

DETERMINATION OF THE POTENTIALS OF ZERO CHARGE OF SOLID METALS BY MEANS OF DIFFERENTIAL CAPACITY MEASUREMENTS*

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Of the many methods of determination of the potentials of zero charge (p.z.c.) for solid electrodes, the method based on determination of the position of the differential capacity minimum¹ has given the most reliable results, the measurements being preferably carried out in dilute (10^{-3} – $10^{-4}M$) solutions of symmetrical singly charged surface-inactive electrolytes^{2,3}. The reliability of the determination of the p.z.c. increases with dilution of solution and decrease of the ion charge.

Measurements of the capacity of the electrical double layer at solid metals for determination of the p.z.c. were carried out for the first time by Borisova *et al.*⁴. The metals chosen were lead, cadmium and thallium. The hydrogen overvoltage at these metals is high, they adsorb hydrogen poorly and in the potential range -0.5 to -1.5 V (NHE) show high polarizability. It was shown for thallium, lead and cadmium in dilute solutions that on the curves of the differential capacity of the double layer *versus* potential there is a minimum, the potential of which coincides approximately with the values of the p.z.c. of these electrodes obtained by other methods. However, the results were described by curves whose shapes differed from those plotted on the basis of the double layer theory and measured experimentally at mercury¹. At solid electrodes the capacity value was found to depend on the a.c. frequency^{4,5}.

It should be stressed that the capacity measurement method gives unambiguous information on the double layer properties only under conditions when the electrode is ideally polarizable. The absence of the frequency dependence of the capacity component of the impedance which is being measured is used as one of the criteria testifying that this quantity corresponds to the double layer capacity. However, for ideally polarizable electrodes as well, the dependence of capacity on frequency can arise due to unequal accessibility of the electrode surface to alternating current, leading to a decrease with increasing frequency in the capacity value being measured. The risk of non-uniform polarization by alternating current increases with electrolyte dilution and increase of its ohmic resistance. It depends also on the geometry of the electrode positions and is particularly great with electrodes of large linear dimensions, as in refs. 1 and 5, which makes it necessary under such conditions to perform measurements with

* Dedicated to Professor Wiktor Kemula on the occasion of his 70th birthday.

low frequency currents. The use of low frequencies increases the requirements on the ideal polarizability of the electrode⁶.

Unequal surface accessibility can be due to formation (creeping in) of a thin electrolyte film between the metal and the insulator on which it is fixed. It is also possible that electrolyte may spread over the solid surface of the electrode freely immersed in liquid. In all these cases two parts of the metal surface, the surface immersed in the electrolyte and that in contact with the thin electrolyte film, are involved in the measurements, which leads to non-uniform polarization of the electrode with alternating current. The influence of electrolyte penetration on the frequency dependence of the capacity being measured can be considered on the basis of a transmission line model^{7,8}. Recently solid electrodes embedded in Teflon holders^{9,10} have been used for the elimination of this influence.

Non-uniform polarization of solid electrodes may be also due to the roughness of the surface being investigated. As shown in ref. 11, insufficient smoothness of the electrode (true surface being 3–4 times larger than visible) distorts the shape of the capacity *vs.* potential curve and is responsible for a greater dependence of the capacity being measured on frequency.

It follows from the electrical double layer theory that the potential of the minimum of the capacity curve in dilute solutions can be identified with the p.z.c. in solutions of symmetrical, specifically inactive electrolytes, the criterion of the absence of specific electrolyte adsorption being in this case the independence of the potential of the minimum of the electrolyte concentration. The conclusion that the potential of the minimum is identical to the p.z.c. is unambiguous in the case when the change in the capacity component of the impedance corresponds to the change in the capacity of the diffuse part of the double layer with changing electrolyte concentration.

