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REAL SURFACE AREA MEASUREMENTS IN ELECTROCHEMISTRY

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Real surface area measurements in electrochemistry

Abstract - Electrode reaction rates and most double layer parameters are extensive quantities and have to be referred to the unit area of the interface. Knowledge of the *real* surface area of electrodes is therefore needed. Comparison of experimental data with theories or of experimental results for different materials and/or from different laboratories to each other is physically groundless without normalization to unit *real* area of the electrode surface. Different methods have been proposed to normalize experimental data specifically with solid electrodes. Some of them are not sufficiently justified from a physical point of view. A few of them are definitely questionable. The purpose of this document is to scrutinize the basis on which the various methods and approaches rest, in order to assess their relevance to the specific electrochemical situation and, as far as possible, their absolute reliability. Methods and approaches are applicable to (a) liquid electrodes, (b) polycrystalline and single crystal face solids, (c) supported, compressed and disperse powders. The applicability of the various techniques to each specific case is to be verified. After an introductory discussion of the "concept" of real surface area, fifteen methods, eleven applied *in situ* and four *ex situ*, are scrutinized. For each of them, after a description of the principles on which it is based, limitations are discussed and recommendations are given.

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1. INTRODUCTION

1.1 Generalities

The surface area which can be determined with ordinary tools designed to measure a length is the *geometric* surface area, A_g . It is defined (ref. 1) as the projection of the real surface on a plane parallel to the macroscopic,

visible phase boundary*. Thus, A_R is calculated on the basis of known geometric dimensions of the object constituting the electrode, whose resolution is normally that of macroscopic measurements. Only for liquids does the real surface coincide *in principle* with the geometric surface. In the case of solids, asperities are normally present whose height may be orders of magnitude greater than the atomic or molecular size, though lower than the visible resolution. In this case the real surface area is higher than A_R and experimental data must be *normalized* to the real surface to become universally comparable.

Electrode reaction rates and most double layer parameters are extensive quantities and have to be referred to the unit area of the interface. Knowledge of the *real* surface area of electrodes is therefore needed. Comparison of experimental data with theories or of experimental results for different materials and/or from different laboratories to each other is physically groundless without normalization to unit *real* area of the electrode surface.

While the surface area, A , is normally expressed as a squared length (SI Units: m^2), it is often expedient to report specific values referred either to unit mass ($A_m/m^2 \text{ g}^{-1}$), or to unit volume ($A_v/m^3 \text{ m}^{-3} \equiv \text{m}^{-1}$); they are related by the following equation:

$$A_v = A/V = A\rho/m = A_m\rho \quad (1)$$

where ρ is the mass density, m the mass and V the volume of the system. Note that the (real) surface area per unit geometric surface area is called the *roughness factor*, $f_r = A/A_R$ (cf ref. 1)

Different methods have been proposed to normalize experimental data specifically with solid electrodes. Some of them are not sufficiently justified from a physical point of view. A few of them are definitely questionable.

The purpose of this document is to scrutinize the basis on which the various methods and approaches rest, in order to assess their relevance to the specific electrochemical situation and, as far as possible, their absolute reliability. Methods and approaches are applicable to (a) liquid electrodes, (b) polycrystalline and single crystal face solids, (c) supported, compressed and disperse powders. The applicability of the various techniques to each specific case is to be verified.

This document is related to previous IUPAC publications, such as the Manual of Symbols and Terminology (ref. 2), its Appendix II (ref. 3), Appendix III (ref. 4), and the papers on adsorption from solution (ref. 5) and on interphases between conducting phases (ref. 1). The final list of references given is not intended to be exhaustive; only a few illustrative and exemplificative papers have been chosen for quotation.

1.2 General concepts

The meaning of real surface area depends on the method of measurement of A , on the theory of this method, and on the conditions of application of the method. Thus, for a given system, various "real surface areas" can in principle be defined, depending on the characteristic dimension of the probe used. This is so even if phenomena of surface reconstruction, relaxation and faceting, which often occur during adsorption or electrochemical measurements, should not be taken into account. The most appropriate is the one estimated using a method which best approaches the experimental situation to which the area determined is to be applied.

Besides the concept of real surface area, other aspects should be taken into consideration when dealing with solid electrodes: (a) surface topography (macro- and microroughness); (b) homogeneity/heterogeneity of the surface; (c) dispersion of the active material, including (d) distribution law of the dispersed active material. These aspects are closely interrelated and are to be thoroughly considered in order to achieve a correct comprehension of the meaning of normalization of data to the unit *real* area of the electrode surface.

* Note that if the surface includes a macroscopic vertical step between two planar regions, also the phase boundary has a step whose area is thus obviously counted in the calculation of A_R . If the step is microscopic, it turns out not to be included into the geometric surface.

Surface heterogeneity and surface roughness are crucial aspects of solid surfaces. The difference between the two concepts lies in the fact that periodicity is not required for surface heterogeneity while for surface roughness it becomes a determining condition. Such irregularities which should not be considered as roughness due to their non-periodic character may be important in the definition of surface quality. The concept of roughness is well illustrated by the above distinction between real and geometric surface area. A surface is ideally homogeneous as its properties do not depend on the position on the surface at the atomic size resolution. The surface of liquids simulates homogeneity at the best since the local properties are smoothed by thermal fluctuations. For solids, ideally ordered single crystal faces may be representative of homogeneous surfaces.

A surface is heterogeneous as its properties depend on the position. The simplest example of a heterogeneous surface is a single crystal face with randomly distributed point defects. The commonest example is a polycrystalline surface where the periodicity of distribution of atoms differs from place to place. In both cases the surface, though heterogeneous, may be ideally smooth. However, pits on a single crystal face entail both heterogeneity and roughness. Consistently, a rough surface may in principle be homogeneous. However, a rough single crystal face implies also surface heterogeneity.

In very general terms, surface roughness may be treated in certain cases using the theory of fractal geometry (ref. 6). Recent developments in the understanding of the *fractal nature* of (especially) surface roughness and of its consequences for all extensive interfacial quantities, complicate the phenomenological approach adopted in the previous paragraphs. For instance, the dimension of a "surface area" is no longer the square of length in the theory of fractals. Also "bulk properties" such as electrical conductivity are no longer merely bulk but they become (partly) interfacial. Since this document is devoted to the experimental determination of the surface area and not to its mathematical description, the customary phenomenological approach to the problem will be followed in the various sections.

Polycrystalline solid materials consist of an ensemble of randomly oriented *crystallites*, which are the smallest units of single crystals. In the case of a disperse material, two or more crystallites may aggregate through grain boundaries to form *particles*. These are characterized by their dimension (size), shape and size distribution function. Patchwise models simulate heterogeneous surfaces as a collection of homogeneous patches. Heterogeneity is thus expressed in terms of a spatial distribution function.

The particle (crystallite) size is normally given in terms of a length, d , whose geometric significance depends on the particle shape. However, d is customarily referred to as the *particle (crystallite) diameter*. For a given material, the experimental value of d is always an average over the number of particles examined.

Various kinds of d may be defined (ref. 7). For crystallites of diameter d_i and number n_i , the *number average diameter* for a given particle size distribution is given by:

$$d = \Sigma n_i d_i / \Sigma n_i \quad (2)$$

the *surface average diameter* by:

$$d_s = \Sigma n_i d_i^3 / \Sigma n_i d_i^2 \quad (3)$$

and the *volume average diameter* by:

$$d_v = \Sigma n_i d_i^4 / \Sigma n_i d_i^3 \quad (4)$$

Which of the three diameters above are experimentally obtained depends on the technique and the procedure used for the determination.

Other examples illustrating the above aspects are: (a) mechanically treated polycrystalline solid electrodes, always involving a disturbed surface layer whose atomic arrangement differs from the equilibrium one in the bulk; (b) dispersed electrode materials usually involving an unknown size distribution of particles whose shape and crystallographic orientation may depend on the nature of the material, and whose surface structure may include different defects depending on the kind of preparation procedure.

The above paragraphs, while not exhausting the problem, are illustrative of the fact that the simple concept of "real surface area" may be misleading if not related to the numerous other parameters which depend on the surface structure and determines the reactivity of an electrode surface.

