AUTOMATIC COMPENSATION OF OHMIC POTENTIAL DIFFERENCE IN POTENTIOSTATIC MEASUREMENTS

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In 1975-1977, under the Council of Mutual Economic Aid (COMECON), in a program of scientific-technical cooperation on the problem of devising measures for protection of metals from corrosion, there have been organized joint international tests of potentiostatic apparatus with automatic compensation of the ohmic potential difference, developed and produced in Hungary and the German Democratic Republic (GDR). The aim of the tests was to elucidate the special features and optimal conditions for the use of these pieces of apparatus and to determine the prospects for further developments. The tests were made in Hungary, the GDR, and the USSR, and involved workers from institutes in these countries.

Valid electrochemical investigations are, of course, possible only with correct registration of the potential of the test electrode. Errors are introduced by the ohmic potential difference (OPD) which arises when a polarizing current flows (the IR error); the OPD is usually localized in the electrolyte between the tip of the measurement capillary and the working electrolyte (WE) or in the surface layers of the electrode itself. The IR error is marked when the current density is high, when the medium has a high resistivity, or when the electrode is covered by a poorly conducting film (e.g., a salt or paint-and-varnish film). The rise in the IR error with the density of the polarizing current leads to an increasing shift in the actual potential, and characteristic distortions arise on an anodic potentiostatic curve recorded without taking account of the OPD (Fig. 1).

During registration of anodic potentiodynamic curves with a constant rate of change of the standard potential, the actual rate of shift of potential continuously changes; in sections AB and DE (Fig. 1) the IR error continuously increases, and $(\partial\varphi/\partial\tau)_{true} < (\partial\varphi/\partial\tau)_{rec}$. In section BC,

$$(\partial\varphi/\partial\tau)_{true} > (\partial\varphi/\partial\tau)_{rec};\ (\partial\varphi/\partial\tau)_{true} \to (\partial\varphi/\partial\tau)_{rec}$$

as IR → 0.

The dynamic effect is especially marked when the behavior of the electrode depends on its history (the mode of approach to the given potential). There may then be distortions in the characteristic values of both

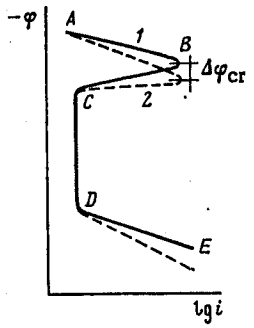

Fig. 1. Schematic anodic potentiostatic curve for passivated metal: 1) true; 2) distorted by uncompensated IR error. $\Delta\varphi_{cr}$) distortion of critical passivation potential.

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the potential and the current density. This can be illustrated by the characteristic curves of the cathodic reaction of reduction of a depolarizer, measured with linear potential sweep or by cyclic voltamperometry. The volt–ampere curves are characterized by the peak of the current i_p, which arises at some characteristic potential φ_p. Near φ_p there is a sharp rise in i_pR, i.e., there is a marked OPD in the measurement circuit, which in turn causes a shift in φ_p toward more negative values. In general, i_p rises in proportion to the rise in the depolarizer concentration C_0 and the rate of shift of potential V_φ [1]. Consequently, the deviation of φ_p from the true value is the higher, the higher C_0 and the more rapid the potential sweep. Since the dependence of φ_p on C_0 and V_φ is one of the main criteria of reversibility of an electrochemical system and of the presence of chemical and adsorption stages in the overall cathode process [1-3], neglect of the distorting influence of OPD can lead to erroneous interpretations of these laws.

An OPD can also distort the actual value of i_p. In the absence of an appreciable OPD, the electrode potential, which is determined by the reaction of reversible reduction of the depolarizer, is a linear function of time,

$$\varphi=\varphi_0-V_\varphi\tau_1, \tag{1}$$

where φ_0 is the potential at the start of the sweep. If there is an appreciable OPD, the time dependence of the potential deviates from Eq. (1) [4]:

$$\varphi=\varphi_0-V_\varphi'\tau_2. \tag{2}$$

In general, the OPD is not a linear function of time. However, to a first approximation we may assume that in some interval $\Delta\varphi$ near φ_p the value of φ_{ohm} varies linearly with τ. Then the time required to overcome the interval $\Delta\varphi$ in the absence of an OPD is

$$\tau_1=\Delta\varphi/V_\varphi, \tag{3}$$

and that with an appreciable OPD is

$$\tau_2=(\Delta\varphi+i_pR)/V_\varphi, \tag{4}$$

where i_p is the true current at the peak of the potentiodynamic curve corresponding to the rate of potential change V'_φ. From Eqs. (1)-(4) it follows that

$$V_\varphi'=V_\varphi\frac{1}{1+Ri_p/\Delta\varphi}. \tag{5}$$

If there is a linear change of potential, i_p is proportional to the product $(V_\varphi)^{1/2}C_0$. From Eq. (5) it follows that owing to the OPD the dependence of the peak current on the potential sweep rate, which is the basis for determination of the experimental kinetic parameters of the reaction of reduction of the depolarizer, will deviate from the theoretical value. This deviation increases with the depolarizer concentration, with the rate of change of potential, and with the electrolyte resistance.

