Translated from *Uspekhi Khimii*, **44**, 2001-2007 (1975) U.D.C. 541.135.4

The Electrical Double Layer Capacitance and the Zero-charge Potentials of Metals in a Solid Electrolyte

S.V.Karpachev, I.D.Remez, V.V.Sal'nikov, and A.T.Filyaev

Studies of the properties of the electrical double layer and of the zero-charge points for certain metals in a solid electrolyte consisting of stabilised zirconium dioxide are reviewed. The influence of the electrode potential, temperature, and composition of the gas phase on the double layer capacitance and the zero-charge point is examined. A correspondence is established on the basis of experimental data between the potential of the minimum on the "capacitance-potential" curve and the zero-charge points for tin and silver.
The bibliography includes 16 references.

CONTENTS

I. Introduction 946
II. Experimental data for the structure of the electrical double layer in solid electrolytes 946
III. Zero-charge potentials of metals 948

I. INTRODUCTION

As a result of research by Frumkin and his school, the importance of studies of the structure of the electrical double layer and zero-charge potentials for electrochemical kinetics has now been demonstrated. In a study of the cathodic evolution of hydrogen from acid aqueous solutions Frumkin et al.[1] discovered the dependence of the overvoltage on the concentration of an extraneous electrolyte at a constant current density and acid concentration. They showed that this is due to the influence of the added neutral electrolyte on the double layer structure (on the ψ_1 potential). Furthermore, Frumkin showed[2] that in the cathodic reduction of complex anions the current decreases sharply until the attainment of the zero-charge potential owing to the increasing diffuseness of the double layer. This effect was established for several metals, the zero-charge potentials of which are appreciably different.

Electrochemical cells with an electrolyte consisting of stabilised zirconium dioxide have now acquired great practical importance and for this reason a more profound study of the electrochemical kinetics in solid electrolytes has become necessary; the investigation of the properties of the electrical double layer and of the zero-charge potentials of metals in the stabilised zirconium dioxide solid electrolyte has begun. The experimental data obtained for this new type of electrolyte are extremely interesting in the light of the theoretical ideas developed by Frumkin and his school.

II. EXPERIMENTAL DATA FOR THE STRUCTURE OF THE ELECTRICAL DOUBLE LAYER IN SOLID ELECTROLYTES

The first measurements of the double layer capacitance in the stabilised zirconium dioxide electrolyte were made by ourselves on a platinum wire electrode[3]. The dependence of the electrical double layer capacitance on potential is presented in Fig. 1. The capacitance–potential curves have a distinct minimum at a specific potential. The measurements were made at 1020°C in an electrolyte having the composition 85 mole % ZrO_2 + 15 mole % CaO in an atmosphere of argon freed from oxygen by being passed over metallic calcium at 650°C. All the measurements were performed at 10 kHz with the capacitance and resistance connected in series in one of the arms of an a.c. bridge. It was subsequently established that at 10 kHz there is still some dispersion of the capacitance and therefore the measured capacitance values involve an error; however, the type of the variation of the capacitance with potential is probably correct.

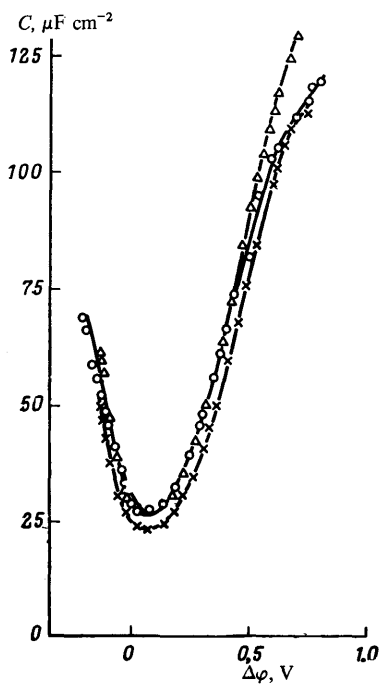


Figure 1. Variation of the differential electrical double layer capacitance with potential on a platinum electrode. The reproducibility of the results for three specimens is indicated.

We assumed that the dispersion of the capacitance at such comparatively high frequencies is due to the low value of the Faraday impedance caused by the high temperature. Hence it was necessary to carry out experiments at higher frequencies. Furthermore, it was desirable to employ as the test electrode a drop of fused metal rather than the solid metal. Evidently in this case the surface area of the junction between the electrode and the electrolyte, determined from geometrical dimensions, is closer to the true value.