2. IN SITU METHODS

2.1 Drop weight (or volume)

This method is that classically used with liquid metal electrodes (refs. 8-11) such as Hg, Ga, amalgams, and gallium liquid alloys (In-Ga, Tl-Ga, etc.). Electrodes may be static (hanging or sessile drop) or dynamic (falling drop). In general terms, the area of such drop electrodes can be calculated as the surface of rotation on the basis of diameters of sections which belong to different fixed levels on the drop drawing. More specific approaches are described below.

2.1.1 Principles. For dropping electrodes, the rate of flow (m) of the liquid metal down a glass capillary is measured by weighing the mass of metal dropped in a given period of time. The area A of the extruded drop at a selected time t of the drop life is calculated, assuming spherical shape, from the equation (refs. 9,12,13):

$$A = 4\pi(3mt/4\pi\rho)^{2/3} \quad (1.1)$$

where ρ is the density of the dropping liquid. With m in g s^{-1} , t in s and ρ in g cm^{-3} the resulting surface area is in cm^2 .

2.1.2 Limitations. Equation (1.1) is strictly valid only for the area of a single drop at the end of the drop life. It may be valid at a different moment of the drop life only if it is allowed to assume that the flow rate is not significantly depending on time. However, the assumption of constant flow rate is rendered invalid by the effect of the back pressure (refs. 12-16) given by $2\gamma/r$ where γ is the surface tension of the liquid metal and r the drop radius. Thus, the action of the back pressure is maximum at the moment of drop detachment. Consequently, the flow rate increases during the growth of a drop. The back pressure is seen to decrease with drop size and drop life. Its relative effect becomes smaller with increasing height of the liquid metal head (pressure) over the capillary. The quantity m , measured as indicated above, will be the average of the time-dependent flow rate, $m(t)$, over the whole drop life, τ , i.e. $m = (1/\tau)\int_0^\tau m(t)dt$. At $T = \tau$ the area is correctly calculated by eqn.(1.1), but at $t < \tau$ the real area will be smaller than the calculated one. Since γ is potential dependent, the back pressure effect is also expected to depend on potential, being greatest at the potential of zero charge (ref. 3). On the other hand, there is a compensating effect caused by the inertia of the Hg stream downwards the capillary.

These problems do not occur if the weight of the drop is measured at exactly the time where the electrochemical quantity is recorded, for instance, at mechanically knocked-off electrodes and at the hanging-drop electrode.

The condition of perfect sphericity of the drop is not met toward the end of the drop life especially with capillaries of relatively large bore. Under similar circumstances the drop will become pear-shaped (refs. 11,12,17).

Part of the surface of the (assumed) sphere is actually excluded at the place where the drop connects with the column in the capillary. Under similar circumstances, the drop can be treated as a "truncated" sphere (refs. 18,19). The excluded area is approximately equal to πr_c^2 , where r_c is the radius of the capillary at the orifice (refs. 12,20).

An experimental approach to the determination of the excluded area resting on the assumption of constant flow rate with drop life is the following. Under similar circumstances it is possible to write:

$$\tau C_1 / (A_1 - A_x) = \tau C_2 / (A_2 - A_x) = \dots = \tau C_n / (A_n - A_x) = \text{const}(E) \quad (1.2)$$

where $\tau C_1, \tau C_2, \dots, \tau C_n$ are the total capacitances (i.e. not referred to unit surface area) measured at some times t_1, t_2, \dots, t_n of the drop life. A_1, A_2, \dots, A_n are the surface areas determined at the various times by means of eqn.(1.1) and A_x is the excluded area. By solving eqn.(1.1), an average value $\langle A_x \rangle$ can

thus be estimated. Strictly, it should result to be a function of potential (cf above). The order of magnitude of A_x is about 1% of the drop surface area.

Other complications which have to be mentioned are shielding effects and solution creeping. If the glass of the capillary shields a part of the drop surface, a non-linear relationship may result between, eg capacitance or current, and the surface area derived from the drop weight. On the other hand, solution may creep into the capillary causing an opposite effect. The occurrence of solution creeping is usually shown by the erratic formation of drops.

2.1.3 Evaluations. The back pressure effect is important only at the birth of a drop. It is observable at short times of the drop life. It is minimized by using relatively high values of t , high pressure over the capillary and relatively high flow rates.

The non-sphericity of the drop becomes important only toward the end of the drop life and is minimized by working at short t values compared to the drop time and with narrow capillaries.

Back-pressure and non-sphericity are usually not a problem with dropping Hg electrodes with flow rates of the order of 0.2 mg s^{-1} and time of measurement of about 7-9 s over a drop life of 12-15 s. Both effects can have some importance with oxidizable liquid electrodes, such as Ga and its alloys, for which high flow rates, low overpressure, and short drop times can be necessary.

Excluded area effects have been reported (refs. 13,20) and have been claimed to be more important than the other two, up to ca 1%. However, its bearing is greater at short times and decreases rapidly with the expanding drop surface area. It is minimized by using very narrow capillary and large drops. With the characteristics specified above, the drop surface area is of the order of 1-2 mm^2 . The excluded area effect becomes negligible with respect to the intrinsic accuracy of the measured quantities ($\ll 0.1\%$) as the radius of the orifice is $\ll 20\text{-}25 \text{ }\mu\text{m}$. Again, this effect may be a problem with oxidizable liquid metals for which large bore capillaries may be necessary.

The recommended procedure to check whether any of the above effects are operative is to carry out measurement at different times with the same capillary under otherwise constant conditions. Corrections for the screened area can be made where necessary by measuring r_0 by a suitable technique.

2.2 Capacitance ratio

This method is normally used with solid electrodes, but it is also applicable to liquid metals and disperse systems. It is widely adopted for the estimation of the surface area ratio for different samples of the same electrode material (eg ref. 21-24).

2.2.1 Principles. The experimental differential capacitance of the electrode under investigation in aqueous solutions is divided by $15\text{-}17 \text{ }\mu\text{F cm}^{-2}$, the empirically established range of capacitance per unit area measured with a Hg electrode at moderately negative charges (around $-12 \text{ }\mu\text{C cm}^{-2}$) where C goes through a shallow minimum. This implies assuming that the structure of the double layer is exactly the same for the investigated electrode as for Hg. The potential of measurement should be the same on the rational scale, viz referred to the potential of zero charge.

A variant of this method consists in measuring the capacitance in very dilute solutions ($\ll 10^{-3} \text{ mol dm}^{-3}$) and in assuming that the minimum value at the potential of zero charge is entirely governed by the diffuse layer capacitance so that the surface area can be obtained by dividing the experimental value by that calculated by means of the Gouy-Chapman theory. This modification implies that the position of the potential of zero charge (the point of zero charge in the case of ionic solids) is experimentally identifiable.

2.2.2 Limitations. Although there is some evidence that the capacitance falls in a narrow range of values at negative charges in the region -10 to $-15 \text{ }\mu\text{C cm}^{-2}$, this value may span from 15 for Hg to 25 for the (111) face of Ag. Moreover, the capacitance is potential dependent in a way which depends dramatically on the nature of the metal. In many cases the position of the potential of zero charge is not known, hence the observation of a plateau does

not necessarily mean that it may be treated as equivalent to the shallow minimum of Hg at negative charges.

In the case of the capacitance minimum at the potential of zero charge, taking it as determined entirely by the diffuse layer is tantamount to assuming that the inner layer capacitance is as low as that on Hg. Results for Ag, Au, Ga and In-Ga have shown that this is definitively not a general case. This approach is even less reliable with ionic solids, whose inner layer capacitance and its potential dependence are as a rule unknown (cf section 7.2).

Since techniques based on alternating electric signals are used for the measurement, for rough solid surfaces the capacitance usually shows a frequency dispersion which prevents the assignment to it of a physically significant value. Also, measured capacitances are often vitiated by some faradaic components due to the fact that most electrochemical interfaces are not ideally polarizable (ref. 5).