Correct measurement and regulation of the potential, especially in dynamic measurements, are far from always possible by existing methods, which involve specially designed capillaries [5] and calculation of the IR error by various methods [6-9].

The most promising method involves potentiostatic apparatus with automatic compensation of the IR error. Such units, based on the current-interruption method [10, 11] or measurement of R with high-frequency ac [12, 13], permit us to take continuous account of the changes in both the resistance and the polarizing current density, and give more complete compensation of the IR error than potentiostats with manual IR compensation in which resistance changes are not automatically compensated.

In the international tests we worked with three types of potentiostatic units with automatic OPD compensation (Table 1).

The Meinsberg Scientific-Research Institute (GDR) has developed a potentiostatic apparatus with automatic IR compensation including a PS-3 potentiostat, a PU-1 interrupter unit [13], a PV-1 programmer, the PT-1 device for checking the potentiostats (equivalent circuit to an electrochemical cell), and a KMTs-1 cell for corrosion tests. Automatic IR compensation is effected with the aid of the PU-1 interrupter unit; interruption is effected by switching a controlled resistance in series with the working electrode. The design and operational principles are described in [14].

At the Jozef Atilla University (Szeged, Hungary) a potentiostat has been developed, based on the principle of interruption of the polarizing current (the AFKEL 407); it differs in design from the Meinsberg SRI

TABLE 1. Comparative Characteristics of Potentiostatic Units with Automatic IR Compensation

Parameter	SRI Meinsberg	AFKEL	ON-405
Maximum output voltage, V	± 10	± 25	± 30
Maximum output current, A	± 0.5	0 0.25	± 1
Maximum compensated voltage, V	± 1.0	± 5.0	± 5.0
Potentiostatic range, V	± 2.0	± 2.4 (with external controller, ± 10.0)	+ 2.0
Compensation principle	Interruption	Interruption	Ac measurement (4-5 kHz)
Interruption time, μsec	10-1000	—	—
Polarization time, msec	Pulse duty factor 1:10	5-50	—
Measurement delay time, μsec	—	0.01-10	—
Measurement time, μsec	—	20	—
Programming in potentiometric conditions	External PV-1 programmer	AFKEL-1800 function generator	Built-in scanning unit, 5-600 mV/min
Additional equipment	—	Logarithmic amplifier	—
Size, mm	540 × 290 × 155; interruptor unit, 375 × 248 × 156	480 × 300 × 100	330 × 140 × 350
Mass, kg	11 (interruptor unit, 7.0)	2 units	2 units, 8 and 5

potentiostat, and is used in conjunction with the previously developed AFKEL 406 potentiostat, the AFKEL 1800 programmer, and the AFKEL 1001 logarithmic amplifier.

The University of the Chemical Industry, Veszprém, Hungary, has developed the ON-405 potentiostat (produced commercially by the "Radelkis" factory), which operates on the principle of ac resistance measurement (4-5 kHz) [12, 13].

To test the potentiostats with IR compensation, identical equivalent circuits (Fig. 2) were used in Hungary, the GDR, and the USSR, differing only in the nominal characteristics of the resistors and capacitors (Table 2).

Joint tests on the potentiostats were made with the NIFKhI* and PT-1 equivalent circuits, which use transistors to reproduce the characteristic changes in the polarization resistance of a passivated metal and can model three main cases encountered in the practice of potentiostatic measurements – in a low-resistance medium with high polarizing current densities of $(10^{-2}$-$1.0)$ A/cm^2; in a high-resistance medium (up to 10^2-10^5 Ω); and in a low-resistance medium with electrodes coated with high-resistance films.

Nonlinear equivalent circuits also enable us to observe the influence of IR compensation on the shape of the polarization curve of a passivated metal (Fig. 3). For comparison, the original curve (curve 1) was obtained with $R_k = 0$ (in the absence of OPD). When $R_k = 0$, we observe a shift of the curve toward positive potentials (with constant height of the maximum), increasing with R_k (curves 4, 5, and 2). With an interrupter unit, all the curves (6 and 3 in Fig. 3) are practically coincident with each other and with the original curve 1.

