interval, owing to the appreciable overpotential of the electrode processes.

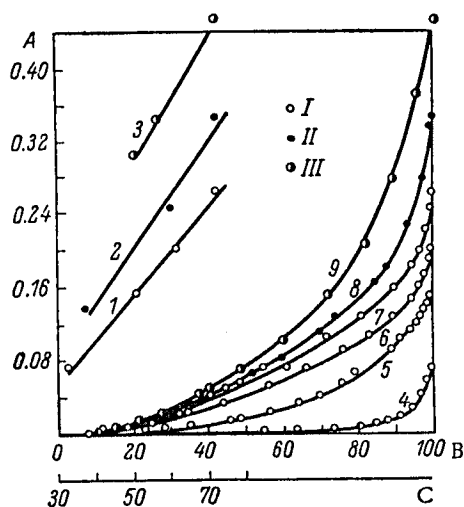


Fig. 4. Relationship of the electrolyte conductivity in porous electrodes to the porosity of the latter (curves 1-3) and the degree of saturation of the porous surface (curves 4-9). A) Corrected conductivity, k_{cor} ; B) degree of saturation, s (%); C) porosity, g (%). Material of electrodes and particle dimensions (microns): I) carbonyl nickel, 65; II) electrolytic nickel, 65; III) nickel turnings, 200. Porosity of electrode (%): 4) 32; 5) 51; 6) 63; 7) 71; 8) 73; 9) 71.

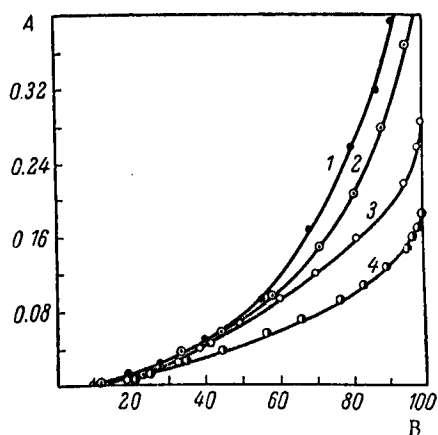


Fig. 5. Effect of particle dimensions of the filler on the conductivity of electrolyte in the pores. A) Corrected conductivity, k_{cor} ; B) degree of saturation, s (%). Porosity of electrodes (%): 1) 71; 2) 71; 3) 62; 4) 62. Dimensions of filler particles (microns): 1) 160; 2, 3) 85; 4) 20.

The neutral solutions, and particularly in acid solutions, the conditions required for measuring the electrical conductivity of the electrolyte in porous nickel electrodes are less favorable, since in such solutions, nickel is not subject to passivation.

To test the conclusions set out above, polarization curves were obtained on porous nickel in solutions of potassium chloride, potassium sulfate, and sodium hydroxide. The curves are shown in Fig. 2; and it is seen that in alkaline solutions the practical range of passivity of the nickel electrode amounts to 500 mV. In the sulfate and chloride solutions, the interval is considerably narrower.

Measurements of the conductivity of the electrolyte in the pores of a nickel electrode were carried out using 1.0 N sodium hydroxide solution.

The apparatus for measuring the electrical conductivity of the electrolyte in the pores of an electrode is shown in Fig. 3. The apparatus consists of two glass vessels 1, sealed to springs in such a way that they may be moved further away from each other. The lower openings of the vessels are closed by means of thin cellophane films 2. In the vertical limbs of the vessels, mercury-oxide electrodes 3 are mounted. These electrodes are the means whereby current is introduced to the electrolyte. The reduction in potential when current passes through the electrolyte in the pores of the electrode is measured by means of a potentiometer or cathodic voltmeter 4, connected with mercury-oxide electrodes 5, mounted in vessel 1, in such a way that the tips of the electrodes are in tight contact with the cellophane film. The whole system is filled with 0.1 N sodium hydroxide solution. To ensure that the cellophane films were in a stretched condition, the electrolyte in the apparatus was maintained under a pressure of around 20 cm water, which was achieved by connecting a pressure vessel 6 to the vessel 1. The current was led to the electrode under investigation 7 from the accumulator 8 through the series-connected resistance and micro-ammeter 9.

