Translated from *Uspekhi Khimii*, 47, 804-818 (1978) U.D.C. 541.138.3:546

Electrochemical Determination of Surface Area of Metals

E.I.Khrushcheva and M.R.Tarasevich

The fundamental principles of the electrochemical determination of the surface area of metals are discussed. Conditions of determination and methods of calculation are analysed for smooth and powdered metals of the platinum group, nickel, the copper subgroup, and carbonaceous materials. A list of 108 references is included.

CONTENTS

I. Introduction 416
II. Fundamental principles of the electrochemical measurement of true surface area 416
III. Determination of true surface area of various materials 418

I. INTRODUCTION

Study of the kinetics of heterogeneous processes requires a knowledge of the true surface area of the solid involved in the reaction. Several methods of determination based on the measurement of adsorption by volume or by weight have now been adequately developed and have been surveyed in detail in monographs and reviews [1-4].

Intensive work during the past decade has led to the widespread use of a new electrochemical method for determining the surface area of several metals in compact and powdered forms [5,6]. The possibility of determining true surface area from electrochemical measurements was first pointed out by Bowden and Rideal [7], and later by Shlygin and Frumkin [8]. Among the merits of this method, discussed quite fully by Brunauer [1], is its great sensitivity, which permits measurements on specimens of surface area down to 0.01 cm^2. The surface area of a catalyst can be measured electrochemically directly during the process when reaction takes place in an electrolyte solution [9,10]. These advantages, together with the rapidity of the measurements and the possibility of using readily available series-produced equipment, has attracted the attention of increasing numbers of research workers. However, no reviews hvve appeared on the electrochemical determination of surface area, which makes it difficult to choose the optimum procedure according to the nature of the metal and the conditions of measurement.

II. FUNDAMENTAL PRINCIPLES OF THE ELECTROCHEMICAL MEASUREMENT OF TRUE SURFACE AREA

The electrochemical method for determining the true surface area of a catalyst is based on measurement of the quantity of electricity consumed in changing the charge on the electrode in a given potential range. The theoretical basis of the method is Frumkin and Petrii's thermodynamic theory [11-13] of the surface state of electrodes that adsorb hydrogen and oxygen. It was shown [11-13] that in general the total (or thermodynamic) charge communicated to an electrode is consumed in charging the electrical double layer at the electrode-solution interface and in the adsorption of hydrogen, oxygen, or components of the electrolyte. The applicability of the thermodynamic theory to the surface state of a metal in an electrolyte solution was confirmed experimentally. In the case of a completely reversible system (e.g. a platinum electrode in the range of potentials for the adsorption of hydrogen) an unambiguous correspondence was established between the charge communicated to the electrode and its potential given by the charging curve. Either the charge consumed in adsorption (mostly of hydrogen) or the free charge (the differential capacitance of the electrical double layer) is determined experimentally. The surface coverage with adsorbed species or the capacitance of the double layer is found from investigations on electrodes of a given metal having a known true surface area (measured e.g. by the Brunauer-Emmett-Teller method). These values are then used as coefficients in determining the surface areas of other specimens of the same metal.

We shall now consider in greater detail the above two groups of methods, estimate their sensitivity, and assess the prospects of using them for various materials and experimental conditions.

1. Method of Charging Curves

Several modifications of the method of measuring charging curves can be used at the present time. They differ in the procedure for establishing conditions under which the whole of the electricity supplied to the electrode is consumed in changing its charge.

Frumkin and Shlygin [8,14,15] developed a technique of slow determination of charging curves on electrodes having a large true surface area. The curves were obtained from a solution saturated with an inert gas, to eliminate involvement in the electrochemical process of hydrogen or oxygen dissolved in the electrolyte. Powdered materials were placed in an electrically conducting gauze [16] to serve as current lead. Charge transfer can be effected by contact between the powder and an inert lead [17]. The quantity of electrochemically active impurities can be diminished [18] by decreasing the volume of the solution. Slow equilibrium charging curves can then be obtained at low current densities even on smooth electrodes.

A method was suggested [7,19] for obtaining rapid galvanostatic charging curves at high current densities. This would eliminate the effect of foreign solutes, which might have diffused to the electrode surface if the curves were determined slowly.

The above methods now find widespread use in electrochemical research.

Fig. 1 shows a typical charging curve for a platinum electrode in 1 *N* sulphuric acid, obtained at low current densities (the rapid galvanostatic curve is similar in shape) [20] (here and subsequently electrode potentials are

given relative to the potential of a reversible hydrogen reference electrode in the same solution). The curve exhibits two arrests (region *I* and *III*) with a high pseudo-capacitance. Ionisation of adsorbed hydrogen takes place in the region of the first arrest:

$$MH_{ads} \rightarrow H^+ + \bar{e} + M.$$

The second arrest corresponds to the discharge of water molecules with the formation of adsorbed oxygen or surface oxides:

$$M + H_2O \rightarrow MO_{ads} + 2H^+ + 2\bar{e}.$$

The two arrests are separated by a region *II* having a low capacitance, where a large proportion of the electricity is consumed in changing the charge on the double layer.

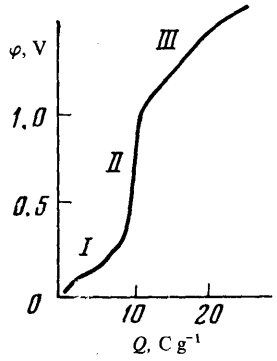


Figure 1. Charging curve for platinum in 1 *N* sulphuric acid at 20°C.[20]

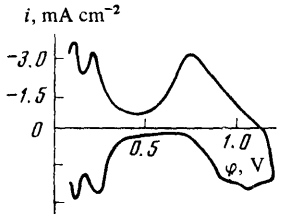


Figure 2. Current–potential curve on platinum in 1 *N* sulphuric acid in argon with a rate of application of potential of 1 V s^{-1}.[28]

Charging curves are now commonly obtained by a potentiodynamic method, first used for this purpose by Will and Knorr[21] and by Kolotyrkin and Chemodanov[22]. Electronic apparatus has been designed for this method[23-25] and investigations have been made on the surface state of various metals[16,24,26,27]. With linear scanning of the potential at a rate $v = \partial\varphi/\partial\tau$ the $i-\varphi$ curves (Fig. 2)[28] determined by means of triangular voltage pulses represent essentially the differential form of the galvanostatic $Q-\varphi$ curves: $I = v\partial Q/\partial\varphi$. Maxima on the potentiodynamic $i-\varphi$ curve therefore correspond to maxima on the galvanostatic curve. The potentiodynamic method can be applied both to smooth[16,29,30] and to finely divided[16,31] electrodes. It yields highly reproducible results, largely because of the reproducible surface state of the electrodes obtained by periodic electrochemical oxidation and reduction[32,33] or by programmed pretreatment of the surface[24]. However, limitations on the rate of application of the potential, due to the disperse character of specimens, must be borne in mind when using this method.