A convenient graphical method for verifying the conformity of the capacity values obtained experimentally with the electrical double layer theory was suggested by Parsons and Zobel¹². According to this method the dependence is plotted as $1/C$ versus $1/C_D$ at constant surface charge (C_D = differential capacity of the diffuse double layer). In the absence of specific adsorption, this dependence is described by a straight line with a slope equal to 1, as was experimentally confirmed for mercury¹². In the case of solid electrodes, the relation between the capacity being measured and the diffuse layer capacity can be represented in accordance with Grahame's model by the relation

$$1/C = 1/fC_H + 1/fC_D$$

where C_H is the capacity of the dense part of the double layer. The coefficient f can characterize both the surface roughness and an insufficient accuracy of the determination of the electrode surface, resulting, for instance, from possible penetration of electrolyte*.

Significant progress has been made in recent years in the development of methods for preparation of smooth surfaces of solid electrodes and provision of

* The possibility of a difference in the dielectric constant of water in the diffuse layer and in the bulk of the solution, which we shall not discuss here further, has also been suggested (see ref. 13).

reliable insulation of the non-operating part of the surface, which has lead to the determination of the p.z.c. of a number of solid electrodes. Reliable and reproducible results can be obtained only after careful removal of oxide layers or adsorbed oxygen from the electrode surface¹⁴. This is achieved by cathodic reduction. However, when cathodic pre-reduction of electrodes in neutral and alkaline solutions is used, it is necessary to take into account the possibility of incorporation of alkali metals and formation of intermetallic compounds on the electrode surface, which may affect the p.z.c. values¹⁵.

In the case of bismuth, measurements were carried out with a drop-shaped electrode^{16,17}, formed upon solidification of a liquid bismuth drop squeezed out by means of a microscrew from a glass capillary. For bismuth this technique proved to be particularly successful on account of the fact that the molar volume of this metal increases upon solidification. The differential capacity measurements on this electrode showed that, just as on mercury, potassium fluoride is not specifically adsorbed¹⁸; the p.z.c. in potassium fluoride solution is -0.39 ± 0.01 V*.

The investigation of the electrical double layer properties on an anodically polished lead electrode showed that sodium fluoride is not specifically adsorbed on lead either⁹. This conclusion was drawn from the independence of the potential of the minimum on the capacity curve of sodium fluoride concentration; an additional proof was a satisfactory agreement between the experimentally obtained differential capacity curves and those calculated from more concentrated solutions with the use of the diffuse double layer theory and Grahame's model¹⁹. The p.z.c. of electropolished lead in sodium fluoride solution is -0.56 ± 0.02 V. Since when this or another method of chemical or electrochemical polishing is used, there is always a possibility of the surface investigated being contaminated by traces of the polishing solution, which may prove to be surface-active, in the case of lead the capacity measurements were also performed on an electrode whose surface had been etched in dilute nitric acid before the experiment. In that case the reproducibility of the absolute capacity values proved to be much worse than on a polished electrode and the frequency dependence to be more pronounced. However, the potential of the minimum on an etched electrode proved to have a value coinciding, within experimental error, with the value on a polished electrode. Good reproducibility in the case of the polished surface of lead enabled the use of the back integration method for the determination of the p.z.c. in solutions containing surface-active ions. The p.z.c. calculated by this method in 0.1 M NaBr and 0.1 M NaI proved to be shifted by -70 and -200 mV, respectively, relative to the p.z.c. in sodium fluoride solution. The p.z.c. value for lead given in ref. 9 (-0.56 V) was 80–100 mV more positive than the values obtained earlier^{4,20}. This seems to be due to the fact that in refs. 4 and 20 the p.z.c. was determined from the position of the minimum on the capacity curves in electrolytes prone to certain specific adsorption on lead. In the case of the SO_4^{2-} ion the fact that the potential of the minimum on the C, ϕ curve differs from the p.z.c. in fluorides is due both to specific adsorption²¹, and to electrolyte asymmetry³. In ref. 22, from the capacity curve measure-

* All potentials are referred to NHE.

ments in dilute KNO_3 , H_2SO_4 , H_3PO_4 and HNO_3 solutions, it is concluded that the SO_4^{2-} and PO_4^{3-} ions are subject to slight specific adsorption on lead. The p.z.c. values obtained from measurements in millinormal solutions (-0.59 ± 0.02 V) are in fair agreement with those given in ref. 9.