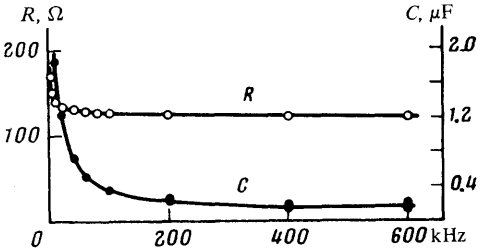


Figure 2. Variation of the capacitance and resistance with frequency.

The double layer capacitance was measured for liquid silver and tin drops at the equilibrium potential in the same electrolyte at 970°C in an atmosphere of purified argon[4]. The electrode potentials were determined with the aid of an electrochemical gas-analyser, which consisted[5] of a ceramic test-tube made of stabilised zirconium dioxide with platinum electrodes attached to its inner and outer surfaces. The test-tube was positioned so that the outer electrode was in the gas space of the electrochemical cell and the inner space of the test-tube communicated with the atmosphere. The potential difference arising in the electrochemical concentration cell between the platinum electrodes made it possible to determine the oxygen pressure in the gas space of the cell; it amounted to 10^{-12}–10^{-14} atm. The impedance of the second platinum electrode (which was deposited on the surface of the solid electrolyte plate on the side opposite to that containing the drop) was neglected because of its large area. Separate experiments established that the auxiliary electrode was virtually unpolarised under the experimental conditions.

Fig. 2 presents curves characterising the dispersion of the resistance R and the capacitance C. The values of R and C were recalculated for a series-connected circuit. Evidently at a frequency of about 500 kHz a constant capacitance is reached and the measurements were made at this frequency. Having estimated the surface area of the junction between the metal drop at the electrolyte, the specific capacitance of the double layer was determined approximately. For silver and tin, it was found to be the same (20 μF cm^{-2}).

Somewhat later we made a detailed study at 970°C of the dispersion of the capacitance and resistance[6] using zirconium dioxide stabilised by yttrium oxide as the electrolyte. The oxygen pressure in the cell was maintained in the range 10^{-12}–10^{-14} atm, as before. The dispersion of the capacitance was investigated as a function of the yttrium oxide content in the solid electrolyte and the electrode potential. It was established that the capacitance in the series-connected circuit becomes constant at a frequency of 600 kHz. In the range of frequencies from 400 to 600 kHz the capacitance changed insignificantly—by up to 10%; therefore all subsequent experiments were performed at a frequency of 400 kHz, since the error in the measurement of the impedance components increased with a.c. frequency. This suggests that, with the series-connected resistance and capacitance, whose impedance is equal to that of the cell, the resistance refers to that of the electrolyte and the capacitance is that of the electrical double layer.

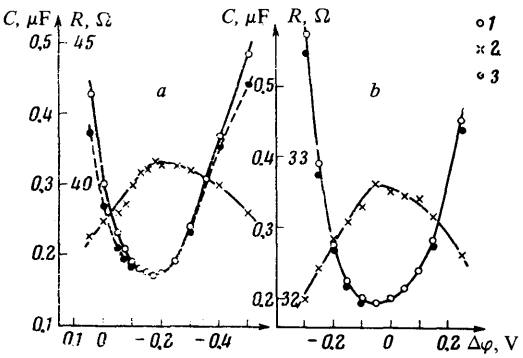


Figure 3. Variation of the differential electrical double layer capacitance (*1*) and of the resistance of the electrolyte (*2*) with polarisation for liquid silver and tin drops: *a*) tin; *b*) silver; points *3* represent the variation of the capacitance with allowance for the change in the area of the electrode/electrolyte junction as a result of the spreading of the drop.

We regarded the method described as satisfactory and used it to investigate the double layer capacitance on liquid silver and tin drops. The electrolyte disc had a diameter of 17 mm and was 1.8 mm thick; the diameter of the metallic drops was 0.7–1.0 mm. The decrease of the potential in the electrolyte may be neglected in view of the low polarising currents and the high conductivity of the electrolyte. Since the surface area of the platinum electrode was large, its contribution to the measured capacitance was neglected. The potential of the test electrode was reckoned relative to an air reference electrode.