The true surface area can be calculated from each of the above regions of the charging curve. However, the hydrogen region is generally used, because the deposition and removal of hydrogen are more reproducible than the corresponding processes with oxygen. In calculating the quantity of electricity corresponding to the hydrogen adsorbed, we must introduce a correction for the charging of the double layer and the evolution of molecular hydrogen. Finding the charge consumed in the evolution of hydrogen is a more difficult problem. In order to prevent the evolution of molecular hydrogen, therefore, the determination of slow charging curves does not extend beyond potentials 30–50 mV more positive than the reversible hydrogen potential.

The quantity of hydrogen adsorbed is determined from the area below the potentiodynamic $i-\varphi$ curve bounding the hydrogen region (Fig. 2). This is equivalent to integrating the $Q-\varphi$ curve:

$$Q = \frac{1}{v}\int_{\varphi_1}^{\varphi_2} i \cdot d\varphi$$

The end-point for measuring the quantity of electricity consumed in the adsorption of hydrogen on platinum was taken[34] to be the potential of the minimum preceding the evolution of hydrogen. This corresponds to the assumption that the quantity of electricity required for the adsorption of hydrogen at $\varphi < \varphi_{min}$ is balanced by the charge involved in the evolution of hydrogen at $\varphi > \varphi_{min}$. A similar postulate was made for other metals[35]. It has been suggested[36] that $i-\varphi$ curves should be obtained at a low temperature (down to −72°C) to diminish the influence of hydrogen evolution on the quantity of hydrogen adsorbed.

The oxygen region of the charging or potentiodynamic curve can also be used to calculate the true surface area[30,37-42]. However, this gives rise to additional complications owing to the non-equilibrium character of the adsorption of oxygen and the time variation of the strength of its bonding to the surface[16,27,43,44]. As a result, the quantity of oxygen adsorbed depends on the current density used to obtain the charging curve or on the rate of application of the potential.

In order to calculate surface coverage of an electrode by hydrogen and oxygen it is necessary to know the quantity of electricity consumed in forming a hydrogen or oxygen monolayer. It is supposed that one hydrogen or oxygen atom is adsorbed on one metal atom. Polycrystalline electrodes are generally used in electrochemical investigations, so that most workers[16,37-40,45-47] start from the interatomic distance in determining the number of surface atoms. In the case of platinum this corresponds to 1.31×10^{15} atoms cm^{-2} true surface. Monolayers of hydrogen or oxygen on platinum then require consumptions respectively of 210 and 420 $\mu C\ cm^{-2}$. These values are used directly to calculate coverage by oxygen θ_H and θ_O. By no means in all cases is it possible to measure separately the quantities of electricity consumed in the adsorption of hydrogen and oxygen and in charging the double layer. If the regions in which these processes occur overlap (e.g. on nickel, silver, and carbonaceous materials), some numerical coefficient, determined by the charge

necessary to change the electrode potential in the given range, must be used in calculating the true surface area.

In the electrochemical determination of surface area it must be borne in mind that the character of the charging curve is influenced significantly by the composition of the electrolyte[11]. This is due to the simultaneous adsorption of hydrogen and oxygen and of components of the electrolyte on the electrode surface. During recent years these phenomena have been investigated in detail on smooth and finely divided platinum[48-51] and palladium[52,53] electrodes. Thus for a palladium electrode in the presence of various anions and cations coverage with hydrogen decreases in the sequences

$$H_2SO_4 > H_3PO_4 > HCl > HBr \qquad KOH > NaOH > CsOH > Ba(OH)_2 > Ca(OH)_2.$$

In determining the surface area of a catalytic electrode, therefore, it is desirable to obtain galvanostatic or potentiodynamic charging curves in a standard electrolyte, whose components do not undergo strong specific adsorption. Organic impurities in the solution influence substantially the character of adsorption and the quantity of hydrogen adsorbed[54]. Special methods of purifying solutions have been described[33,52,55-57], ensuring that experiments can be conducted under sufficiently uncontaminated conditions. This is especially important in the investigation of smooth electrodes.

2. Measurement of Differential Capacitance

Another method for determining true surface area involves measuring the differential capacitance of the double layer. The relaxation time of the double layer is considerably shorter than typical times of adsorption and exchange accompanied by complete or partial transfer of charge across the interface. We can measure the capacitance of the double layer by high-frequency a.c.[58,59] or pulse[59] methods with short resolving times ($\sim 10^{-6}$ s), and use the result to estimate true surface area. It is usually assumed in this method[60-65] that the capacitance of the double layer is the same on different metals, equal to the capacitance of the mercury electrode (16–20 μF cm^{-2}). However, recent accurate measurements indicate[66] that different metal electrodes may differ in capacitance by 50–100%. Relaxation methods for measuring the differential capacitance of the double layer are applicable only to smooth electrodes, which is an important restriction on their use for determining true surface area.

Isolated attempts were made[8] to determine the capacitance of the double layer by means of slow charging curves. However, these methods cannot be regarded as successful, since in most cases processes involving adsorption of electrochemically active species also occur in the "double layer" region. It was shown[67] by Frumkin's thermodynamic method[11] that oxygen already begins to be adsorbed on platinum at potentials more positive than 0.3 V.