The measurements were carried out using porous nickel specimens of different structures. The samples were prepared in the form of discs of diameter 17-20 mm and thickness 4.6 mm by pressing and sintering in an atmosphere of hydrogen. The nickel used for the preparation of these electrodes consisted of powders of three kinds: carbonyl nickel, with particle dimensions of 6 ± 2 microns,* electrolytic nickel with particle dimensions of 65 ± 15 microns, and nickel turnings with dimensions of 205 ± 25 microns. Ammonium bicarbonate was used as powdered filler, the bicarbonate having mean particle dimensions of 20, 85, and 160 microns. Thirty eight samples of porous nickel in all were investigated, the porosity of which varied within the limits 32-77%, the samples having various structures.

Measurements of the conductivity of the electrolyte in the pores of the electrodes were determined for various degrees of saturation of the porous space by means of the liquid. Complete saturation of the pores with the electrolyte was attained by sucking the

* The theoretical dimensions were determined on the basis of statistical examination of micro-photographs of the powders.

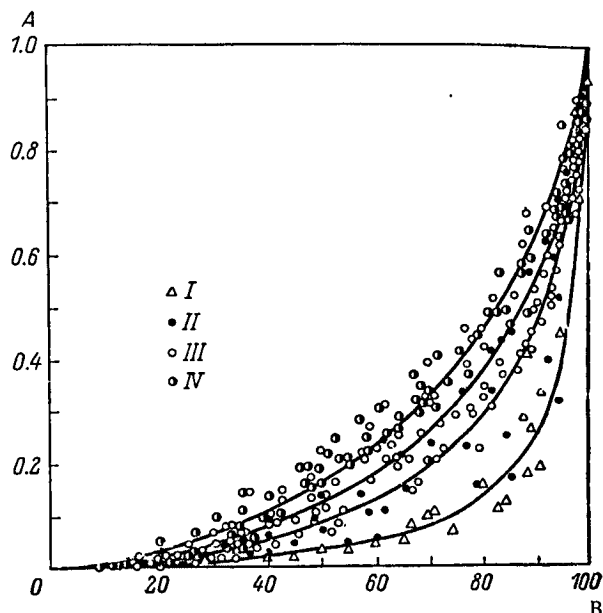


Fig. 6. Relationship between the relative conductivity of the electrolyte in the pores of the electrodes (k_{rel}) and the degree of saturation of the porous space with the liquid. A) Relative conductivity, k_{rel} ; B) degree of saturation of the porous space with liquid. Porosity of electrodes (%): I) 32-38, II) 45-53; III) 57-66; IV) 70-77. The curves, reading downwards, are calculated for porosities of 35, 49, 60, and 73% respectively.

along its thickness. The resistance of the electrolyte in the pores was calculated on the basis of the linear relationship between current and potential difference, and a correction was applied for the resistance of the cellophane films (around 3 ohms).

Some of the experimental results are shown in Figs. 4 and 5 in the form of curves showing the relationship between the conductivity of the electrolyte in the pores and the degree of saturation of the porous space by the electrolyte. The conductivity (k_{cor} - the corrected value) was expressed in fractions of the specific conductivity of the electrolyte applied to the electrode: $k_{cor} = k_{exp}/k_{sp}$.

Figures 4 and 5 show that the electrolyte shows an appreciable conductivity in the pores of the specimen only when the degree of saturation of the porous space amounts to at least 8-10%. Increase in the degree of saturation causes the conductivity to increase. The overall nature of the curves for different electrodes is similar, though the actual values of the conductivity for a given degree of saturation depends considerably on the structure of the electrodes. Thus, it is seen from Fig. 4 that at constant saturation, the conductivity increases with increase of the porosity of the electrodes, while for constant porosity, the conductivity increases with increase in dimensions in the particles from which the electrodes were prepared. The same figure also gives curves showing the relationship between conductivity of completely saturated electrodes and the porosity of the latter for samples prepared from three nickel powders of different dispersivity. This graph illustrates the same relationship, that is, increase in conductivity with increase in porosity and particle dimensions.

Figure 5 shows the effect of the dimensions of the filler particles (ammonium bicarbonate). It is seen that samples prepared using coarse-grained filler show somewhat higher conductivity than those using fine-grained filler under uniform conditions of porosity.

The structure of the porous electrodes depends on a great number of different factors, including dispersivity of the metal powders, and of the filler, the ratio of the two, and conditions of mixing, pressing, and sintering. The conductivity of the electrolyte in the pores of the electrode is determined by the structure of the latter, and depends on all three factors which influence the formation of one or other structural type. A detailed study of the interplay of

samples under vacuum. Partial removal of the liquid from the pores was carried out by centrifuging the samples. By changing the rate of rotation of the centrifuge, it was possible to attain any desired degree of saturation of the porous samples by means of an electrolyte. After centrifuging the samples for some minutes, these were allowed to stand in order to attain uniform distribution of the liquid throughout. Determination of the degree of saturation was carried out by weighing the samples before and after measuring the electrical conductivity. Experiments showed that, during the time of measurement, if the samples were maintained in contact with the electrolyte through the cellophane films, the change in the degree of saturation through filtration of the liquid through the films was negligible. During all the manipulations, involving passage of electrolyte, equations were taken to minimize evaporation.