Differences between the p.z.c. values of a cadmium electrode obtained by various authors^{4,10,23} reach 200 mV. It was shown in ref. 24 that these differences are associated with the ready oxidizability of the cadmium electrode. On anodically polished and cathodically carefully reduced cadmium¹⁰ the p.z.c. in solutions of sodium fluoride, which is not specifically adsorbed, is equal to -0.72 ± 0.02 V and does not depend on the solution pH in the pH range in which the specific adsorption of OH^- ions on cadmium^{14,25} can be neglected. As shown recently^{14,26}, the p.z.c. of chemically polished cadmium is -0.75 ± 0.02 V. The adsorption of other halogen ions increases¹⁰ in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$. In 0.1 M NaBr and NaI solutions the p.z.c. calculated by the back integration method shift by -100 and -200 mV, respectively, relative to the p.z.c. in NaF.

The influence of temperature on the p.z.c. of cadmium has also been studied. In 0.01 M KF solution the change with temperature of the p.z.c. measured *versus* NCE kept at the temperature of the solution being investigated²⁷ is $+0.15 \text{ mV K}^{-1}$.

In refs. 28 and 29 the p.z.c. of a drop-shaped antimony electrode was determined. This electrode was prepared by a method similar to that used for bismuth electrodes¹⁶. As shown in these references, the NO_3^- , ClO_4^- , F^- and SO_4^{2-} anions are not specifically adsorbed on antimony. The authors conclude that the p.z.c. of antimony in the absence of specific adsorption has a value close to -0.15 V. The Cl^- , Br^- , I^- , CH_3COO^- and SCN^- anions are specifically adsorbed, the adsorption extent increasing in the sequence $\text{Cl}^- < \text{CH}_3\text{COO}^- < \text{Br}^- < \text{SCN}^- < \text{I}^-$. In solutions containing surface-active anions the p.z.c. determined by back integration depends linearly on the logarithm of the anion concentration.

The p.z.c. of a polished tin electrode determined in 0.025 N Na_2SO_4 solution, corrected for the electrolyte asymmetry³⁰ is equal to -0.43 V. This value agrees with the results obtained earlier³¹. In ref. 32 for a previously fused and solidified tin electrode the p.z.c. value was found to be -0.38 V. Determination of the p.z.c. of tin must be carried out with SO_4^{2-} or ClO_4^- solutions, as F^- ions show some specific adsorption on tin.

For a polished copper electrode a satisfactory series of the C , ϕ curves changing regularly with electrolyte concentration could be obtained³³ only in NaF solutions at pH=5.2–6.2 and, less satisfactorily³⁴, in NaClO_4 solutions. In other solutions, including those of sulphates, the C , ϕ curves are strongly distorted by the anion adsorption. The p.z.c. in 0.001 M NaF is 0.09 ± 0.015 V, in 0.001 M NaClO_4 0.025 V. Measurements were also carried out³⁴ on separate faces of a single copper crystal. However, judging by the shape of the C , ϕ curves, the surface preparation had not in that case been as good as that achieved for polycrystalline copper. In NaF solutions all p.z.c. values for single crystal faces proved to be more negative than those obtained for a polycrystalline sample.

The most accurate measurements of p.z.c. of indium were made in ref. 35. For an electropolished indium electrode in NaF solutions the p.z.c. was found to be -0.65 ± 0.02 V. According to ref. 36 the p.z.c. of an indium electrode from which a thin surface layer had been cut before measurements is -0.67 ± 0.02 V.

In ref. 37 the p.z.c. of a chemically polished thallium electrode in 0.001 M NaF was found to be -0.71 V and in 0.01 M potassium chloride solution -0.76 V.