Comparison of the two groups of electrochemical methods for determining true surface area—by obtaining charging curves and by measuring differential capacitance—indicates that the former are simpler, more generally applicable, and reliable. It therefore forms the basis of most electrochemical techniques for measuring true surface area. Recently the possibility has been discussed of determining this property from the rate of an electrode reaction with a known specific exchange current[68].

III. DETERMINATION OF TRUE SURFACE AREA OF VARIOUS MATERIALS

Specific methods for measuring true surface area of various metals are governed by the nature of the latter, the ability to adsorb hydrogen and oxygen. Specific surfaces of most metals that have been investigated electrochemically are determined from the adsorption of hydrogen. They include metals of the platinum group—platinum, palladium, rhodium, iridium, ruthenium, and osmium—together with nickel. With platinum and rhodium the potential range for the adsorption and desorption of hydrogen is quite clearly defined. With ruthenium and nickel the potential ranges for the adsorption of hydrogen and oxygen overlap. The adsorption of hydrogen on palladium (and to some extent also on nickel) is complicated by the dissolution of hydrogen in the bulk of the electrode. Hydrogen is hardly adsorbed at all on gold, copper, and silver, on which surface area is determined from the adsorption of oxygen or the polarisation capacitance in a certain potential range. The last method is used also to determine surface areas of carbonaceous materials.

1. Platinum Metals and Nickel

Platinum and rhodium

Galvanostatic charging curves have been used to investigate the surface coverage of finely divided platinum and rhodium powders by adsorbed hydrogen and oxygen[10,16]. The potentials at which adsorbed hydrogen is completely removed from the surfaces of these metals are respectively 0.40 and 0.27 V (in 1 *N* sulphuric acid). The quantity of hydrogen adsorbed was determined by the method of tangents. No correction was made for the capacitance of the double layer, so that values of θ_H were rather too high.

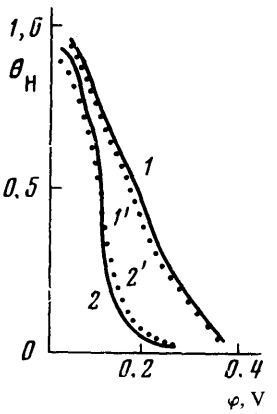


Figure 3. Potential dependence of surface coverage with hydrogen of: 1) platinum powder ($s = 20$ m^2 g^{-1}); 1') smooth platinum electrode; 2) rhodium powder (20 m^2 g^{-1}); 2') smooth rhodium electrode[16].

However, the contribution of this capacitance does not[51] exceed 5–7%, which is smaller than the error in the BET method. Knowing the true surface area of powders measured by the BET method, we can calculate values of θ_H on platinum and rhodium at various potentials.

Monolayers of hydrogen on platinum and rhodium surfaces correspond in electrical units to 210 and 220 $\mu C\,cm^{-2}$ respectively. Fig. 3 shows that surface coverage of both platinum and rhodium powders with hydrogen reaches a monolayer ($\theta_H \approx 1$) near the reversible hydrogen potential. Similar results have been obtained on a single crystal of platinum[70]. The surface area of platinum and rhodium is independent of the method of obtaining the powders or their degree of dispersion, so that the hydrogen region of the charging curve can be used to determine the true surface area of these powdered metals[16]. Galvanostatic charging curves on the powders were compared with $i-\varphi$ curves obtained by means of triangular voltage pulses on smooth electrodes. Good agreement was obtained for $\theta_H-\varphi$ curves on smooth and dispersed electrodes (Fig. 3). The technique can be used also to determine the true surface area of platinum–rhodium alloys[71].

The possibility has been considered[37-41] of measuring the true surface area of platinum from the adsorption of oxygen. Surface coverage was then determined as the ratio of the quantity of electricity consumed in the adsorption of oxygen to double the quantity corresponding to a monolayer of hydrogen: $\theta_O = Q_O/2Q_H$. However, diverse values have been published—1.76,[37] 1.83,[38] 1.05,[41] and 1.24 [40] V—for the potential at which $\theta_O \approx 1$. Such divergence is due to the non-equilibrium character of the adsorption of oxygen and to accumulation of the gas on the electrode surface with time.

Ruthenium

Comparison of the electrochemical determination of the true surface area of ruthenium black[72] with the BET method showed that the quantities of electricity consumed in adsorption of hydrogen near the reversible hydrogen potential are 280 and 218 $\mu C\,cm^{-2}$ in aqueous sulphuric and hydrochloric acids respectively. The former value corresponds to a monolayer. Determination of true surface area from the charge consumed in the double-layer region gave markedly overestimated values, owing to the presence of adsorbed oxygen on the ruthenium surface in this range.

Palladium

The possibility of determining the true surface area of palladium powders from the adsorption of hydrogen has been subjected to detailed investigation[16,52,53,73]. The complexity of such determination is due to the dissolution of hydrogen in the bulk of the metal. A typical charging curve obtained on powdered palladium in 1 *N* sulphuric acid is reproduced in Fig. 4. Over the range of potentials 0–0.08 V hydrogen dissolves with the formation of α and β phases. It is adsorbed at $0.08\,V < \varphi < 0.28$ V; some adsorption of hydrogen is observed also at $\varphi < 0.08$ V.[52] A technique was proposed[52,53] for separating the quantity of hydrogen adsorbed and desorbed in the potential range of chemisorption, and determining the surface coverage with chemisorbed hydrogen at each potential on the assumption that θ_H is independent of the degree of dispersion of the specimens. This assumption was confirmed for palladium powders of true surface area 0.3–100 $m^2\,g^{-1}$. Fig. 5 illustrates the dependence of surface coverage of palladium with hydrogen over the potential range 0–0.28 V in 1 *N* sulphuric acid (curve *1*). It follows from these results that the quantity of hydrogen chemisorbed at 0.075 V corresponds to $\theta_H = 0.82$, but at potentials close to zero $\theta \approx 1$. The calculations were based on the hypothesis that the quantity of electricity consumed in coverage with a monolayer of hydrogen was 210 $\mu C\,cm^{-2}$.