Fig. 3 presents curves relating to the capacitance of the liquid silver and tin electrodes to polarisation. They have a deep minimum at specified potentials. The potentials of the minima on the capacitance curves for silver and tin are respectively −1.08 and −1.29 V. Curves relating the capacitance to the potential at different oxygen pressures in the gas phase were also obtained and it was found that a change in oxygen pressure does not affect the shape of the curves and the positions of the potential minima. One may conclude that the test electrodes are reversible with respect to oxygen. For this reason, regulation of the potential by altering the oxygen pressure in the gas phase or by polarisation with a direct current leads to the same result.

Fig. 3 also presents curves for the variation of the resistance of the electrolyte with electrode polarisation,

which has a distinct maximum. This can be explained by the fact that the surface tension at the boundary between the liquid drop and the solid electrolyte varies with polarisation, and hence the area of the junction between the drop and the electrolyte also varies. There is reason to believe that the resistance maximum corresponds to the interfacial tension maximum, i.e. to the zero-charge potential of the metal. Since the minimum on the capacitance curve and the maximum on the resistance curve occur at virtually the same potential, one may say that the potential of minimum capacitance coincides with the zero-charge potential. It might have been supposed that, owing to the variation of the area of the junction mentioned above, there is a change in the dependence of the capacitance on the potential and in the potential of minimum capacitance. However, the electrolyte resistances at different potentials show that this effect is very small and does not alter either the potential of minimum capacitance or the variation of the capacitance with potential (Fig. 3, dashed curve).

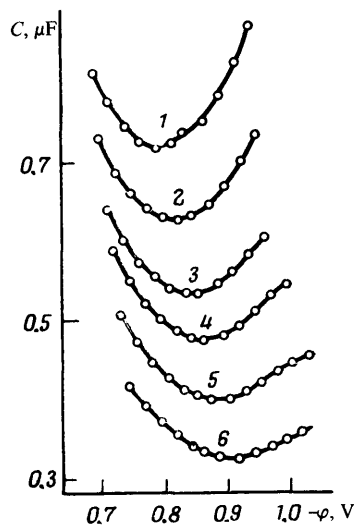


Figure 4. Variation of the electrical double layer capacitance with potential for a liquid silver electrode at different temperatures (°C): 1) 1123; 2) 1093; 3) 1060; 4) 1032; 5) 1001; 6) 969.

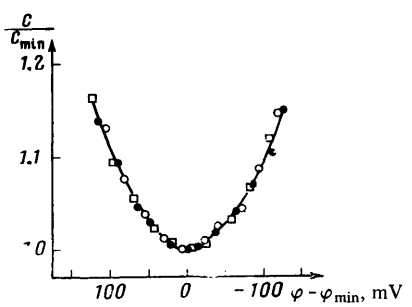


Figure 5. Variation of C/C_{min} with $\varphi - \varphi_{min}$ for three temperatures (1123°, 1060°, and 969°C); C is the electrical double layer capacitance at a potential φ and C_{min} and φ_{min} are the capacitance and potential corresponding to the minimum on the curve (see Fig. 4).

The temperature variation of the double layer capacitance was studied in the temperature range 970–720°C in an atmosphere of helium at a frequency of 400 kHz for a silver electrode in an electrolyte to which 8 mole % of yttrium oxide had been added[7]. The results (Fig. 4) show that the minimum capacitance increases with temperature and the minimum itself becomes somewhat sharper on the corresponding curves. However, when the capacitance is referred to its minimum value at a given temperature, then the points for all six temperatures fit on the same curve (Fig. 5). Hence one may conclude that the variation of the capacitance with potential is of the same type over the entire experimental temperature range. Indeed, if the shape of the curves were partly determined by the Faraday process, it would be difficult to expect such an agreement. Since the points on the $\lg C - 1/T$ curve fit satisfactorily on a straight line, one may conclude that the double layer capacitance increases exponentially with temperature over the entire experimental range of potentials. Similar capacitance–potential curves were obtained also in fused electrolytes[8].

III. ZERO-CHARGE POTENTIALS OF METALS

The capacitance–potential curves for dilute aqueous solutions also have a minimum coinciding with the zero-charge potential in the case of a symmetrical electrolyte. For aqueous solutions, a theory of this phenomenon was devised by Frumkin. However, there is as yet no corresponding theory for solid and fused electrolytes. Therefore further studies on the double layer capacitance at the boundary between liquid metals and a solid electrolyte are necessary, measurements of this kind in electrolytes with different defective structures and for a wider range of metals being particularly needed.