Much attention has been and is being given to the determination of the p.z.c. of silver from the position of the differential capacity minimum. In ref. 38 the p.z.c. value of carefully cathodically reduced silver in dilute sulphate solutions was found to be -0.7 ± 0.05 V. This result was at variance with the determinations of the p.z.c. of silver by the null solution method³⁹ and with earlier capacity measurements⁴⁰, but was supported by the comparison of the shape and position of the C, ϕ curves of mercury and silver⁵⁸ in 0.01 N and 0.001 N solutions and by independent measurements by English authors⁴¹. In ref. 42, from the C, ϕ curves measured practically at one concentration, the p.z.c. value -0.44 V was found, which coincides with results ($\phi_{\varepsilon=0} = -0.45$ V) obtained by the scraping method⁴³ (however the p.z.c. value of silver recommended in a later conclusive paper by the same authors⁴⁴ was -0.64 V). This led Trassati⁴⁵ to recommend the value $\phi_{\varepsilon=0} = -0.44$ V for "normal" silver, i.e. silver with a purity no higher than 99.99%, believing that the p.z.c. of silver of higher purity could be more negative. However, this conclusion is at variance with the data of ref. 38 and later papers⁴⁶⁻⁴⁸.

Further progress was made in the determination of the p.z.c. of silver when it became possible to pass from the measurements on polycrystalline silver to those on separate faces of silver grown electrolytically in capillaries⁴⁹ and obtained by other methods⁵⁰⁻⁵³. The main results are listed in Table 1. The p.z.c. values obtained for the same face show good coincidence. For a single crystal on whose surface there are faces with different indices the value $\phi_{\varepsilon=0} = -0.66 \pm 0.03$ V was determined. It follows from Table 1 that the p.z.c. of separate faces of silver can lie both more positive and more negative than the p.z.c. of polycrystalline silver: the p.z.c. lies more negative the lower the packing density of the face⁴⁹.

The value -0.7 ± 0.05 V for the p.z.c. of polycrystalline silver can be considered to be firmly established, but it remains yet to explain the much more positive values obtained in earlier papers. It is most likely that those values refer to an oxidized surface. Thus, it was shown⁴² that the minimum on the differential capacity curve shifts sharply towards positive values (up to 0.0 V) upon application of anodic and cathodic pulses, after which adsorbed oxygen is certain to remain on the silver surface.

The differential capacity measurements carried out on a gold electrode show that, just as for silver, the crystallographic orientation of the face affects the electrical double layer properties⁵⁴⁻⁵⁶. However, it has been impossible so far to interpret all the results obtained. The C, ϕ curves in diluted NaF solutions show minima which smooth out, but do not disappear completely, with rising solution concentration. The potentials of the minima are 0.19, 0.38, 0.50 V for the (110), (100) and (111) faces, respectively. According to the

TABLE 1

P.Z.C. OF THE FACES OF SILVER SINGLE CRYSTALS AND POLYCRYSTALLINE SILVER

Face	Method of surface preparation	Electrolyte	P.z.c./V	Reference
(111)	1 Faces electrolytically grown in glass capillaries, cathodically polarized at -0.6 to -0.7 V	$0.005\text{ }N$ Na_2SO_4	-0.48 ± 0.02^a	49
	2 Electropolished in cyanide solution, cathodically polarized at -1.26 V	$0.0025\text{ }M$ K_2SO_4	-0.52 ± 0.03^a	50
	3 Electropolished in cyanide solution, cathodically polarized at -1.46 V	$0.005\text{ }M$ NaF	-0.45 ± 0.01	51
	4 Electropolished in pyrophosphate solution, cathodically polarized at -0.8 to -0.9 V	$0.001\text{ }M$ KF	-0.46 ± 0.02	53
	5 Electropolished in pyrophosphate solution, cathodically polarized at -0.8 to -0.9 V	$0.01\text{ }N$ Na_2SO_4	-0.46 ± 0.02^a	53
(100)	1 Electrolytically grown faces, cathodically polarized at -0.6 to -0.7 V	$0.005\text{ }N$ Na_2SO_4	-0.63 ± 0.02^a	49
	2 Electropolished in pyrophosphate solution, cathodically polarized at -0.8 to -0.9 V	$0.01\text{ }N$ Na_2SO_4 $0.005\text{ }M$ NaF	-0.65 ± 0.02^a -0.61 ± 0.02	53 59
	3 Electropolished in cyanide solution, cathodically polarized at -1.26 V	$0.0025\text{ }M$ K_2SO_4	-0.66 ± 0.02^a	50
(110)	1 Electropolished in cyanide solution, cathodically polarized at -1.26 V	$0.0025\text{ }N$ K_2SO_4	-0.74 ± 0.02^a	50
	2 Electropolished in cyanide solution	$0.005\text{ }M$ NaF	-0.77 ± 0.01	52
Polycrystalline silver	1 Etched in HNO_3 , polished with glass powder, degreased by boiling in 10% NaOH , cathodically polarized at -0.9 V	$0.002\text{ }N$ Na_2SO_4	-0.7 ± 0.05	38
	2 Etched in HNO_3 , polished with glass powder, degreased by boiling in 10% NaOH , cathodically polarized at -0.9 V	$0.001\text{ }N$ Na_2SO_4 + $0.0001\text{ }N$ H_2SO_4 ; $0.01\text{ }M$ KOH	-0.7 ± 0.05	58
	3 Mechanically polished, etched in 10% HClO_4 , cathodically polarized at -0.3 V	$0.01\text{ }M$ NaClO_4	-0.7	41
	4 Sprayed under vacuum	$0.01\text{ }N$ Na_2SO_4	-0.68 ± 0.02	47
	5 Electropolished in cyanide solution, cathodically polarized at -1.26 V	$0.005\text{ }M$ NaF	-0.72 ± 0.01	48
Single crystal faces with different indices	Electropolished in pyrophosphate solution, cathodically polarized at -0.8 to -0.9 V	$0.01\text{ }N$ Na_2SO_4	-0.66 ± 0.03^a	53