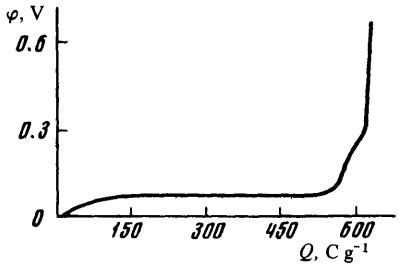


Figure 4. Charging curve on palladium powder ($30\,m^2\,g^{-1}$) over the range 0–0.7 V in [1 N] sulphuric acid at 25 °C.[73]

Investigation of the influence of anions (PO_4^{3-}, Cl^-, Br^-, and SO_4^{2-}) [52] and of cations (K^+, Na^+, Cs^+, Ca^{2+}, and Ba^{2+})[53] on the adsorption of hydrogen on palladium showed that the course of the charging curves in the region of the $\alpha-\beta$ phase transition is almost independent of solution composition, whereas the chemisorption of hydrogen is affected significantly by the nature of anion and cation. The surface coverage θ_H diminishes with increase in the adsorbability of the anions (Fig. 5). A similar pattern is observed with cations[53].

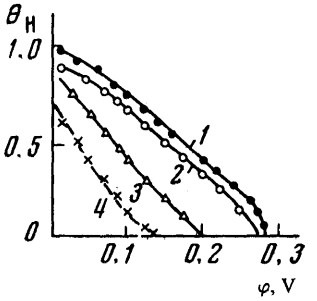


Figure 5. Potential dependence of surface coverage of palladium powder with hydrogen in 1 *N* acids: 1) sulphuric; 2) orthophosphoric; 3) hydrochloric; 4) hydrobromic.[52]

Thus the true surface area of palladium powders can be determined from the adsorption of hydrogen. The divergence between the results and values obtained by the BET method does not exceed 10%.[16]

The $\theta-\varphi$ curves calculated for smooth palladium electrodes from potentiodynamic $i-\varphi$ curves obtained with the potential applied at 20 mV s^{-1} were found[16] to coincide with $\theta-\varphi$ curves for finely divided powders. This indicates the possibility of using potentiodynamic curves to determine true surface areas of smooth palladium electrodes.

The total quantity of electricity representing the adsorption of hydrogen dissolved in and adsorbed on palladium in the range 0–0.3 V cannot be used to measure the surface area of palladium, as had been suggested[74], since the quantity of hydrogen dissolved is independent of the surface area. Thus this quantity is approximately the same for powders having surface areas of 39 and 3 m^2, whereas the quantity of hydrogen adsorbed differs more than tenfold[16].

The true surface area of smooth palladium has been determined[42] from the adsorption of oxygen under conditions such that in 1 *N* sulphuric acid a monolayer is formed at $\varphi \simeq 1.0$ V, in agreement with results obtained by other workers[52,53,73].

Nickel

The electrochemical behaviour of nickel near the potential of the reversible hydrogen electrode has been less well studied than that of the platinum metals. There is no generally accepted view on the mechanism of the adsorption and dissolution of hydrogen and the formation of oxide layers in this potential region[75–85]. The widespread use of nickel in electrocatalysis (liquid-phase hydrogenation, chemical current sources, etc.) has given rise to repeated attempts to develop electrochemical methods for determining its true surface area. These methods usually involved determining the capacitance of the double layer (using alternating current[86–88], from the fall in potential after polarisation had been switched off[89], and from charging curves[90]). The calculation was based on various values for the differential capacitance of the double layer (from 10 [91] to 100 μF cm^{-2}).[90] Therefore these procedures can hardly be recommended for determining the true surface area of nickel without adequate experimental support. A method based[92] on measurement of the adsorption of thallium and sodium ions is merely comparative.

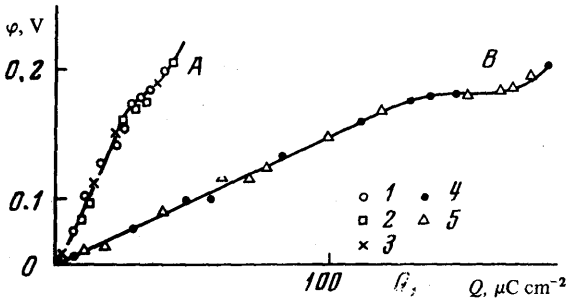


Figure 6. Charging curve per unit surface area (measured by the BET method) of nickel: A) Raney; B) carbonyl; 1) sintered electrode of A; 2) sintered electrode of a mixture of 50% A + 50% B; 3) powder in a grid of A; 4) powder in a grid of B; 5) sintered electrode of B.[81]

The most soundly based method for determining the true surface area of smooth and finely divided nickel was developed by workers who showed[81–85] that hydrogen does not undergo bulk dissolution in nickel at $\varphi \geq 0.03$ V. A similar conclusion was reached by another worker[79].

Surface areas (measured by the chemisorption of oxygen from the gas phase) of various nickel powders were compared[81–83] with the slopes of the linear portion of the equilibrium galvanostatic charging curve (Fig. 6) over the range 0.03–0.17 V. The pseudocapacitance calculated per unit true surface area was 1120 μF cm^{-2}. Such a value was explained by the occurrence of electrochemical processes involving adsorbed layers of neutral species.

$$H_{ads} + OH^- \rightarrow H_2O + \bar{e},$$

$$Ni + x\,OH^- \rightarrow Ni(OH)_2 + x\,\bar{e}.$$

Determination by a vacuum–electrochemical method of the surface coverage of nickel with hydrogen and with oxygen showed that $\theta_H > 0.95$ and that $\theta_{OH} < 0.5$ and 0.2 at $\varphi \simeq 0$ and 0.17 V respectively. These results make it possible to determine the true surface area of finely divided nickel in this potential range.