*The NIFKhI equivalent circuit was developed in collaboration with workers at the All-Union Scientific-Research Institute of Automation of Apparatus for Metrology (Tbilisi).

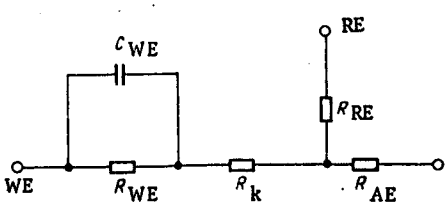

Fig. 2. Equivalent linear circuit of electrochemical cell: WE) working electrode; AE) auxiliary electrode; RE) reference electrode.

TABLE 2. Principal Parameters of Equivalent Circuits of Electrochemical Cells

Type of equivalent	R_{WE}, Ω	C_{WE}, μF	R_k	R_{RE}	R_{AE}
			Ω		
PT-1	2; 20; 200; 2000, 20000	0; 0,1; 1,0; 10; 50 External	0; 0,1; 1,0; 10; 100; 1000; 10 000 0–1000	0; 100; 10^3; 10^4 10^5; 10^6	0; 7; 70; 700; 7000; 70 000
NIFKhI	6; 600	0; 0,1; 1,0 2,0; 4,0	1; 2,5; 5,0; 500 0–1000	0; 10^2; 10^4; 10^7	20; 2000
IATÉ	10; 100	0,1; 1,0; 10; 100	0; 1; 10; 20; 100	0; 100; 10^4; 10^7	70;
AFKI			0–200		7000

Such tests not only permit us to monitor the correctness of the automatic compensator, but also to find its best operating conditions (interruption time) according to the parameters of the electrochemical cell.

With the equivalent circuits we also checked the dynamic characteristics of the potentiostats in the compensation mode. With a linear equivalent circuit we recorded the potential–current dependences for automatic linear rise and fall of the standard voltage with different fixed rates and compared them with the original curve measured with $R_k = 0$ (without compensation).

In the course of the experiment we varied $(RC)_{WE}$. The agreement between the forward and reverse curves over the whole working range of the equivalent-circuit parameters at maximum potential variation rate shows that the action is sufficiently rapid for potentiodynamic measurements. For the PS-3 potentiostat with the PU-1 unit good compensation is attained with maximum variation of the sweep rate (2 V in 3.33 min); the ON-405 potentiostat gives satisfactory compensation for the maximum available sweep rate of 0.6 V/min. The AFKEL set can be used for dynamic investigations up to 10 V/h.

Measurements on the equivalent circuits embraced the entire range of operation of the devices when the various parameters are varied. In each series of measurements, at constant values of R_{WE}, R_{RE}, and R_{AE}, the interruption time t, and the preset potential, the capacitance of the working electrode, and the value of R_k were varied. To keep the potential at a given level while the potentiostats are working with interruption, the

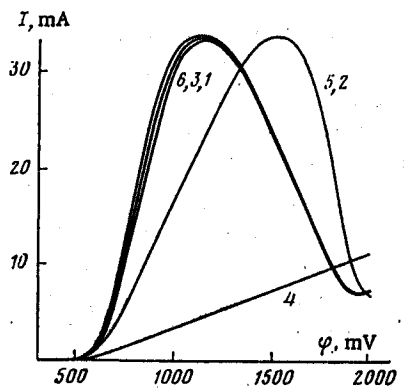

Fig. 3

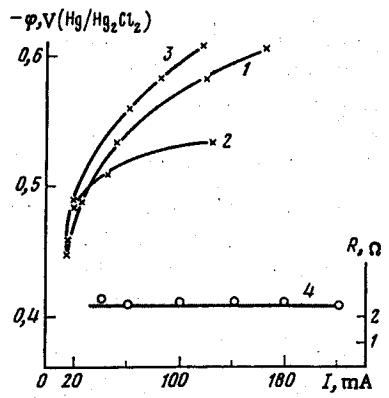

Fig. 4

Fig. 3. Polarization curves (10 mV/sec) obtained on PS-3 potentiostat with PU-1 interrupter unit and on PT-1 equivalent circuit (R_{AE} = 7 Ω, R_{RE} = 10 kΩ, interruption time 20 μsec). 1, 2, 4, 5) No compensation; 3, 6) with compensation. Values of C_{WE} (μF): 1-4) 50; 5, 6) 10. Values of R_k (Ω): 1) 0; 2, 3, 5, 6) 10; 4) 100.