In measuring the electrical conductivity of samples of a given porosity, the apparatus (Fig. 3) was inserted between the cellophane films, and current was passed through. The value of the current was varied between such limits that the potential difference at opposite sides of the specimen did not exceed about 300 mV. In all cases a strictly linear relationship was observed between the reduction of potential at the sample and the current (that is, Ohm's Law was followed). When the direction of the current was changed there was usually a slight shift (amounting to a few millivolts) of the current-potential difference line, though the slope of this was preserved unchanged. This asymmetry is apparently due to non-uniform polarization of the electrode

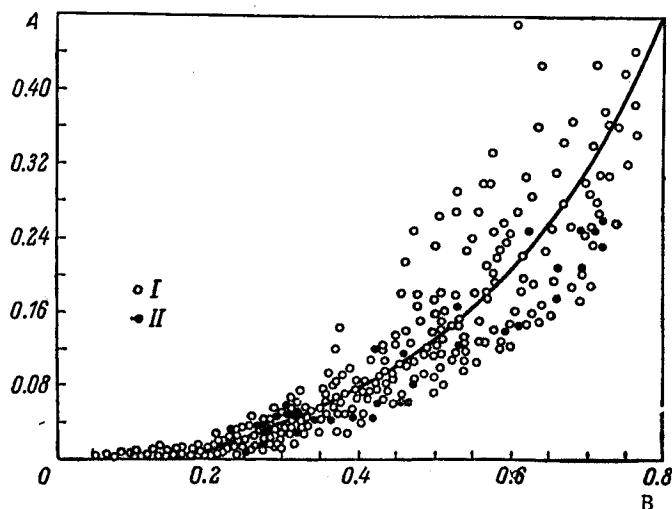


Fig. 7. Correlation between the total electrolyte content in porous electrodes, S and the corrected conductivity. A) Corrected conductivity, k_{cor} ; B) total volume content of electrolyte per unit volume of the porous electrode; S (cm^3/cm^3). Electrodes: I) nickel; II) graphite.

these complex factors would be very difficult and thankless task, and was not envisaged in the course of this investigation. Our purpose was to use a comparatively limited range of material to elucidate the most characteristic regularities determining the conductivity of the electrolyte within porous electrodes. For this purpose, it was necessary to limit the investigation to determining the correlations between fundamental structural characteristics of the electrodes and the conductivity of the electrolyte within its pores. Such relationships should be suitable for determining the probable values of electrolyte conductivity in pores of electrodes on the basis of the most general information about their structure.

Figure 6 gives experimental points obtained in investigating 38 different electrodes of various structures. On the axis of ordinates, the relative conductivity (k_{rel}) is shown, that is, the conductivity of the electrolyte in incompletely saturated porous space, compared with the value in fully saturated pores, the latter taken as 1.

The electrodes were divided into four groups in accordance with the porosity: from 32 to 38% (point I), from 45 to 53% (point II), from 57 to 66% (point III), and from 70 to 77% (point IV). In spite of a certain scatter, the points corresponding to each group have a tendency to be distributed within a limited area of the graph. The curves given on the graph correspond approximately to the centers of these zones. The curves approximate well to functions of the type:

$$k_{\text{rel}} = \frac{(a-1)s}{a-s}, \quad (1)$$

where s is the degree of the saturation of the porous space with liquid (as a fraction of unity); and a is a parameter depending on the porosity of the electrode. The connection between the parameter a and the porosity, for values of the latter greater than 30%, may be regarded as linear:

$$a = 0.5g + 0.875, \quad (2)$$

where g is the porosity (as a fraction of unity).

Inserting the value from Eq. (2) in Eq. (1) we obtain an equation expressing the relationship between the relative conductivity of the electrode and the porosity, and the degree of saturation of the porous space with electrolyte:

$$k_{\text{rel}} = s \cdot \frac{g - 0.25}{g + 1.75 - 2s}. \quad (3)$$

Experimental test of Eq. (3) showed that it was quite satisfactory for many practical purposes in its agreement with experiment. The discrepancy between the calculated values of the relative conductivity and the measured values for all the electrodes investigated never exceeded $\sim 20\%$, and in the majority of cases was appreciably less than this. If account is taken of the fact that electrodes with quite a wide range of structure were investigated the result can be

regarded as satisfactory. The applicability of Eq. (3) is limited by the range of structure-variation within which the electrodes investigated lies. The results of calculations on the basis of Eq. (3) for electrode porosities less than 30%, and degrees of saturation less than 15%, must be regarded as doubtful.