If it is assumed that the nature of the adsorbed species is the same on smooth and powdered specimens, the results can be used to investigate smooth electrodes[83,85]. Potentiodynamic i–φ curves are then obtained in alkaline solution over the range 0.03–0.18 V, and the quantities of electricity at different rates V of application of the potential are extrapolated to $V = 0$. The result is compared with the value 1120 μF cm^{-2}. The electrode must be subjected to a special (stepwise) treatment at 0.2, 0.1, and 0 V in order to obtain reproducible results[83]: otherwise a different value may be obtained for the pseudocapacitance per unit surface area of the nickel powder[80].

The electrochemical method for determining the true surface areas of platinum metals and nickel has found practical application in investigating electrocatalytic processes on porous gas-diffusion and liquid electrodes. It has been used to determine the surface area of the catalyst in porous electrodes[93] during preparation and operation[41,94,95], in measuring the distribution of liquid and gas porosity[94], for determining the surface area of platinum metals on a carrier[96], and also in calculating the kinetic parameters of electrochemical reactions[93].

2. Metals of the Copper Subgroup

Hydrogen is not readily adsorbed on copper, silver, and gold, in contrast to metals of the platinum group, so that surface coverage with hydrogen cannot be used to determine the true surface areas. Therefore either the potential range corresponding to the adsorption of oxygen is used (copper and gold), or else some segment of the charging or potentiodynamic i–φ curves on which the polarisation capacitance has been determined in preliminary experiments (silver).

Gold

An electrochemical method has been developed[16,29] for determining the true surface area of finely divided and smooth gold from the adsorption of oxygen. The surface coverage in acid solutions was calculated from charging curves or from potentiodynamic curves over the range 1.3–1.7 V. On the assumption that one oxygen atom is adsorbed on one metal atom the coverage of finely divided gold reaches a monolayer at 1.7 V. The adsorption of oxygen obeys similar laws on smooth and finely divided gold: the specific adsorption is the same on such electrodes. Good agreement is found between surface areas obtained from charging curves and by the BET method.

Copper

The quantity of surface oxide Cu_2O forming a monolayer in a given potential range is determined[97]. Conditions required[97] indicate that surface area is most conveniently measured in alkaline solutions. The quantity of electricity corresponding to a monolayer of copper(I) oxide is 180 $\mu C\ cm^{-2}$.[98] The quantity of oxide is calculated from the arrest on the charging curve in the range 0.87–0.47 V. It can be found also by obtaining potentiodynamic curves with the potential applied at 2–10 mV s^{-1}. This method has been used to determine the true surface area of copper coatings having a roughness factor of 2–10. It has found application in studies of the corrosion of copper[99].

Silver

Determination of true surface area from the adsorption of oxygen on silver, in contrast to gold and copper, is difficult because of the formation of multilayer deposits. The adsorption of oxygen on silver powders in the range 0.25–0.8 V gives in several cases[100] good agreement with BET results. The roughness factor of smooth silver electrodes has been estimated [101,102] from the quantity of electricity determined from i–φ curves obtained by the application of triangular voltage pulses over the potential range 0–0.2 V, in which it was assumed [101,102] that the quantity of electricity was consumed only in charging the double layer of the silver electrode.

A more rapid method proposed[31] for determining the surface area of silver powders involves applying the triangular pulse to the electrode after cathodic reduction of the latter at negative potentials, with i–φ curves obtained in the range 0.2–0 V applied at the rate 3–40 mV s^{-1}. As before [101,102] this potential range is regarded[31] as corresponding to charging of the double layer. It was assumed for the calculation that the true capacitance of silver in this potential range is 50 $\mu F\ cm^{-2}$. The results agree well with those obtained by the BET method.

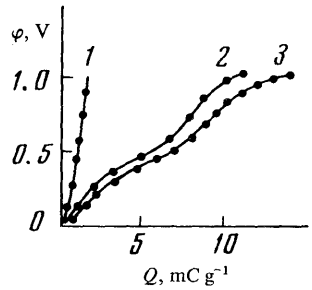


Figure 7. Charging curves on silver powders differing in specific surface ($m^2\ g^{-1}$): 1) 2.5; 2) 3.0; 3) 10.[100]

The true surface areas of silver powders prepared in various ways were measured[100] by the BET method and compared with electrochemical measurements by means of slow charging curves in 0.1 N aqueous potassium hydroxide. Charging curves on silver powders are plotted for various specific surfaces in Fig. 7. Comparison of BET surface areas with the quantity of electricity consumed in the range 0–0.25 V showed that for almost all the silver powders $Q/s_{BET} = 0.02 \pm 0.003$ mC cm^{-2}. Hence the true surface area of silver can be determined from the polarisation capacitance in the potential range 0–0.25 V.

3. Carbonaceous Materials

Measurement of the specific surface of carbonaceous materials is one of the most important and difficult tasks. Development of an electrochemical method is impeded by the existence of such materials in various modifications (coal, carbon black, graphite, pyrographite, vitreous carbon), whose electrochemical properties depend in considerable degree on their structure and the method of measurement. Appreciable difficulties may result also from the presence of micropores, of dimensions comparable with the radii of hydrated ions, in several carbonaceous materials (e.g. in activated carbon). This would lead to a change in the capacitance of the double layer.

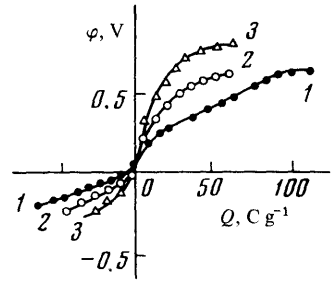


Figure 8. Charging curves obtained in 0.01 N sulphuric acid on: 1) activated carbon (surface area 710 $m^2\ g^{-1}$); 2) carbon black (760); 3) graphite (670).[107]