Fig. 4. Cathodic polarization curves of platinum in 1 N H_2SO_4, recorded without compensation for ohmic potential difference (1, 3) and with automatic compensation (2); 3) with Luggin capillary removed about 10 mm from Pt surface; 4) ohmic resistance vs current density.

working electrode must have a sufficiently large time constant RC. It can be shown that in working with a linear equivalent circuit, in the absence of an ohmic component ($R_k = 0$) the relative error of the potentiostat is $\Delta \approx t/(RC)_{WE}$.

When $R_k \neq 0$, the error depends on many factors, including the preset potential. Both the potentiostats (the PU-1 and the AFKEL) operate satisfactorily when $(RC)_{WE} \geq 2 \cdot 10^{-3}$ sec. To reduce the error it is necessary to make an appropriate choice of the interruption time.

The ON-405 potentiostat operates satisfactorily at low values of C_{WE}; at high values of C_{WE} (e.g., for electrodes with coatings or surface films) the ON-405 potentiostat cannot be used.

Together with the measurements based on equivalent circuits, the effectiveness of the automatic compensation was checked by determining the stationary and potentiodynamic characteristics of the reaction of cathodic reduction of hydrogen ions and water and anodic solution of nickel in aqueous, water – dimethylsulfoxide, and dimethylsulfoxide (DMSO) media.

In aqueous media with high electrical conductivity (1 N H_2SO_4), the influence of OPD on the stationary curves of discharge of ions with maximum approach of the Luggin capillary to the electrode surface is manifested only with currents of the order of 30 mA ($\varphi_{ohm} = 10$ mV), and is 41 mV when $I_k = 100$ mA (Fig. 4, curves 1 and 2). The ohmic resistances of the system, calculated from the cathodic polarization curves measured in the usual way and with automatic OPD compensation, are practically independent of the cathodic current density and do not exceed 0.5 Ω (Fig. 4, curve 4). Withdrawal of the Luggin capillary from the electrode surface leads to a marked distortion of the curves owing to a rise in the IR error in the measurement circuit (Fig. 4, curve 3). In the automatic compensation mode, polarization curve 3 coincides with curve 2. In the graph of φ vs $\log i_k$ the slope of the linear section of the corrected polarization curve in the region of high cathodic current densities ($i_k > 50$ mA/cm^2) is 0.06 ± 0.005 V, in agreement with the results of the polarization measurements at low overvoltages and with the data in [15] on the kinetics of reduction of hydrogen on a platinum electrode.* The anodic polarization curves of a nickel electrode in aqueous media have active solution and passivation sections (Fig. 5, curve 1). In this case, imposition of automatic compensation has no appreciable influence on the results of the polarization measurements, apparently owing to the relatively low passivation current density and the high electrical conductivity of the electrolyte and the passivating layers on the nickel electrode.

A change from aqueous solutions to H_2O – DMSO mixtures is accompanied by a change in the shape of the anodic polarization curve of nickel (Fig. 5, curve 2): The passivation region disappears. At the same time the influence of OPD becomes more marked.† With automatic OPD compensation, the polarization curve shifts toward higher current densities, and is linear when plotted in logarithmic coordinates. The principal difference between the behavior of a nickel anode in these solutions and that in aqueous solutions consists in a marked increase in the ohmic resistance of the system with i_a; in aqueous media it is independent of the current density, just as in the case of discharge of H^+ ions (Fig. 4, curve 4).

*The slope of the Tafel section depends on the previous treatment of the Pt. In our work, as also in [15], the electrode was subjected to preliminary cathodic polarization for 20 min with a current density of 10^{-3} A/cm^2.
†The potentials are given without allowance for the diffusion potential at the DMSO – H_2O phase interface.

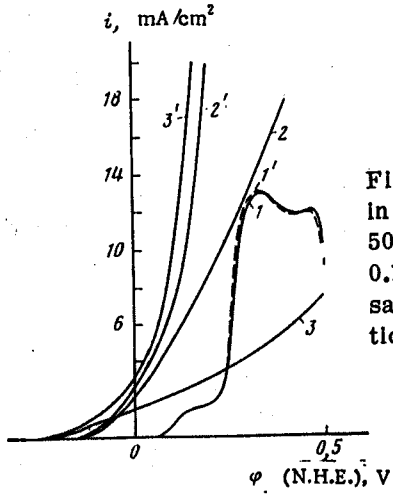

Fig. 5. Anodic polarization curves of Ni in 1 N H_2SO_4 solution in H_2O (1, 1') and 50% H_2O + 50% DMSO (2, 2'); 3, 3') in 0.1 M HCl (DMSO); 1-3) without compensation; 1'-3') with automatic compensation of ohmic potential difference.