2.2.3 Evaluations. This method has no physical basis; it cannot even be defined as empiric since it goes against the experimental evidence. Apart from the nature of the electrode, the electrolyte may have unpredictable effects. For instance, F⁻ ions are not specifically adsorbed on Hg but they are on Ag and other *sp*-metals. The potential of zero charge of *d*-metals is mainly unknown and the behaviour of the double layer capacitance with potential has not been investigated. In the case of oxidizable transition metals like Ni and Fe, the capacitance depends dramatically on the presence of oxide films. In non-aqueous solvents the difference between Hg and *d*-metals (cf Pt and Pd in DMSO and ACN) is even more striking and use of this method to estimate surface areas may be in error by even an order of magnitude.

The method is more reasonable in its variant. However, the approximation of constancy in the inner layer capacitance must be verifiable and can anyway lead to inaccuracy of 10-20%. The method is acceptable as an internal check (or for the estimation of the relative surface area) for different samples of the same metal or of the same ionic solid (eg oxide), provided the repeatability of the experimental results is ascertained at a given constant frequency of the alternating signal. With liquid metals, it is a correct way to normalize experimental data to unit surface area, provided accepted values for exactly the same system and the same conditions are available, and the measuring apparatus is known to give correct results. Experimental difficulties may arise from the high ohmic resistance due to the low electrolyte concentrations needed. Moreover, double layer charging may become a diffusion-controlled process.

2.3 Parsons-Zobel plot

This method rests on the comparison of the experimental data with the double layer theory. The difference with respect to the previous one is that this is a multiple-point and not a single-point method.

2.3.1 Principles. Originally, the method stemmed from the application of the Gouy-Chapman-Stern theory of the double layer refined by Grahame (GCSG model), according to which the interface is depicted as equivalent to two capacitors in series. The interfacial capacitance per unit surface area is given by (ref. 25):

$$1/C = 1/C^i + 1/C^d \quad (3.1)$$

where C^d is the capacitance associated with the diffuse layer (on the solution side of the interface) and C^i is the inner layer capacitance associated with an ion-free layer of solution adjacent to the solid surface. The model predicts that C^d depends on the electrolyte concentration while C^i is not directly measurable but it can be derived from eqn.(3.1) provided the ions are not specifically adsorbed. If the interface has an area A , eqn.(3.1) may be rewritten as:

$$1/\tau C = 1/\tau C^i - 1/AC^d \quad (3.2)$$

where C^d is given by the Gouy-Chapman theory in terms of the unit surface area (SI units: F m⁻²). Subscript T has been introduced - cf eqn.(1.2) - to denote the total capacitance, ie $\tau C = CA$ (SI units: F). The experimental evidence indicates that C^i is in fact independent of electrolyte concentration in the

absence of ionic specific adsorption (refs. 25,26). Thus, a plot of $1/\tau C$ (experimental quantity) vs $1/C^d$ (calculated for different concentrations of the electrolyte) will result in a straight line whose slope and intercept give $1/A$ and τC^i , respectively (refs. 27,28).

In more recent theories the physical separation of the interface into an inner and a diffuse layer is not included as a necessary concept (ref. 29). The reciprocal of the capacitance of the electrode/solution interface turns out to be described by a power series with respect to the Debye length, x^{-1} :

$$1/C = ax^{-1} + bx^0 + cx^1 + \dots \quad (3.3)$$

If the surface area is made explicit, eqn.(3.3) becomes:

$$1/\tau C = ax^{-1}/A + bx^0/A + cx^1/A + \dots \quad (3.4)$$

The first term depends on the square root of the electrolyte concentration as in the Gouy-Chapman theory, the second term is independent of the electrolyte concentration as the inner layer capacity does in the GCSG model, and the third term becomes important only at high electrolyte concentrations, say $>1 \text{ mol dm}^{-3}$.

Although some evidence for the importance of the third term is experimentally available (ref. 30), in the electrolyte concentration range up to ca 1 mol dm^{-3} eqn.(3.4) is equivalent to eqn.(3.2) and can be used to derive the real surface area. Thus, this method is in fact not bound to the validity of any existing specific double layer theory.

2.3.2 Limitations. Equation (3.2) has been verified in the case of liquid electrodes, including Ga. It is however inconvenient for such electrodes since a single-point experiment at the diffuse layer minimum may be sufficient (cf section 2). For liquid electrodes conformation to eqn.(3.2) is often used to verify the absence of specific adsorption (ref. 25).

For the applicability of the method to solid electrodes the electrode surface must be absolutely homogeneous and the measured capacitance must be frequency independent. Thus, it is strictly valid only for single crystal face electrodes (ref. 31).

Inhomogeneities on the surface result in a marked curvature of the plot of $1/\tau C$ vs $1/C^d$ (refs. 31,32). Paradoxically, the method is useful to measure surface roughness, but rough surfaces of single crystal faces are inhomogeneous so that the requirements for the applicability of the method are lost. In any case the asperities which can be "seen" by this method are those of height greater than the diffuse layer thickness at the highest concentration (normally 1 mol dm^{-3} since the model probably breaks down in more concentrated solutions), i.e. of the order of 1 nm .

2.3.3 Evaluations. While the method is unacceptable for polycrystalline surfaces in principle, it can be reasonably used with polycrystalline metals of low melting points (soft surfaces) since inhomogeneities are of minor effect on the electronic structure of these surfaces. Thus, the method is to a first approximation acceptable with Pb, Sn, Cd, In, Bi.

With single crystal faces the applicability of the method depends on the extent of the surface defects. If the surface is perfect, the method serves to give an exact measure of the geometric surface which in case of complex electrode shape is difficult to determine optically. If the surface shows only small deviations from ideality (roughness factor < 1.1), the method will give the real surface within a few percent (2-3%). Better resolution is probably possible by a somewhat different approach based on trials (refs. 26,32). The most probable roughness factor is that resulting in the most regular variation of C^i with potential. The approach is more empiric because it is not based on a model but on an intuitive view of how a capacitance curve should be as a function of potential around the zero charge. It seems to work with silver, but there are problems with Au. At the moment the latter approach lacks the general validity necessary to be recommended here. It necessitates further investigation.

The applicability of the method to disperse systems (mainly ionic solids) is still under evaluation (refs. 33,34).

2.4 Hydrogen adsorption from solution

The method is used as a rule with a few transition metals showing hydrogen adsorption in potential regions prior to massive H₂ evolution. The experimental technique may be cyclic voltammetry or current step (chronopotentiometry) (refs. 35,36). The method has been established mainly with Pt electrodes (ref. 37), but it has been extended to Rh and Ir (refs. 38,39), and to Ni (refs. 40,41).

2.4.1 Principles. The charge under the voltammetric peaks for hydrogen adsorption or desorption (or associated with the appropriate section of the potential-time curves), corrected for double layer charging (ie the capacitive component), is assumed to correspond to adsorption of one hydrogen atom on each metal atom of the surface (Q_H). The charge associated with a one-to-one H-M correspondence per unit surface area (Q_H^*) is calculated on the basis of the distribution of metal atoms on the surface. This is well defined for a perfect single crystal face (ref. 42), whereas it is taken as an average value between the main low-index faces for polycrystalline surfaces. The resulting value is as a rule very close to that pertaining to the (100) face (ref. 43). The true surface area is thus derived from:

$$A = Q_H / Q_H^* \quad (4.1)$$

In the case of polycrystalline Pt the accepted value is 210 $\mu\text{C cm}^{-2}$, based on the assumption that the density of atoms on such a surface is $1.31 \times 10^{15} \text{ cm}^{-2}$ (refs. 44,45).

The validity of the method implies that the point where hydrogen adsorption is complete can be exactly identified, and that the coverage is completed before the rate of hydrogen evolution becomes significant. In addition, it rests on the assumption that there is a definite quantitative relation between the charge measured and the amount of substance deposited, ie total charge transfer takes place from the adsorbate to the metal. Finally, no alteration of the surface upon adsorption is assumed to take place. These assumptions are common also to methods 5 and 6.

2.4.2 Limitations. Some of the assumptions on which the method rests may not be valid. In particular, adsorption may take place with partial charge transfer, and phenomena related to surface alteration may also occur upon deposition of species from the solution.