The adsorption of oxygen and hydrogen on various carbonaceous materials has been investigated in electrolyte solutions [103–108]. Fig. 8 shows typical charging curves on activated sugar charcoal, PM-100 carbon black, and graphite in 0.01 N sulphuric acid[107]. The capacitance is minimal in the potential range 0.05–0.25 V. This segment of the charging curve corresponds to the capacitance of the double layer. Values of the capacitance for coal, carbon black, and graphite are 7.0, 4.5, and 2.5 $\mu F\ cm^{-2}$ true surface area. Hydrogen is adsorbed at potentials more negative than those corresponding to the double-layer region, and oxygen at more positive potentials. Results obtained for coal and carbon blacks having different surfaces in 0.1 N sulphuric acid indicate that the "oxygen" portion of the charging curve can be used to determine the true surface areas of these adsorbents. With coal the mean polarisation capacitance is $28 \pm 2\ \mu F\ cm^{-2}$ for surface areas of 450 and 710 $m^2\ g^{-1}$, which corresponds to an accuracy of 10%; but with carbon black the mean value is $13 \pm 2\ \mu F\ cm^{-2}$ over the range 160–760 $m^2\ g^{-1}$, corresponding to an accuracy of 15%. For KhS-72 carbon black and AG-3 carbon the polarisation capacitance in the same potential range was respectively 15 and 19 $\mu F\ cm^{-2}$.[108] Deviations from the results of

Ref. 107 may be due to technical differences in the production of the carbonaceous materials.

An attempt was made[106] to use a.c. polarisation to measure the surface area of porous carbonaceous materials (coal and graphite of various brands), which reduces to determining the capacitance of the double layer. As noted above, however, the specific capacitance of the double layer depends on the nature of the carbonaceous material[107]. Hence the capacitance values used to calculate specific surface area from electrochemical data require special experimental justification.

oOo

The electrochemical method for determining true surface area is now sufficiently developed for platinum metals, the copper subgroup, nickel, and certain types of carbonaceous materials. It has been successfully used to study several electrolytic processes at electrodes of these materials. The number of research topics to which the electrochemical determination of surface area is applicable will increase as investigation of the structure of the double layer and of adsorption from electrolyte solutions on other metals and alloys is extended. Another important line of development of the electrochemical method is to measure the surface area of metallic or semiconducting catalysts on carriers, of platinum on carbon, oxides on carbon, and nickel and silver powders stabilised by oxides.

REFERENCES

1. S. Brunauer, "The Adsorption of Gases and Vapours" (Princetown University Press) (Translated into Russian), 1948.
2. S. J. Gregg and K. S. W. Sing, "Adsorption, Specific Surface, and Porosity" (Translated into Russian), Mir, Moscow, 1970.
3. R. Anderson (Editor), "Experimental Methods for the Investigation of Catalysis" (Translated into Russian), Mir, Moscow, 1972, p. 48.
4. M. M. Dubinin, Izv. Akad. Nauk SSSR, Ser. Khim., 996 (1974).
5. D. V. Sokol'skii and A. M. Sokol'skaya, "Metally—Katalizatory Gidrogenizatsii" (Metals—Hydrogenation Catalysts), Nauka, Alma-Ata, 1970.
6. D. V. Sokol'skii and G. D. Zakumbaeva, "Adsorbtsiya i Kataliz na Metallakh VIII Gruppy v Rastvorakh" (Adsorption and Catalysis on Group VIII Metals in Solution), Nauka, Alma-Ata, 1973.
7. F. P. Bowden and E. K. Rideal, Proc. Roy. Soc. A, 120, 59, 90 (1928).
8. A. Shlygin and A. N. Frumkin, Acta Physicochim. URSS, 4, 911 (1936).