The zero-charge potentials of liquid silver, tin, gold, and copper were determined in the electrolyte 0.887 ZrO_2 + 0.08 Y_2O_3 + 0.04 Al_2O_3.[9] The solid electrolyte consisted of a disc 17 mm in diameter and 2–3 mm thick. The metal drop diameter was 2–3 mm. The electrolyte discs were prepared by the method already described. The measurements on silver and tin were made at 1085°C, on gold at 1190°, and on copper at 1174°C in an atmosphere of purified helium. The pressure of oxygen in helium was 10^{-12}–10^{-14} atm. The helium was freed from oxygen and the residual oxygen pressure was determined as in the measurements of the electrical double layer capacitance.

The zero-charge potential was determined by measuring the variation of the wetting angle θ with the potential. The wetting angle was determined from photographs of the drop profile, and $\cos\theta$ was plotted against φ. Under the conditions of a constant composition of the gas atmosphere, at the potential corresponding to zero charge the angle θ has the minimum value and the $\cos\theta - \varphi$ curves passed through a maximum. The platinum electrode, deposited on the lower side of the disc, was used to polarise the drop with a direct current. The test electrode potential was measured relative to an air reference electrode.

The curves obtained for silver and tin are presented in Fig. 6. Relative to the air reference electrode, the zero-charge potentials of silver and tin are respectively −0.97 and −1.23 V.[9] The high experimental temperature and the test metals were chosen so that the equilibrium oxygen pressure over the metal oxides was greater than the residual oxygen pressure in the cell at a given temperature. The following factor is striking. The difference between the zero-charge potentials of silver and tin

is $\varphi_0^{Ag} - \varphi_0^{Sn} = 0.26$ V. On the other hand, the difference between the potentials corresponding to the minimum double layer capacitances on the same metals is $\varphi_C^{Ag} - \varphi_C^{Sn} = 0.21$ V. These results show that the difference between the potentials of minimum capacitance for silver and tin is approximately the same as the difference between their zero-charge potentials. The agreement may be regarded as satisfactory bearing in mind that the accuracy of the determination of the zero-charge potentials is to within 25 mV.

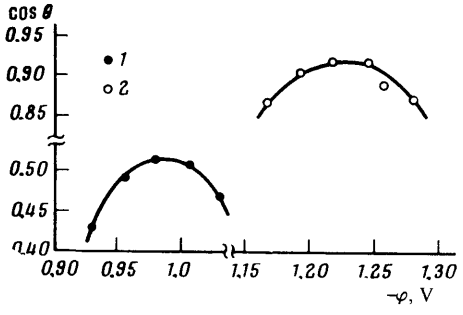


Figure 6. Variation of the cosine of the wetting angle with potential: 1) silver; 2) tin.

In a study of the correspondence between the potential of minimum double layer capacitance and the zero-charge potential in solid electrolytes[10] it was shown that such agreement can be accounted for when certain assumptions are made concerning the structure of the surface solid electrolyte. It is quite possible that such correspondence does not always obtain in solid and fused electrolytes.

The results of the measurements of the zero-charge potentials were adjusted to the same temperature (1085°C) by the procedure of Remez et al.[11] and are given in the Table.

The zero-charge potentials φ_0^M (M = metal).

Metal	Solid electrolyte		Aqueous electrolyte
	φ_0^M relative to air electrode, V	φ_0^M relative to φ_0^{Sn}, V	φ_0^M relative to φ_0^{Sn}, V
Silver	−0.97	+0.26	−0.32
Gold	−0.99	+0.24	+0.56
Copper	−0.85	+0.38	+0.47
Tin	−1.23	0.00	0.00

The values recommended by Leikis et al.[12] were used as the zero-charge potentials in aqueous solutions. The greatest difference relative to aqueous solutions is observed for silver. The zero-charge potentials of gold are of the same sign, but differ by 0.32 V. The difference for copper is a minimum (0.09 V). The experimental data obtained are insufficiently extensive to reach general conclusions on their basis. However, one may say a few words about the tabulated data.

Frumkin[1] demonstrated convincingly the role of the adsorption of not only ions but also neutral molecules both with and without intrinsic dipole moments. Furthermore, Frumkin[13] put forward the idea that, under certain conditions, the difference between the zero-charge potentials of two metals may be equal to the difference between their electrode work functions. Later Frumkin and coworkers[14] devised a detailed theory of this effect in which account is taken of the different degrees of adsorption of solvent molecules, particularly water molecules, on different metals. However, it is hardly useful to make such a comparison under the conditions of our experiments, since the electrode work functions of the metals investigated were determined at room temperature and our experimental temperature was in excess of 1000°C; it is necessary to determine the electrode work functions of the metals at high temperatures. Nor can one rule out the possibility that in our case adsorption, which may be different for different metals, plays a role in the zero-charge potential jump. For example, one may postulate the adsorption of oxygen ions or their vacancies.