The completion of the monolayer probably takes place only with Pt electrodes whereas with Rh and Ir such condition is not fulfilled. This involves some independent determination of coverage by pseudo-capacitance measurements which introduces additional uncertainties. The identification of the end-point for adsorption is also a problem since its position depends on the operating conditions (eg the partial pressure of H₂ gas). It has been suggested that this point is better seen at very low temperatures (ref. 39), which introduces the assumption that the temperature does not modify the situation essentially. Alternatively, the end-point can be attained by extrapolating Q_H to infinite sweep rate which enables a separation between adsorption and faradaic charges for H₂ evolution to be achieved (ref. 46).

The method cannot be used with metals *absorbing* hydrogen such as Pd. Hydrogen absorption at low potential sweep rates (eg $< 5 \text{ mV s}^{-1}$) is also a problem with highly porous electrodes (ref. 47). The independence of Q_H on the sweep rate should be ascertained to find out the best experimental conditions. Extrapolation to infinite sweep rate (or current pulse) could in principle separate adsorption from absorption. However, distortion of the voltammogram due to ohmic drops and/or kinetic restrictions may appear at high sweep rates, especially with highly porous materials. The problem of the overlapping of the hydrogen and oxygen adsorption regions is more serious and prevents the application of the method to easily oxidizable transition metal such as Ni, Fe, Ru, Os, etc.

The method has been applied also to finely divided powders (ref. 48). In the case of supported metals, the H atoms deposited on the metallic particles may diffuse along the surface to regions where the support is uncovered (spillover). Spillover effects may render the results of hydrogen adsorption ambiguous, thus invalidating the quantitative significance of the measured Q_H .

The absolute significance of the accepted Q_H^* is questionable. Apart from the distribution of the adsorbate which might be verified spectroscopically (but

adsorption in solution does differ from the gas phase situation because of the competition with solvent molecules), the assumption that the surface density of atoms is a constant for a given metal is inconsistent with the widely diffuse idea of basic unreproducibility of polycrystalline surface structures. The adsorbability of hydrogen varies very much on different crystal faces (refs. 42,49). In addition, the double layer correction, as usually made, is arbitrary. Besides being in principle unfeasible, the separation of "faradaic" and the capacitive charges rests on the assumption that the interfacial capacitance is constant over the potential region of hydrogen adsorption, and equal to its magnitude in the potential region prior to hydrogen discharge. However, the very presence of the adsorbate may modify the capacitive parameters of the phase boundary.

Another aspect to be taken into account is the influence of ions on hydrogen adsorption (ref. 50). The height of the peaks and their position are influenced by the nature of the electrolyte. Ionic adsorption may be significant at the potentials where hydrogen is adsorbed or even evolved.

2.4.3 Evaluations. This is the only method which enables an *in situ* approach to the real surface area of *d*-metal electrodes to be attempted. The total inaccuracy and unreproducibility of these measurements can be expected to be about $\pm 10\%$ (refs. 43,46), which is quite satisfactory in this case. Although surface area values for different metals estimated with this approach may not bear the same physical significance, the method allows a good normalization of experimental data for the same metal. The reliability of the method depends very much on the cleanliness of the electrode surface (hence of the solution) which should be ascertained before conducting the specific determinations for the measurement of the real surface area.

2.5 Oxygen adsorption from solution

The method is applicable to metals showing well developed regions for oxide monolayer formation and reduction. In addition to some *d*-metals, it has been used with Au for which the previous technique cannot be applied since no hydrogen adsorption region is recognizable.

2.5.1 Principles. The method rests on the same grounds as the previous one (ref. 51). Oxygen is assumed to be chemisorbed in a monoatomic layer prior to O_2 evolution with a one-to-one correspondence with surface metal atoms (ref. 52). This implies that the charge associated with the formation or reduction of the layer is:

$$Q_0 = 2eN_A \Gamma_0 A \quad (5.1)$$

where N_A is the Avogadro constant, and Γ_0 , the surface concentration of atomic oxygen, is assumed to be equal to N_M , the surface density of metal atoms. From the value of N_M per unit surface area, the value of Q_0^* , the reference charge, is calculated so that:

$$A = Q_0 / Q_0^* \quad (5.2)$$

The approach implies that:

$$Q_0^* / Q_H^* = 2 \quad (5.3)$$

so that the accepted value for polycrystalline Pt is $420 \mu C \text{ cm}^{-2}$. A value of $390 \pm 10 \mu C \text{ cm}^{-2}$ has been suggested for polycrystalline Au (refs. 52,53). Calculated values of Q_0^* for Au single crystal faces are also available (ref. 54).

2.5.2 Limitations. Oxygen adsorption usually results in oxide formation by a *place-exchange* mechanism. This leads to Q_0 being a function of time. The potential where the monolayer is completed is difficult to assess. Sometimes overlapping of oxygen and hydrogen adsorption regions occurs.

Q_0 may be measured either during oxygen adsorption (positive potential sweep or positive current pulse) (ref. 52) or during adsorbed oxygen reduction (refs. 55,56). In the former case Q_0 may include oxidizable impurity effects and some charge associated with evolved O_2 . In the latter case, the adsorbed monolayer may in fact be a multilayer (oxide film) of undefined stoichiometry.

The double layer correction usually implies that C_{dl} is constant and equal to

that in the double layer region prior to oxide formation. The correction may come out to differ depending on the direction of potential sweep (or on the sign of the current pulse).

As for the absolute value of Q_0^* , the method suffers from the same shortcomings as Q_H^* (cf section 4).

2.5.3 Evaluations. The method is less reliable than that based on H adsorption, but in some cases it is the only applicable of the two (eg Au, Pd). The reliability decreases as the affinity of the metal for oxygen increases. Thus, it should be the best for Au, for which however the stoichiometry of the oxide formed is uncertain. If anodic sweeps or current pulses are used, Q_0 should be determined down to constant values as the experimental parameter is varied. Also, the determination of the potential range where eqn.(5.3) is verified (for the metals allowing that) may constitute an indicative criterion of the absence of anomalous effects. This entails a careful selection of the limits of the potential range where Q_0 should be determined. The cleanliness of the surface and the solution should be ensured. Using cathodic sweep or current pulses may enable a single-point experiment to suffice. However, the condition of $\theta_0 = 1$ should be ascertained if an accepted praxis does not exist.

The method can be used with Au electrodes since H adsorption does not take place, but it is to be borne in mind that the treatment the surface is subjected to may not be without any effect on its structure, especially in the case of single crystal faces.

2.6 Underpotential deposition of metals

This method has been used for electrodes for which neither of the previous ones can be applied, eg Ag (ref. 57), Cu (ref. 58), and for metals for which a better separation between H and O adsorption cannot be achieved, eg Ru (ref. 59). An advantage of this method over method 4 (hydrogen adsorption) is that no spillover effects are expected, hence selective deposition is possible. Thus, the method may be particularly convenient to determine the (active) surface of supported electrodes where the (inactive) support comes in contact with the solution (ref. 60).

2.6.1 Principles. The charge associated with the underpotential deposition of a suitable metal ion is measured usually by voltammetry. The maximum adsorption in a monolayer is calculated on the basis of a chosen model so that the surface area of the sample is given by:

$$A = Q_H / Q_H^* \quad (6.1)$$

Usually, Ag and Cu adatoms are used.

2.6.2 Limitations. This method suffers from the same shortcomings as method 4, in particular the correction for double layer charging is arbitrary and the identification of the end point for the metal adsorption is uncertain. In addition, (i) the UPD region may interfere with hydrogen or oxygen adsorption, (ii) the surface distribution of the UPD species may be unknown, (iii) the adatom deposition may occur with partial charge transfer thus making the value of Q_H^* specifically system-dependent, and (iv) the usual assumption of one-to-one correspondence with H and O adsorption may not be valid in the case of UPD because the new phase formation may result in more condensed monolayers, multilayers or cluster growth (ref. 61). Thus, in the case of Pb on Cu (111) the coverage has been found (ref. 58) to correspond to a close-packed configuration, while in the case of Pb on Ru the one-to-one correspondence (epitaxial growth) is more probable (ref. 59). The occurrence of the one or the other possibilities depends on a number of factors including size ratio between supporting metal and UPD metal, strength of the bond between overlayer and support in comparison with lateral interactions in the monolayer, etc.