9. D. V. Sokol'skii, "Gidrirovanie v Rastvorakh" (Hydrogenation in Solution), Izd. Akad. Nauk Kazakh. SSR, Alma-Ata, 1962.
10. A. M. Sokol'skaya, "Rodii—Katalizator Gidrogenizatsii" (Rhodium—Hydrogenation Catalyst), Nauka, Alma-Ata, 1974.
11. A. N. Frumkin, in "Advances in Electrochemistry and Electrochemical Engineering", edited by P. Delahay, Interscience, New York, 1963, Vol. 3, p. 287.
12. A. N. Frumkin, Elektrokhimiya, 2, 387 (1966).
13. O. A. Petrii, Uspekhi Khim., 44, 2048 (1975) [Russ. Chem. Rev., No. 11 (1975)].
14. A. N. Frumkin and A. I. Shlygin, Izv. Akad. Nauk SSSR, Ser. Khim., 773 (1936).
15. A. N. Frumkin and A. I. Shlygin, Dokl. Akad. Nauk SSSR, 2, 173 (1934).
16. R. Kh. Burshtein, M. R. Tarasevich, V. S. Vilinskaya, and K. A. Radyushkina, "Kataliticheskie Reaktsii v Zhidkoi Faze (Trudy II Vsesoyuznoi Konferentsii)" (Catalytic Reactions in the Liquid Phase—Proceedings of the Second All-Union Conference), Nauka, Alma-Ata, 1967, p. 315.
17. Yu. A. Podvyazkin and A. I. Shlygin, Zhur. Fiz. Khim., 31, 1305 (1957).
18. G. A. Deborin and B. V. Ershler, Zhur. Fiz. Khim., 14, 708 (1940).
19. J. A. V. Butler and G. Armstrong, Proc. Roy. Soc., A, 137, 604 (1932).
20. O. A. Petrii, R. V. Marvet, and Zh. N. Malysheva, Elektrokhimiya, 3, 962 (1967).
21. F. G. Will and C. A. Knorr, Z. Elektrochem., 64, 258, 270 (1960).
22. Ya. M. Kolotyrkin and A. N. Chemodanov, Dokl. Akad. Nauk SSSR, 134, 128 (1960).
23. V. N. Alekseev, L. L. Knots, M. R. Tarasevich, and N. A. Shumilova, Zhur. Fiz. Khim., 38, 1048 (1964) [Russ. J. Phys. Chem., No. 4 (1964)].
24. V. S. Vilinskaya, B. I. Lentsner, L. L. Knots, and M. R. Tarasevich, Elektrokhimiya, 7, 1763 (1971).
25. M. R. Tarasevich, F. Z. Sabirov, B. I. Lentsner, and L. L. Knots, Elektrokhimiya, 7, 586 (1971).
26. N. A. Shumilova, G. V. Zhutaeva, M. R. Tarasevich, and R. Kh. Burshtein, Zhur. Fiz. Khim., 39, 1012 (1965) [Russ. J. Phys. Chem., No. 4 (1965)].
27. E. I. Khrushcheva, N. A. Shumilova, and M. R. Tarasevich, Elektrokhimiya, 2, 277 (1966).
28. A. N. Frumkin, E. I. Khrushcheva, M. R. Tarasevich, and N. A. Shumilova, Elektrokhimiya, 1, 17 (1965).
29. A. A. Michri, A. G. Pshenichnikov, and R. Kh. Burshtein, Elektrokhimiya, 8, 364 (1972).
30. D. A. J. Rand and R. Woods, J. Electroanalyt. Chem., 31, 29 (1971).
31. V. S. Bagotskii, G. V. Zhutaeva, L. S. Kanevskii, G. V. Boikova, and N. A. Shumilova, Kinetika i Kataliz, 16, 264 (1975).
32. O. A. Petrii and I. G. Shchigorev, Elektrokhimiya, 4, 370 (1968).
33. S. D. James, J. Electrochem. Soc., 114, 1113 (1967).
34. S. Gilman, J. Electroanalyt. Chem., 7, 382 (1964).
35. S. Gilman, J. Phys. Chem., 71, 4339 (1967).
36. R. Woods, J. Electroanalyt. Chem., 49, 217 (1974).
37. S. Schuldiner and R. M. Roe, J. Electrochem. Soc., 110, 332 (1963).
38. S. Trasatti, Electrochim. Metal, 2, 12 (1967).
39. R. Thacher and J. P. Hoare, J. Electroanalyt. Chem., 30, 1 (1971).
40. J. S. Mayerll and S. H. Langer, J. Electrochem. Soc., 111, 438 (1964).
41. J. Giner, J. M. Parry, S. Smith, and M. Turchan, J. Electrochem. Soc., 116, 1692 (1969).
42. S. H. Cadle, J. Electrochem. Soc., 14, 645 (1974) [sic.].
43. M. R. Tarasevich, V. A. Bogdanovskaya, and V. S. Vilinskaya, Elektrokhimiya, 8, 89 (1972).
44. G. M. Alipova, E. I. Khrushcheva, G. P. Samoilov, N. A. Shumilova, and E. I. Zimakov, Elektrokhimiya, 8, 1537 (1972).
45. S. B. Brummer, J. Phys. Chem., 69, 562 (1965).
46. M. W. Breiter and S. Gilman, J. Electrochem. Soc., 109, 622 (1962).
47. T. Beigler, D. A. J. Rand, and R. Woods, J. Electroanalyt. Chem., 29, 269 (1971).
48. V. Ya. Veber, Dzh. Pirtskhalava, Yu. B. Vasil'ev, and V. S. Bagotskii, Elektrokhimiya, 5, 1037 (1969).