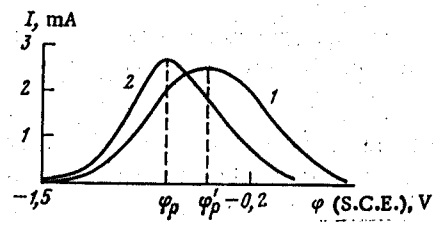

Fig. 6. Cathodic volt–ampere curves of platinum in solution in DMSO + 0.01 HCl + 1 M LiCl + 0.04% H_2O with potential shift rate of 20 mV/sec: 1) without compensation; 2) with automatic compensation of ohmic potential difference.

The influence of the OPD is particularly marked in an anhydrous solution in DMSO (Fig. 5, curve 3). Here the ohmic resistance of the system reaches high values even at low current densities and rises appreciably with the anodic polarization. Apparently when nickel interacts with organic molecules, layers form on its surface with low electrical resistance.

As remarked above, the distorting influence of the IR error is particularly marked when volt–ampere characteristics are measured by the linear potential variation method. Figure 6 shows potentiodynamic curves for the reaction of reduction of water from DMSO solutions [16], measured by the usual method (Fig. 6, curve 1) and with automatic potential compensation (Fig. 6, curve 2). We see that in conformity with the above theoretical analysis, the OPD has a twofold influence on the measurement results – it shifts φ_p toward the negative and slightly reduces the value of i_p.

The PU-1 interrupter unit was tested with the PI-50-1 and P-5827M potentiostats (made in USSR) and was found to operate stably over a wide range of potentials and currents. It is desirable to augment the potentiostats with units of similar type, extending the possibilities for investigation.

The use of potentiostats with automatic OPD compensation enables us to make reliable polarization measurements when the contribution made by the OPD is appreciable and can distort the given potential.

Comparison of the characteristics of the tested instruments reveals that there is still an urgent requirement to design a potentiostat with automatic OPD compensation and high output voltage (at least 100 V).

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THE PRESENT STATE OF RESEARCH INTO ATMOSPHERIC CORROSION IN THE MEMBER-NATIONS OF THE COUNCIL OF MUTUAL ECONOMIC AID (COMECON)*

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This report contains a survey of information on the forms, directions, and certain results of the cooperation of the member-nations of COMECON in research on atmospheric corrosion. Their collaboration embraces practically all the aspects which are at present considered important everywhere in the world.

In the member-nations of the Council of Mutual Economic Aid (COMECON), as indeed everywhere in the world, much attention is being paid to research on atmospheric corrosion, and much money is being spent on this work. Owing to the rapid expansion of large-scale construction work and the development of machine-building, the number of objects requiring protection from atmospheric corrosion has increased by an order of magnitude since World War Two. The aggressiveness of the atmosphere has also increased sharply. At the same time, the continual tendency toward rise in the quality, cost, and reliability of machine parts means that the severity of the requirements for corrosion protection is always increasing.

This problem is especially important when we are dealing with export of products to the world market, in which it is sometimes corrosion protection quality which determines the competitiveness of the goods. A considerable proportion of the exports of machine parts and equipment from the COMECON countries is sent to the developing countries, in which the climates are far different from those in central Europe. Thus, it is necessary to find new ways of protecting export goods.

However, even for the climatic conditions of the COMECON countries an important limiting factor in the improvement of anticorrosion methods is the manpower needed to deposit and particularly to repair certain protective coatings as the protected areas continually grow. Analyses made in Czechoslovakia have revealed that even now it is difficult to obtain enough men to protect all the existing steel structures with paint, and in the near future it will become altogether impossible.

Research on atmospheric corrosion in the COMECON countries has a long tradition and a solid scientific basis. A number of theoretical researches, mainly by Soviet and Czechoslovakian research institutes, have made a recognized contribution to world knowledge of the causes, mechanism, and kinetics of corrosion of metals by the atmosphere. The plans for further work in this direction should in many ways become definitive outside the COMECON countries. The prospective expansion of theoretical knowledge in the program of research into atmospheric corrosion is not regarded as an end in itself, but is coordinated with the tasks of technical innovation as a whole in conformity with the requirements of the national economy, including the development of common COMECON standard in the field of corrosion protection.

This conception of research work can be successfully realized only given maximum utilization of all forms of cooperation in COMECON. Immediately after World War Two there arose working contacts between institutes in the socialist countries, and in time these led to the signing of an agreement for scientific–technical cooperation on the problem of development of measures to protect metals from corrosion. Research on atmospheric corrosion is included in Project VI of this program, "Corrosion in Natural Conditions."

* Report to symposium of specialists of COMECON countries and Mexico on Devising Measures to Protect Metals from Corrosion.

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