The calculation of Q_H^* for polycrystalline surfaces is based on empirical considerations. The same is also the case of single crystal faces for which the method gives strictly the number of surface active sites rather than the true surface area. The response of the single crystal face is however different from that of the polycrystalline surface of a given metal because of the possible penetration of the discharged atoms into grain boundaries in the latter case.

2.6.3 Evaluations. The reproducibility of the measurements is usually high. If established knowledge about the system does not exist, the formation of a monolayer should be checked experimentally. The surface distribution of UPD metal atoms should be assessed also on the basis of spectroscopic data for the same system in gas phase adsorption, where however the situation may not be the same in view of the absence of the competitive effect of solvent adsorption at the solid/liquid interface (ref. 62).

In the case of epitaxial growth, the value of Q_m^* is expected to depend on the surface structure of the sample, whereas this is not the case if close-packed monolayers are formed.

The methods of monolayer formation are claimed (ref. 57) to be more sensitive than those based on double layer charging since the charge spent in UPD is as a rule one order of magnitude higher. However, this consideration is tenable only in case double layer charging is operated by the same technique as that used to measure Q_m .

It is to be borne in mind that UPD may have undesired effects on the properties of the electrode surface owing to retention of some UPD atoms in the metal lattice even after complete desorption, and to possible surface reconstruction (refs. 63-65).

2.7 Voltammetry

In some cases none of methods 4-6 can be used because neither hydrogen nor oxygen adsorption, nor UPD takes place. This may be the case of non-metallic electrodes (refs. 66-68). Voltammetry, chronopotentiometry, current step and potential step techniques, differential chrono-potentiometry, etc. (ref. 69,70), can be used to determine the apparent total capacitance of the electrode surface. The voltammetric approach, which is the most popular, is described in some details below.

2.7.1 Principles. Voltammetric curves are recorded in a narrow potential range (a few tens of mV) at different sweep rates (ref. 69). The current in the middle of the potential range is then plotted as a function of the sweep rate. Under the assumption that double layer charging is the only process, a straight line should be obtained, whose slope gives the differential capacitance (total value) of the interface:

$$\tau C = dQ/dE = Idt/dE = I/(dE/dt) \quad (7.1)$$

The capacitance thus obtained is then compared to some reference value C^* so that the surface area is obtained from:

$$A = \tau C / C^* \quad (7.2)$$

The method is not different in substance from that in sec. 2 except for the fact that the technique used is not specific for capacitance measurement and is generally applied to large surface area and porous electrodes.

2.7.2 Limitations. This method has been several times applied to oxide electrodes. The assumption of $C^* = 60 \mu\text{F cm}^{-2}$ for the capacitance of the unit true surface area of an oxide (irrespective of its nature) (ref. 67) is not established. The dependence of capacitance on potential for oxides is unknown, so that the error may be very large. Since voltammetric curves of oxides show maxima related to surface redox processes, the value of capacitance may differ in different potential regions (ref. 71).

Porous materials or oxide electrodes usually show a dependence of I on sweep rate due to exclusion of some less accessible surface at the highest rate (ref. 71). The mechanism of charging of oxide electrodes is more complex than that of metals since it is also governed by pH through surface proton exchange (ref. 72). The state of charge of a surface is thus strongly dependent on the solution pH. Therefore, the determinations should at least be normalized to a reference pH.

2.7.3 Evaluations. The method has no universal significance since C^* has only an empiric validity. No comparison is quantitatively possible between different oxides since the physical meaning of the charge may change in the different cases. Nevertheless, the method is useful for an internal comparison for a given material, provided the technique is normalized to appropriate

experimental conditions.

The comparison of capacitance values between different oxides is also invalidated by the fact that the fraction of surface sites being oxidised or reduced in a given potential range may differ for different systems. The determination of an absolute capacity has been attempted in some cases by using an independently determined BET surface area (ref. 68). However, while this approach does not add anything to the validity of an internal comparison, it adds the vexing question of the relative meaning of *in situ* and *ex situ* surface area determinations, relevant also to other methods dealt with in this document.

2.8 Negative adsorption

The method has been proposed for large surface area solids suspended or colloiddally dispersed in an electrolyte solution (ref. 73). *In principle*, it can also be used with massive systems.

2.8.1 Principles. The method assumes the validity of the diffuse layer model. Ions are repelled from surfaces carrying charges of like sign. The Gouy-Chapman theory predicts that their negative surface excess (depletion) is charge (potential) dependent and reaches asymptotically an almost constant value at relatively small charges (at potentials in the OHP, outer Helmholtz plane, not too far from zero). As a consequence of the repulsion into the solution, the concentration level of these species is increased in the bulk since they are excluded from all the interfacial regions (refs. 74-76).

The method usually employed involves the analytical determination of the change in the concentration of the negatively adsorbed ion in the solution. The surface area is proportional to the measured Δc through the following equation:

$$A = B V_t (\Delta c / c) c^{1/2} \quad (8.1)$$

V_t is the total liquid volume where the solid is suspended and B is a constant for a given electrolyte type and charge sign on the solid surface. Normally, negative adsorption is measured at negatively charged surface since the probability of specific adsorption of cations is more remote.

2.8.2 Limitations. Since the increase in concentration (Δc) is usually small, this sets a lower size limit to the specific area that can be measured. The potential at the OHP or the charge of the diffuse double layer must be known to apply the method not far enough from the zero charge condition where negative adsorption has not yet reached its limiting value. With porous solids, the negative adsorption from the pores is incomplete because of double layer overlap. In some cases the response of the method is unreliable because the technique is extremely sensitive to the release of traces of impurities from the solid.

Different equations have to be used depending on whether flat or spherical double layers are best approximated (ref. 77). The results can be unreliable if inhomogeneous suspensions are dealt with. In any case, being a double layer technique, it can reveal surface asperities whose height is comparable to the diffuse layer thickness.

2.8.3 Evaluations. The particle size of the disperse solid should be as homogeneous as possible. The method is best suited for crystalline non-porous solids. In general, negative adsorption measurements can be performed at one concentration, but a check of the applicability of the technique is obtained by plotting $V_t B (\Delta c / c)$ vs $c^{-1/2}$. A straight line of slope A should be obtained.

The potential at the OHP should not be <150 mV, otherwise it should be fairly accurately known (cf sec. 8.2); the surface area to be measured must be greater than $1 \text{ m}^2 \text{ g}^{-1}$; the interparticle distance in the suspension should be more than 10 times the diffuse layer thickness. The analytical technique to determine Δc should be precise owing to the small value of Δc . A method to alleviate the strict analytical requirements has been proposed (ref. 78). However, if all recommended conditions are met, the accuracy may be of the order of $\pm 10\%$.

The method is not a routine one and must be assessed case by case.

2.9 Ion-exchange capacity

This method has been specifically suggested for some oxides such as MnO₂ (ref. 79) and tested also for SiO₂ (ref. 80). Compared to the previous method, it is still a double layer approach, but based on positive adsorption.

2.9.1 Principles. Specific adsorption on oxides is substantially an ion-exchange process (ref. 72). Surface complexation of the surface OH groups takes place through the release of acidity (ref. 81). For instance:



The method is based on the determination (radiochemically or by other analytical means) of the amount of complexing ions taken up by the oxide surface. The surface area is then calculated by assigning a given cross-section to the adsorbate (ref. 82).

2.9.2 Limitations. Specific adsorption does not necessarily go to completion, i.e. not all available surface sites undergo ion exchange (cf 9.3). This has been ascertained even in the case of MnO₂. The maximum amount taken up by the oxide surface depends on the nature of the solid, presumably on its acid-base properties (ref. 81). The pH of the solution plays a paramount role and the amount adsorbed will depend on it (ref. 79).

The cross-sectional area assigned to the adsorbate (Zn²⁺ is that usually recommended) will depend on the distribution of the adsorbing sites on the oxide surface and has no definite physical meaning, since it is as a rule established so as to bring the calculated area into agreement with the BET surface area. This makes the method not an absolute one, since the results are complicated by the problem of identity between BET and *in situ* wet surface area.