^a Corrected for the electrolyte asymmetry.

authors of ref. 56 only on the (110) face can the potential of the capacity curve minimum be identified with the p.z.c. In ref. 55 the p.z.c. of polycrystalline gold was determined. The curves obtained satisfy the Parsons-Zobel criterion if the roughness factor is taken to be equal to two. The value $\varphi_{\varepsilon=0}=0.18$ V is close to that on the (110) face. According to ref. 57, the p.z.c. of gold in 10^{-3} M HClO_4 is 0.19 V on the (100) face and 0.24 V on the (110) face. However, the shape of the C, φ curves obtained in ref. 57 makes these results questionable. Table 2 lists the p.z.c. values which we believe to be the most reliable of those metals considered above.

TABLE 2

POTENTIAL OF ZERO CHARGE OF SOLID METALS WHICH DO NOT ADSORB HYDROGEN (RECOMMENDED VALUES)

<i>Metal</i>	<i>Solution</i>	<i>P.z.c./V</i>	<i>Reference</i>
Bismuth	0.002 M KF	-0.39 ± 0.02	18
Lead	0.001 M NaF	-0.56 ± 0.02	9
Cadmium	0.001 M NaF	-0.75 ± 0.02	14, 26
Antimony	0.002 M KClO_4	-0.15 ± 0.02	28, 29
Tin	0.002 M KClO_4	-0.38 ± 0.02	32
Thallium	0.001 M NaF	-0.71 ± 0.04	37
Indium	0.003 M NaF	-0.65 ± 0.02	35
Copper	0.001 M NaF	0.09 ± 0.02	33
Gold (polycryst.)	0.002 M NaF	0.18 ± 0.01	55
Gold (110)	0.005 M NaF	0.19 ± 0.01	56
Silver (polycryst.)	0.001 N Na_2SO_4	-0.7 ± 0.05	58
Silver (single cryst.)	0.01 N Na_2SO_4	-0.66 ± 0.03^a	53
Silver (111)	0.001 M KF	-0.46 ± 0.02	51, 53
Silver (100)	0.005 M KF	-0.61 ± 0.02	59
Silver (110)	0.005 M NaF	-0.77 ± 0.01	52

^a Corrected for the electrolyte asymmetry.

SUMMARY

The results of the determination of the potentials of zero charge of solid metals from the position of the minimum on the electrode differential capacity-potential curve in dilute surface-inactive electrolyte solutions have been considered. Possible sources of error in such determinations have been pointed out. On the basis of an analysis of the experimental data, those values have been recommended which at present seem to be the most reliable.

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