The quite clear correlation between the porosity, degree of saturation, and relative conductivity, expressed in Eq. (3), shows that the shape and dimensions of the nickel particles and the filler particles used in preparing the electrodes exercises no clear influence on the value of k_{rel} . However, as can be seen from Figs. 4 and 5, the structure of the initial materials has an appreciable effect on the value of the corrected conductivity (k_{cor}). The latter may be expressed in the form of the product: $k_{cor} = k_{rel} \cdot k_{cor(max)}$ where $k_{cor(max)}$ is the corrected conductivity of the liquid phase in completely saturated electrodes. The actual conductivity of the electrolyte in the pores of the electrode (k_{eff}) may be expressed by the relative conductivity k_{rel} and the maximum corrected conductivity ($k_{cor(max)}$) in the following way:

$$k_{eff} = k_0 \cdot k_{rel} \cdot k_{cor(max)} \quad (4)$$

where k_0 is the specific conductivity of the electrolyte used to penetrate the porous electrode.

Of the three factors in Eq. (4), the first is determined only by the composition of the electrolyte and the temperature; the second depends on the porosity of the electrode and the degree of saturation of the porous space by liquid (Eq. (3)). The last factor ($k_{cor(max)}$) is connected with the porosity of the electrode and the dimensions of the particles. On the basis of an analysis of the experimental data, this relationship may be expressed in the form:

$$k_{cor(max)} = 0.8g + 4 \cdot 10^{-4}d - 0.18, \quad (5)$$

where d is the mean diameter of the particles of the nickel powder, expressed in microns.

However, the relationship given in Eq. (5) is not very clearly expressed; the correlation coefficient for Eq. (5) amounts to not more than 0.34. This is presumably due to the fact that the magnitude of $k_{cor(max)}$ is determined also by the shape of the nickel particles as well, perhaps, as by other factors not taken into account.

Practical calculation of the effective conductivity of the electrolyte in the electrode pores may be carried out successively using Eqs. (5), (3), and (4). For this purpose, it is necessary to know the porosity of the electrode, an approximate value of the particle size of the particles for which the electrode is prepared, the specific conductivity of the electrolyte, and the degree of saturation of the porous space with the electrolyte.

An approximate calculation of the effective conductivity of the electrode in the pores may be obtained, starting from the total electrolyte per unit volume of the porous electrode. There seems to be reason to suppose that the conductivity of the electrolyte in the pores should depend directly on its concentration within the electrode. It is seen from Fig. 7 that this relationship is actually found. In the present case, the solid and the gaseous phases within the porous electrode are to be considered as operating together to reduce the effective conductivity of the liquid phase. The experimental points (I) obtained during the investigation of the 38 electrodes of different structures and porosities, and for different degrees of saturation, form a rather wide but limited band. Within this band, we have drawn a curve showing the relationship between the most probable values of the corrected conductivity and the total liquid content in the pores of the electrode. The curve was constructed according to the equation:

$$k_{cor} = S^3, \quad (6)$$

where S is the volume content of liquid in the electrode: $S = sg$.

Equation (6) and Fig. 7 may be used to estimate the effective conductivity of the electrolyte in the pores of the electrode. For this purpose, it is sufficient to know only the total liquid content within the electrode. The spread of the experimental points in Fig. 7 gives some indication of the size of the possible error in such calculations. Figure 7 also contains the experimental points (II) obtained in one of our experiments during the investigation of the conductivity of the electrolyte in porous graphite in electrodes [7]. These data show qualitatively the same type of relationship as those obtained for nickel electrodes. This "universality" of the relationship expressed by Eq. (6) compensates to some degree for the low accuracy.

SUMMARY

The method has been described for measuring the conductivity of an electrolyte within the pores of metallic electrodes, based upon choosing the experimental conditions in such a way that the metal is passive in relation to possible electro-chemical processes.

On the basis of the experimental data obtained, empirical formulae have been derived which permit of calculating the effective conductivity of the electrolyte in porous electrodes, starting from information about the porosity and the degree of saturation of the porous space by the electrolyte.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.