2.9.3 Evaluations. This method has been scrutinized only for MnO₂ and the procedure has been normalized to this particular oxide. The maximum surface coverage on Al₂O₃ has been found to be lower than on MnO₂ (ref. 81). An attempt with RuO₂ has resulted in a surface area three times lower than the BET value (ref. 83). Moreover, also in the case of MnO₂, the claimed 1 to 1 correlation between BET and Zn²⁺ adsorption surface area deviates at high surface area values probably because of pore exclusion (ref. 81). Finally, the adsorbability of Zn²⁺ decreases with increasing calcination temperature, a fact which makes this method fully applicable (reliability apart) only with hydrous oxides (ref. 80).

Since this method is insufficiently established, it is not recommended for routine use.

2.10 Adsorption of probe molecules from solution

The method is usually applied to high surface area and/or disperse solids (refs. 84-86). While ionic species are used as probe species in previous methods, neutral compounds are essentially used here. The amount of adsorbate may be detected directly or indirectly using electrochemical or non-electrochemical techniques.

2.10.1 Principles. A probe molecule is adsorbed on the solid in solution and the extent of adsorption is determined analytically from the depletion in the solution. Dyes, surfactants, fatty acids and polyalcohols are generally suggested as suitable probe molecules (refs. 81,82). From the (apparent) monolayer surface concentration the surface area of the solid is derived by the equation:

$$A = \Gamma_s N_A A^* \quad (10.1)$$

where Γ_s is the saturation coverage in mol cm⁻² and A^* is the projected area assigned to one adsorbed probe molecule.

In the electrochemical variant, for instance, CO and I₂ have been used as probe molecules (refs. 45,89-91). A monolayer of atomic iodine is assumed to form in the case of I₂ adsorption. The amount of adsorption is determined from the charge required to anodically oxidize the adsorbate (anodic stripping).

The electrode surface area is obtained by the equation:

$$A = (Q - Q_b) / nF\Gamma_s \quad (10.2)$$

where Q is the charge associated with the anodic oxidation of the probe molecule, Q_b is the charge spent in the same potential range in the absence of adsorbate (background charge), n is the charge number of the oxidation reaction ($\text{CO} \rightarrow \text{CO}_2$; $\text{I} \rightarrow \text{IO}_3^-$), F the Faraday constant, and Γ_s the calculated saturation coverage in mol cm^{-2} .

2.10.2 Limitations. In the non-electrochemical version of this method, the major drawback is that the orientation and conformation of the adsorbate may depend on surface charge, on surface coverage, and on the nature of the adsorbent and of the solvent (refs. 62,92). Therefore the value of A^* does not possess a certain physical significance. In addition, the adsorbing species may produce micelles in solution and at the surface, as well as multilayers, so that it is often necessary to introduce a correcting factor (refs. 93,94).

The value of Γ_s is usually derived from extrapolation procedures based on a specific isotherm. The obtained value may not correspond to a complete monolayer if the competition with the solvent is strong. Finally, adsorption of hydrophilic molecules on hydrophobic surfaces is generally weak and gives no practical basis for surface area determinations.

The electrochemical detection of the adsorbate by "anodic stripping" (in the case of CO and I_2) suffers from the same shortcomings as the methods based on H, O and metal adsorption (methods 4 to 6) with the additional problem that the "background charge" usually includes processes of surface oxidation which may be affected by the presence of the adsorbate. The surface stoichiometry of the adsorbed layer has been found to depend on the metal nature and on the crystallite size in the case of CO (ref. 45). The assumption of a close-packed monolayer of unassociated atoms of iodine or of CO may not be straightforwardly extensible to all systems.

2.10.3 Evaluations. Large molecules may generally not have access to pores, cracks or grain boundaries so that different surface areas can be obtained by using different molecules (ref. 87). This may enable the external from the internal surface area to be separated. Another possibility is to follow the rate of adsorption; the area accessible to the adsorbate can then be evaluated as a function of time.

As in previous cases, this method can be used to assess the relative size of two or more solids of the same nature. The absolute values of surface area are vitiated by the assumption of complete coverage at saturation or of a given molecular orientation and conformation. This makes the comparison of the results for different solids rather difficult.

The electrochemical variant should be used only with electrode materials for which the surface stoichiometry of adsorption and the structure of the adsorbed layer have been reliably established, bearing in mind that, due to its nature, the approach is particularly affected by the presence of oxidizable organic impurities.

2.11 Mass transfer

This method has been particularly suggested for surface area determination of complicated objects in galvanic depositions (ref. 95) but it is in fact used much more frequently, even in research situations. It can in principle be used for any system irrespective of the extent of the surface area.

2.11.1 Principles. Under the assumption of homogeneous current distribution, the current associated with the charge transfer to a reactant whose supply is controlled by diffusion is given by (refs. 96-99):

$$I = nFADc/\delta \quad (11.1)$$

where D is the diffusion coefficient, c the bulk concentration and δ the thickness of the diffusion layer. Under the proviso that $c = c$ at $t = 0$ and $c = 0$ at the electrode surface at $t > 0$, δ at time t is given by:

$$\delta = (\pi Dt)^{1/2} \quad (11.2)$$

From (11.1) and (11.2) the measured current is related to the surface area by:

$$A = I(\pi Dt)^{1/2} / nFDC \quad (11.3)$$

The measurement is carried out potentiostatically by recording the current as a function of time.

Equation (11.3) is strictly valid only for linear diffusion at a plane electrode. For non-linear diffusion the complete equations are the following:

$$I = nFADc[(\pi Dt)^{-1/2} + r^{-1}] \text{ (spherical electrode)} \quad (11.4)$$

$$I = nFADc[(\pi Dt)^{-1/2} + r^{-1} + \dots] \text{ (disk electrode)} \quad (11.5)$$

$$I = nFADc[(\pi Dt)^{-1/2} + 0.5r^{-1} - \dots] \text{ (cylindrical electrode)} \quad (11.6)$$

where r is the radius of the sphere, the disk or the cylinder, respectively. Thus, a plot of I vs $t^{-1/2}$ will give a straight line of slope $nFAC(D/\pi)^{1/2}$ for linear diffusion (cf eqn.(11.3)), while it can be approximated to a straight line with the same slope for non-linear diffusion.

A variant of this method (mainly applied to voltammetric situations) makes use of a linear potential-time scan instead of stationary potentiostatic conditions. If the solution is quiescent, the current as a function of potential goes through a maximum (j_p) given by (ref. 100):

$$j_p = A(kn^3/2D_B^{1/2}c_B)v^{1/2} \quad (11.7)$$

where D_B and c_B are the diffusion coefficient and the bulk concentration of the reacting species B, respectively. n is the charge number of the electrode reaction, v the potential sweep rate and k a numerical constant which is determined empirically. The method is tested by checking the functional dependence of j_p on the two parameters, A and v .

Equation (11.7) was originally derived for one-dimensional convection-free linear diffusion, but it is also obeyed in experiments with unshielded electrodes possessing a hemispherical diffusion domain in chronopotentiometry and chronoamperometry for short transition times.

2.11.2 Limitations. The method is not limited by the surface size but simply by the sensitivity of the measuring apparatus. Nevertheless, the applicability calls for an homogeneous distribution of current which is difficult to achieve precisely at surface asperities. Since the diffusion layer thickness has a macroscopic order of magnitude, the surface roughness detected by this technique is of the same order of magnitude, i.e. >10 - $100 \mu\text{m}$.

The current measured may contain an unknown contribution from surface modifications of the electrode, although cathodic polarization is usually suggested. For the correct applicability of the method, the current yield of the probe reaction must be strictly unity.

For purely diffusive systems, the thickness of the diffusion layer varies with time; this may be a problem for rough and porous electrodes, in that different effective surface areas may be determined at different times. Using convective systems (eg pipe flow, rotating disc, etc) for which the thickness of the diffusion layer can be controlled although it will depend on the convection conditions. This will make the experimental approach simpler but the ambiguity of the physical meaning of the measured surface area remains.