49. Dzh. Pirtskhalava, Yu. B. Vasil'ev, and V.S.Bagotskii, Elektrokhimiya, 6, 110 (1970).
50. N. A. Balashova, Elektrokhimiya, 3, 750 (1967).
51. V. E. Kazarinov and N. A. Balashova, Coll. Czech. Chem. Comm., 30, 4184 (1965).
52. V. S. Vilinskaya, R. Kh. Burshtein, and M. R. Tarasevich, Elektrokhimiya, 6, 1497 (1970).
53. R. Kh. Burshtein, V. S. Vilinskaya, and M. R. Tarasevich, Elektrokhimiya, 6, 1861 (1970).
54. O. A. Petrii, B. I. Podlovchenko, A. N. Frumkin, and Hira Lal, J. Electroanalyt. Chem., 10, 253 (1965).
55. M. L. Kronenberg, J. Electroanalyt. Chem., 12, 122 (1966).
56. A. Damjanovic, A. Dey, and J. O'M. Bockris, Electrochim. Acta, 11, 791 (1966).
57. N. P. Berezina and N. V. Nikolaeva-Fedorovich, Elektrokhimiya, 3, 3 (1967).
58. B. B. Damaskin, "Printsipy Sovremennykh Metodov Izucheniya Elektrokhimicheskikh Reaktsii" (Principles of Modern Methods for the Study of Electrochemical Reactions), Izd. Moskov. Gos. Univ., Moscow, 1965, p. 61.
59. B. B. Damaskin, O. A. Petrii, and V. V. Batrakov, "Adsorbtsiya Organicheskikh Soedinenii na Elektrodakh" (Adsorption of Organic Compounds on Electrodes), Nauka, Moscow, 1968, p. 12.
60. H. Dahms and J. O'M. Bockris, J. Electrochem. Soc., 111, 728 (1964).
61. E. Gilleadi, B. T. Rubin, and J. O'M. Bockris, J. Phys. Chem., 69, 3335 (1965).
62. J. P. Hoare, Nature, 204, 71 (1964).
63. J. N. Sarmousakis and M. J. Prager, J. Electrochem. Soc., 104, 454 (1957).
64. P. V. Popat and N. Hacherman, J. Phys. Chem., 62, 1198 (1958).
65. M. H. Gottlieb, J. Electrochem. Soc., 111, 465 (1964).
66. D. I. Leikis, K. V. Rybalka, and E. S. Sevast'yanov, in "Adsorbtsiya i Dvoinoi Elektricheskii Sloi v Elektrokhimii" (Adsorption and the Electrical Double Layer in Electrochemistry), Nauka, Moscow, 1972, p. 5.
67. R. V. Marvet and O. A. Petrii, Elektrokhimiya, 3, 901 (1967).
68. M. Prazak and B. Eremias, Corrosion Sci., 12, 463 (1972).
69. M. R. Tarasevich, K. A. Radyushkina, and R. Kh. Burshtein, Elektrokhimiya, 3, 455 (1967).
70. A. T. Hubbard, R. M. Ishikawa, and J. Katekaru, J. Electroanalyt. Chem., 86, 271 (1978).
71. K. A. Radyushkina and M. R. Tarasevich, Elektrokhimiya, 6, 1703 (1970).
72. T. N. Stoyanovskaya, G. P. Khomchenko, A. I. Pletyushkina, and G. D. Vovchenko, Vestnik Moskov. Univ., Ser. Khim., No. 6, 50 (1963).
73. R. Kh. Burshtein, M. R. Tarasevich, and V. S. Vilinskaya, Elektrokhimiya, 3, 349 (1967).
74. G. A. Bogdanovskii, G. P. Khomchenko, and G. D. Vovchenko, Zhur. Fiz. Khim., 39, 1408 (1965).
75. L. Tokhver, Yu. Tamm, and V. E. Past, Uch. Zap. Tartusk. Univ., Trudy Khim., No. 289, 3 (1971).
76. J. L. Weininger and M. W. Breiter, J. Electrochem. Soc., 111, 707 (1964).
77. V. R. Loodmaa, M. E. Khaga, and V. E. Past, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 9, 794 (1966).
78. G. P. Samoilov, E. I. Khrushcheva, N. A. Shumilova, and V. S. Bagotskii, Elektrokhimiya, 8, 1169 (1972).
79. H. H. Ewe, Electrochim. Acta, 17, 2267 (1972).
80. H. H. Ewe, E. W. Yusti, and K. Stephan, Energy Conversion, 13, 109 (1973).
81. R. Kh. Burshtein, A. G. Pshenichnikov, V. D. Kovalevskaya, and M. E. Belyaeva, Elektrokhimiya, 6, 1756 (1970).
82. R. Kh. Burshtein, V. D. Kovalevskaya, and A. G. Pshenichnikov, Elektrokhimiya, 8, 1388 (1972).
83. A. G. Pshenichnikov, R. Kh. Burshtein, V. D. Kovalevskaya, and L. A. Burkal'tseva, "Kataliticheskie Reaktsii v Zhidkoi Faze (Trudy III Vsesoyuznoi Konferentsii)" (Catalytic Reactions in the Liquid Phase—Proceedings of the Third All-Union Conference), Nauka, Alma-Ata, 1974, Part 2, p. 441.
84. A. G. Pshenichnikov and L. A. Burkal'tseva, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh, Materialy Simpoziuma" (The Double Layer and Adsorption on Solid Electrodes—Proceedings of a Symposium), Tartu, 1975, p. 261.
85. L. A. Burkal'tseva and A. G. Pshenichnikov, Elektrokhimiya, 12, 42 (1976).
86. R. J. Brodd and N. Hackerman, J. Electrochem. Soc., 104, 704 (1957).
87. G. N. Trusov, V. M. Novakovskii, and M. F. Fadeeva, "Dvoinoi Sloi i Adsorbtsiya na Tverdykh Elektrodakh, Materialy Simpoziuma" (The Double Layer and Adsorption on Solid Electrodes—Proceedings of a Symposium), Tartu, 1970, p. 368.
88. O. Rüsoën, Acta Chem. Scand., 18, 1961 (1964).
89. L. Tokhver, Yu. Tamm, and V. Past, Uch. Zap. Tartusk. Univ., Trudy Khim., No. 302, 3 (1972).
90. S. E. S. El Wakkad and Sayeda H. Emara, J. Chem. Soc., 3504 (1953).
91. D. Berndt, Electrochim. Acta, 10, 1067 (1965).
92. S. A. Lilin and N. A. Balashova, Izv. Vys. Ucheb. Zaved., Khim. i Khim. Tekhnol., 16, 1395 (1973).
93. O. S. Abramzon, S. F. Chernyshov, and A. G. Pshenichnikov, Elektrokhimiya, 11, 1307 (1975).
94. R. Kh. Burshtein, A. V. Dribinskii, Yu. I. Kryukov, A. G. Pshenichnikov, and M. R. Tarasevich, Elektrokhimiya, 6, 1356 (1970).
95. N. M. Kagan, G. F. Muchnik, Yu. N. Pisarev, Ya. A. Kaller, and V. A. Panchenko, Elektrokhimiya, 9, 1498 (1973).
96. N. A. Urisson, L. N. Mokrousov, G. V. Shteinberg, Z. I. Kudryavtseva, I. I. Astakhov, and V. S. Bagotskii, Kinetika i Kataliz, 15, 1009 (1974).
97. A. Vashkyalis and D. Kimtene, Elektrokhimiya, 10, 834 (1974).
98. T. Heumann and In. Hyung Monn, Surface Sci., 24, 370 (1971).
99. L. M. Blanco, G. Cabrera, C. Lariot, and M. R. Tarasevich, Memoruia 10 Aniversario del CENIC 5 Seminario Cientifico, Editorial ORBE, Havana, 1975, p. 785.
100. R. Kh. Burshtein, M. R. Tarasevich, E. A. Ponomarenko, and V. V. Karonik, Elektrokhimiya, 7, 1295 (1971).
101. G. V. Zhutaeva and N. A. Shumilova, Elektrokhimiya, 4, 99 (1968).
102. G. V. Zhutaeva, L. L. Knots, B. I. Lentsner, N. D. Merkulova, and N. A. Shumilova, Elektrokhimiya, 4, 482 (1968).

103. E. M. Kuchinskii, R. Kh. Burshtein, and A.N.Frumkin, Acta Physicochim. URSS., 12, 795 (1940).
104. E. A. Ponomarenko, A. N. Frumkin, and R. Kh. Burshtein, Izv. Akad. Nauk SSSR, Ser. Khim., 1549 (1963).
105. J. F. Connolly, R. J. Frannery, and G. Aronowitz, J. Electrochem. Soc., 113, 577 (1966).
106. A. A. Yankovskii, T. D. Bessalova, and I. A. Kedrinskii, Elektrokhimiya, 4, 1483 (1968).
107. R. Kh. Burshtein, V. S. Vilinskaya, N. M. Zagudaeva, and M. R. Tarasevich, Elektrokhimiya, 10, 1094 (1974).
108. L. N. Mokrousov, N. A. Urisson, and G. V. Shteinberg, Elektrokhimiya, 9, 683 (1973).

Institute of Electrochemistry,
USSR Academy of Sciences,
Moscow