The results of a study of the effect of carbon monoxide at the zero-charge potentials of silver and tin must be considered[15]. The experimental technique was as described above. When the gas phase contained 50 mole % of carbon monoxide, the zero-charge potential of silver was found to be −1.16 V relative to the air reference electrode. As stated above, in an atmosphere of helium this potential is −0.97 V. Thus the zero-charge potential of silver was displaced in the negative direction by 0.19 V as a result of the presence of carbon monoxide in the gas phase. The zero-charge potential of tin in the presence of 50 mole % of carbon monoxide was found to be −1.21 V, the corresponding value in helium being −1.23 V. The difference of 0.02 V is within the limits of the error of the measurements and one may assume that the change in the gas phase did not affect the position of the zero-charge point for tin.

The above shift of the zero-charge potential of silver can be tentatively explained by the adsorption of carbon monoxide molecules at the interface. Possibly chemisorption takes place in the present instance. The carbon monoxide molecule has a comparatively small dipole moment (0.12×10^{-18} absolute electrostatic units), but one cannot rule out the possibility that, as a result of adsorption, it acquires a larger dipole moment. It is appropriate to mention here our studies of the differential double layer capacitance on silver in an atmosphere of CO_2 and CO at 970°C.[16] The dependence of the capacitance on the potential was investigated and, as in an atmosphere of helium, curves with a deep minimum were obtained. The minimum capacitance increases with the CO content in the gas phase and the potential corresponding to the minimum on the curves also shifts in the negative direction.

REFERENCES

1. A. N. Frumkin, V. S. Bagotskii, Z. A. Iofa, and V. N. Kabanov, "Kinetika Elektrodnykh Protesessov" (Kinetics of Electrode Processes), Izd. Moskov. Gos. Univ., 1952.
2. A. N. Frumkin, Svensk. kemisk Tidskr., 77, 6 (1965).
3. A. T. Filyaev, S. V. Karpachev, and S. F. Pal'guev, Dokl. Akad. Nauk SSSR, 149, 909 (1963).
4. A. T. Filyaev, S. V. Karpachev, and I. D. Remez, Elektrokhimiya, 11, 293 (1975).

5. H. Peters and H.-H. Möbius, DDR. P. No. 21673 (1961).
6. I. D. Remez, A. T. Filyaev, and S. V. Karpachev, Elektrokhimiya, 10, 337 (1974).
7. I. D. Remez, S. V. Karpachev, L. M. Solov'eva, V. N. Chebotin, and A. T. Filyaev, Elektrokhimiya, 11, 292 (1975).
8. E. A. Ukshe, N. G. Bukun, and D. I. Leikis, Zhur. Fiz. Khim., 36, 2322 (1962) [Russ. J. Phys. Chem., No. 11 (1962)].
9. S. V. Karpachev, V. V. Sal'nikov, and A. T. Filyaev, Elektrokhimiya, 8, 1856 (1972).
10. V. N. Chebotin and L. M. Solov'eva, Elektrokhimiya, 4, 858 (1968).
11. I. D. Remez, V. N. Chebotin, L. M. Solov'eva, and S. V. Karpachev, Elektrokhimiya, 11, 296 (1975).
12. D. I. Leikis, K. V. Rybalka, E. S. Sevastyanov, and A. N. Frumkin, Electroan. Chem. Interfac. Electrochem., 46, 161 (1973).
13. A. Frumkin, Svensk Kemisk Tidskr., 77, 300 (1965).
14. A. Frumkin, B. Damaskin, I. Bagotskaya, and N. Grigor'ev, Electrochim. Acta, 19, 75 (1974).
15. V. V. Sal'nikov, S. V. Karpachev, and A. T. Filyaev, Elektrokhimiya, 10, 1384 (1974).
16. I. D. Remez, V. N. Chebotin, and S. V. Karpachev, Elektrokhimiya, 11, 642 (1975).

Institute of Electrochemistry,
The Urals Scientific Centre,
USSR Academy of Sciences,
Sverdlovsk