2.11.3 Evaluations. This method is not suitable for surface area determinations to be used in systems where atomic roughness is important. It is applicable to systems for which knowledge of a self-consistent macroscopic surface area, which may be higher than A_k , but lower than the real surface area, (eg large electrode surfaces of complicated shapes) is all that is needed.

3. EX SITU METHODS

3.1 Adsorption of probe molecules from gas phase

The well-known BET (from Brunauer, Emmett and Teller) (ref. 101) method belongs to this category; it is undoubtedly the most popular technique to measure surface areas in all branches of surface chemistry.

3.1.1 Principles. Probe molecules are adsorbed from the gas phase onto the solid surface as a function of gas pressure. The amount adsorbed in a monolayer (saturation surface concentration, Γ_s) is derived from an appropriate treatment of the adsorption data on the basis of a specific adsorption isotherm. Finally, the surface area is calculated from Γ_s after assignment of an effective cross-sectional area A^* to the adsorbate molecule (ref. 102).

The most popular treatment makes use of the BET isotherm to derive Γ_s , but variants have been suggested and used (ref. 103). In particular, Γ_s is derived from the first monolayer region, but it can also be obtained from the multilayer region (ref. 104). Selective adsorption on some specific sites can be achieved by using molecules undergoing chemisorption instead of physisorption as implied in the BET treatment. In this case the experimental data are as a rule worked out on the basis of different isotherms (eg Freundlich's) (ref. 105).

3.1.2 Limitations. It is not the purpose of this document to discuss the basic validity of this method. Being an *ex situ* technique, what is to be assessed is its relevance to the electrochemical situation.

Various kinds of probe molecules can be used: N_2 , Kr, Ar mostly (ref. 106), but also H_2O (refs. 107,108) and *n*-butane (ref. 109), and for chemisorption CO_2 , O_2 , CO, N_2O , (refs. 105, 110,111) etc. Different surface area values are usually obtained with different adsorbates. This is especially true for porous solids since the accessibility of probe molecules to inner surfaces depends of course on their size. Thus, the surface area on the basis of N_2 (assigned area 0.162 nm^2) (ref. 102,109), the classic probe molecule in this technique, may be lower than that with Kr or H_2O . Accordingly, hydrocarbons are large molecules and can only give the external surface. The use of two judiciously chosen probe molecules can enable external and internal surfaces to be distinguished (ref. 107).

The most vexing question in this method is obviously the value of A^* (ref. 102,112). Hexagonal close packing is usually assumed to calculate the cross-sectional area:

$$A^* = 1.091 (M/\rho N_A)^{2/3} \quad (12.1)$$

where 1.091 is a packing factor, M is the molar mass of the adsorbate, ρ is its density and N_A the Avogadro constant (a cube of space was instead originally suggested by Emmett and Brunauer to be occupied by each adsorbate molecule). However, there is the possibility of choosing between the density of the liquid and the density of the solid, depending on the degree of localization of adsorption. This is tantamount to implying that the cross-sectional area of the adsorbate may depend on the strength of the interaction with the solid adsorbent. Despite the usual claim that in the case of N_2 the constancy of A^* can be taken with confidence over a large class of solid surfaces, it is now well established (refs. 109,112) that there exists an inverse proportionality between A^* and the C constant in the BET equation (which is a measure of the degree of interaction between adsorbent and adsorbate). Therefore the same value of A^* might not be valid with different surfaces. Moreover, for sufficiently strong interaction, adsorption may become localized so that also the assumption of close arrangements may break down.

3.1.3 Evaluations. If disperse solids are the working systems under investigation, the BET surface area may be too low due to some packing of the grains during the surface area measurement. The situation may be opposite if a packed layer is scraped from the support to measure its specific area, or if the powder on which the BET measurement has been carried out is then used to prepare pellets, since packing may be lower under the conditions of surface area determination.

Use of H_2O as the probe molecule may appear as most appropriate for studies relevant to electrochemical interfaces. However, H_2O is reactive towards most catalysts so that localized adsorption, and sometimes decomposition, may take place. Moreover, liquid water may have a different access to the more internal surface than the vapour at relatively low pressure due to surface tension and hydrostatic pressure effects.

It is very difficult to establish a firm correlation between the BET (or other) surface area and the electrochemical active surface area, each method measuring a surface which responds to the specific probing. However, the BET is a routine method and its use for a first approximation assessment is always

welcome. Caution should be exerted in treating the obtained values on a quantitative (or semi-quantitative) basis. Attempts should always be made to complement the BET surface area measurements with other independent approaches.

It is to be mentioned in this context that modern surface spectroscopic techniques such as AES, have been recently used to extract information about adsorbate absolute packing density (ref. 113). Although not explicitly developed for surface area measurements, the approach contains such a potentiality implicitly (ref. 92).

3.2 X-ray diffraction

The method, which gives information on crystallite size, is as a rule applied to crystalline powders (refs. 114,115) although it can be extended to supported microcrystalline layers (ref. 116). A variant, the small-angle X-ray scattering (SAXS), will not be treated here because its use is not common with electrode systems.

3.2.1 Principles. X-ray diffraction lines broaden (ref. 117) when the crystallite size falls below about 100 nm: at this size broadening in excess of the instrumental width is as a rule not obtained. If Gaussian shape is assumed for the diffraction lines, then (ref. 118):

$$w_{ex}^2 = w_{in}^2 + w_{ps}^2 \quad (13.1)$$

where subscripts refer to experimental, instrumental and particle-size width, respectively. w_{in} is usually obtainable by a calibration procedure. Thus, w_{ps} can be derived. The average crystallite diameter d is then obtained by the classical Scherrer equation (refs. 119,120):

$$d = K\lambda/w_{ex} \cos \theta \quad (13.2)$$

where λ is the X-ray wavelength, w_{ex} is here expressed in radians and K (Scherrer's constant) depends on how the peak width is measured; as a rule, the full width at half maximum (FWHM) is measured, for which K takes a value close to 0.9. More sophisticated deconvolution procedures have also been proposed (ref. 121).

Once d is known, A can be calculated by assuming a particular geometry for the particles (refs. 122,123). Thus, for cubic particles, the surface area is a maximum:

$$A = 6d^2 \quad (13.3)$$

whereas it is a minimum for spherical particles:

$$A = \pi d^2 \quad (13.4)$$

3.2.2 Limitations. The method is restricted to crystalline solids of about 3.5–60 nm particle size. Below 3.5 nm the diffraction line is very broad and diffuse or even absent, while above ca 60 nm the change in lineshape is too small. The crystallite size obtained with this approach is averaged over the sample volume penetrated by the incident radiation, therefore the resulting value is a volume average diameter (cf method 15). Strictly, the surface area calculated by means of eqns.(13.3) and (13.4) is thus not the true surface area since the latter is related to the surface average crystallite size.

Other factors may contribute to the observed linewidth, eg difference in lattice parameters of the individual particles. Moreover, the exact geometrical shape of the particles is not known. The size distribution may be very wide (ref. 124).

In the case of supported material, pellets and layers the whole surface of each single particle is not exposed to the environment. A packing factor is to be adopted to take account of the excluded area (ref. 122). Also in the case of disperse systems and powders, the grains may be composed of more than one crystallite which causes the real surface area to deviate from the calculated one the more the smaller the particle size (ref. 125).

3.2.3 Evaluations. This technique is very useful to obtain rapid information about the dispersion degree of a catalyst present at the surface of a support

or even embedded in it (ref. 126). However, for surface area measurements it should be used only in conjunction with other more appropriate techniques, mainly to obtain a more complete analysis of the morphology of a solid surface.

3.3 Porosimetry

The methods considered above make it possible to estimate the specific area of solids and also in principle to find the pore distribution according to the radius. These methods could be named molecular or atomic probe methods (ref. 127). In addition, a number of nonadsorptive methods of porosity determination have been developed to estimate the real surface area.

3.3.1 Principles. The method is based on the relation between the real surface area of a sample and its porosity θ :

$$A_V = (1 - \theta_0)^{-1} \int_{r_{\min}}^{r_{\max}} (\beta_f / r) d\theta \quad (14.1)$$

where r_{\min} and r_{\max} are the minimal and maximal pore radii, and β_f is the shape factor. For cylindrical pores, $\beta_f = 2$, for pores between globula, $\beta_f = 1.45$. A_V is the surface area per unit volume of the material. Therefore, $(1 - \theta_0)$ is the true volume occupied by the solid phase (total volume minus pore volume). Porosity θ_0 is the ratio of the volume of open pores (connected with the outer surface of a solid) to the total volume of the porous solid. According to the eqn. (14.1), the real surface area can be calculated from the integration of the integral curve of radius pore distribution $\theta(r)$. Such a curve is called an integral porosimetric curve or a *porogram*.

Actually there are many methods for measuring porograms: (1) the method of pressing mercury into mercury unwettable porous solids (mercury porosimetry); (2) small angle X-ray scattering; (3) electron and optical microscopy; (4) centrifugal porosimetry; (5) capillary displacement of wetting liquids by gas; (6) methods based on gas penetration; (7) method of standard porosimetry. While in individual concrete cases each of these methods can be used, the methods of mercury and standard porosimetry are the most universal ones.

When using the method of mercury porosimetry (ref. 128) the side surface of pores into which mercury is pressed can be obtained directly by integration of the Young-Dupré equation:

$$A = -(\gamma \cos \theta)^{-1} \int_0^{P_{\max}} p dV_p \quad (14.2)$$

where θ is the contact angle of mercury on the solid boundary, γ the mercury surface tension, p the pressure, V_p the volume of mercury pressed into the sample, P_{\max} the pressure as the pores are completely filled with mercury.

The method of standard porosimetry (ref. 129) is based on the measurement of the equilibrium curve of relative moisture capacity, that is the relationship between the liquid contents of a test sample and of a standard one with a known pore distribution. The moisture capacity is the ratio of the volume of the liquid content in a solid to the volume of the solid. If the sample contains hydrophilic (metal, oxide, etc) and hydrophobic (polymeric binder) components, when using the method of standard porosimetry with two different wetting liquids (eg, water and liquid hydrocarbons) it is possible to identify hydrophilic, hydrophobic and mixed pores. Thus, the possibility arises of characterizing the real surface areas with the above-mentioned different types of pores.

3.3.2. Limitations. The main difficulty lies in the determination of micropores with radii (< 2 nm, ie of molecular sizes (ref. 130). Such pores could form the main part of the real surface area value in some materials. The lower limit in pore diameter measurable by the Hg porosimeter is set by the highest pressure at which the Hg can be forced into the pores of the sample. In this respect, the technique presents the difficulty that high pressure can disrupt the pore system to be measured.

Another complication is related to the difficulty of choosing the shape factor for real materials. In the method of mercury porosimetry the value of A

depends on the θ estimation. The latter depends on the nature of the material and also whether during the measurements mercury is pressed into pores or, on the contrary, it leaves them (ref. 131), and on the possibility of amalgamation and contamination of mercury. The last two factors also change γ . The often observed hysteresis phenomena also complicate the measurements and the interpretation of the results (ref. 132).

3.3.3. Evaluations. The method can be applied to materials with sufficiently extended surface. The reliability of results depends largely on the choice of the method of porogram measurement and of its conditions. For electrode materials, especially multicomponent porous electrodes, the most promising is the standard porosimetry method, which allows to distinguish the surface by the hydrophobicity factor. Other advantages of this method are its relative simplicity, the possibility of achieving conditions of measurement resembling most closely the real operating ones and of monitoring the surface area during the measurements thanks to the nondestructive nature of this method.

3.4 Microscopy

Microscopy is one of the direct physical methods of determination of the real surface area. The capacity of resolution goes from the macroscopic to the atomic size depending on the technique. Thus, the order of magnitude of the range of observation of the optical microscopy is the millimeter, that of the scanning electron microscopy (SEM) the micrometer, and that of the scanning tunneling microscopy (STM) the nanometer. The progress in the development of STM is making its use *in situ* possible (ref. 133).

3.4.1 Principles. The method is based on the determination of the particle size of the material by optical or electron microscopes (refs. 7,134). In its simplest version the specific surface area is calculated according to the equation:

$$A_m = (\beta_d / \rho) (\sum n_i d_i^2 / \sum n_i d_i^3) \quad (15.1)$$

where ρ is the real density of the material, and n_i is the number of particles with size d_i . The shape factor β_d amounts to 6 for strictly spheric and cubic particles, while it exceeds 6 for any other shape. Since the size of individual particles can be determined with this technique, the results of the microscope can be compared both with data from direct surface area measurements, giving values based on ds , and with those from the X-ray analysis, giving values based on dv .

In the method of projections, the surface area is calculated via the Cauchy expression:

$$A = (4 \sum \alpha_p / n) \quad (15.2)$$

or

$$A_v = (4 \pi \rho N_m \sum \alpha_p / n) \quad (15.3)$$

where $\sum \alpha_p$ is the sum of the plane projected areas of n randomly oriented convex particles and N_m is the number of particles per unit mass.

The modification of the microscopic method based on the interference phenomenon makes it possible to determine the real surface area without dispersion of material.

Electron microscopy can be used for surface roughness measurements with lateral and vertical resolution of 1 nm. Transmission electron microscopy (TEM) offers the possibility of providing direct imaging of individual metal particles and is one of the most used and useful tool to characterize size, shape and distribution of supported metal particles (refs. 135,136). Crystallites as small as 1 nm have been resolved and average crystallite diameters of less than 2 nm have been obtained by TEM in its bright-field and dark-field versions.

The fullest data on the surface profile of massive electrodes and *in principle* on the A value can be obtained by means of the scanning tunneling microscopy (STM) with a high resolving power (nanotopography). At ambient pressure, lateral and vertical resolutions of 1 nm and better than 0.1 nm, respectively, can be achieved (refs. 137-139).

3.4.2 Limitations. Eqns. (15.1) to (15.3) are statistical and their use gives satisfactory results in cases where the size of a great number of particles (at least hundreds) is known, and especially when the particle size distribution is sufficiently wide-ranging. The method is limited to materials with particles of no porosity and roughness. The reliability of A determination depends on the accuracy of the β_a estimation. When electron microscopy is used, samples have to withstand high vacuum treatment without showing structural changes. Electron bombardment should not affect the material. In transmission electron microscopy the accelerating voltage may be up to several hundred kV. The presence of contaminations (vacuum is rarely better than 10^{-10} bar) and the heating due to the incident electron beam could result in adsorbate-induced changes of the surface structure. In the STM method, where the electron energy lies in the meV and eV range and is *in principle* non-destructive, the accuracy of surface area determination depends on the accuracy of the corresponding shape approximation of surface formation. STM is a promising new tool for surface characterization (refs. 140-143), but as a technique for *quantitative* measurement of real surface areas it has not yet been unambiguously established.

3.4.3 Evaluations. In the simplest version, the method is applicable for estimating the surface of some types of nonporous powder-like electrode materials. It gives reliable results if the particle size exceeds (by one order of magnitude or more) the distance resolved by the microscope (1 μm for optical and 1 nm for electron microscopes). The best results are obtained for solid samples with a narrow distribution of particles and shape close to spherical. The sample observed in the microscope must be representative of the original material. Therefore, several samples should be examined.

3.5 Other methods

This group includes methods, that are relatively seldom used in surface area estimations or are limited to special cases (refs. 86,126,144-146), such as (1) weighing of saturated vapour adsorbed on a solid, (2) thermodesorption methods, (3) determining the surface area by measurement of the wetting heat (absolute Harkins-Jura method), (4) gravimetric and volumetric methods, (5) methods based on liquid or gas permeability and displacement, (6) radioisotopic methods, (7) methods of surface potential measurement of pure metal thin films, (8) methods based on the measurement of metal dissolution rate, (9) methods based on the hysteresis of adsorption isotherms, (10) methods for one-dimensional roughness (profile) determination (profilometer, stereoscan, etc.), (11) optical techniques affected by surface roughness (scattering or diffuse reflectance of light), (12) measurements based on NMR spin-lattice relaxation.

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