DIGITAL POLAROGRAPH-IMPEDANCEMETERS
FOR FREQUENCY RANGE OF 10^{-3}—10^{-5} Hz

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Design, principal function and technical parameters of two polarograph-impendancemeters are given. The instruments are suitable both for analytical applications and for investigation of the kinetics and mechanism of electrode processes.

The combination of polarographic and impendance methods enables to obtain the most complete information on electrode processes, necessary for determination of kinetics and mechanism of these processes and composition of investigated solutions[1,2].

At present a number of polarograph-impedancemeters[3–5] has been developed. However, such meters are either almost unaccessible to a wide circle of investigators (*e.g.*, those using specific Fourier converter[3]), or in the case of the balancing bridge methods[4,5], they are time consuming and therefore, they are suitable only for a limited number of electrochemical systems. At the same time it becomes difficult to study electrode processes on solid electrodes because of the lack of polarographic sensors that could provide reproducibility of a solid electrode under investigation matching with that of the mercury dropping electrode which is almost ideal from this point of view.

The present paper describes principles of two polarograph-impedancemeters which are solving the afore-mentioned difficulties to a great extent.

The block diagram of a high-speed low-frequency meter of complex conductance[6] is shown in Fig. 1. The electrochemical cell C is an object of investigation. Counter electrode CE of the cell is connected to the potentiostat output P through the switch S_1 and the reference resistor R_0; the working electrode WE is connected to the ground and the reference electrode RE to one of the potentiostat inputs (*via* the voltage follower VF).

AC voltage U_0 from the sine-wave oscillator SWO and the polarizing voltage E from the voltage reference source VRS (in predetermined potential regime) or the potential difference between the reference and working electrodes are applied to the other input of the potentiostat through the summing amplifier A_1 from holder of potential HP (in a balancing regime). The potential equal to the output voltage of the adder is maintained on the working electrode (in predetermined potential regime). In this case an AC voltage on the reference resistor R_0 is directly proportional

to the complex conductance between the working and reference electrodes, while the DC voltage is proportional to the value of direct (polarizing) current flowing through the cell. Voltage from the resistor R_0 is fed to the signal processing block SPB which provides the sampling and converts these voltage samples to a number of pulses (Fig. 2: signal plots; *I*. Signal processing). The train passes to the counting-storage device CSD where pulses are subject to a mathematical processing (Fig. 2. *II*. Sample processing). As a result of this digital codes processing the following parameters are obtained: the voltage difference between the working and the reference electrode, the real (G) and the imaginary (Y) components of the measured complex conductance, the polarizing current I_0 of the working electrode. SPB and CSD are synchronized by means of a synchronous generator SC, providing the in-phase and the quadrature pulses derived from zero-crossings of the reference voltage. Digital codes of the measured parameters arrive to the digital output and to the indicating device ID. Suitable recorders or a computer could be connected to the digital-to-analog convertor DAC and digital output of the meter.

The instrument is characterized by the following specifications: frequency range $10^{-3} - 10^3$ Hz; range of measured complex conductances $10^{-1} - 10^{-6}\ \Omega^{-1}$; potential
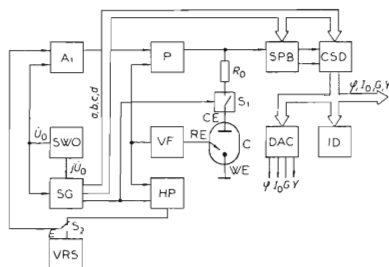

Fig. 1

Block-diagram of polarograph-admitancemeter. A_1 summing amplifier; SWO sine-wave oscillator delivering two signals $\dot{U}_0$ and jU_0; SG synchronous generator; VRS voltage reference source; P potentiostat; VF voltage follower; HP holder of potential; R_0 reference resistor; S_1, S_2 switches; C electrochemical cell; CE, RE and WE counter, reference and working electrodes, respectively; SPB signal processing block; DAC digital-to-analog convertor; CSD counting-storage device; ID indicating device

range ± 2 V; polarizing current range ± 100 mA; duration of one measurement: 30 ms for frequency above 20 H, 3/4 of period of the measured signal for frequency
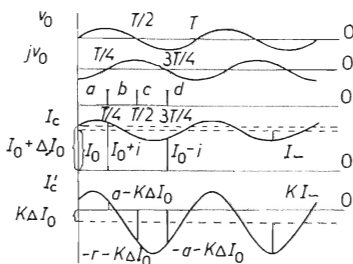

FIG. 2

Diagram of signal timing and processing

I. Signal processing

	Time period	0	$T/4$	$T/2$	$3T/4$
Signal	Samples	$I_0 - \Delta I_0$	$I_0 + i$	—	$I_0 - i$
	Coeff. of transform.	1	0·5	—	0·5
	Amplit. of samples	$I_0 - \Delta I_0$	$\frac{1}{2}(I_0 + i)$	—	$\frac{1}{2}(I_0 - i)$
Amplif. test of signal	Samples	—	$a - K\Delta I_0$	$-rK\Delta I_0$	$-a - K\Delta I_0$
	Coeff. of transform.	—	0·5	1	0·5
	Amplit. of samples	—	$\frac{1}{2}(a - K\Delta I_0)$	$-r - K\Delta I_0$	$\frac{1}{2}(-a - K\Delta I_0)$

II. Sample processing

1)
$$\frac{I_0 + i}{2} + \frac{I_0 - i}{2} = I_0$$

2)
$$-\frac{a - K\Delta I_0}{2} + (r - K\Delta I_0) - \frac{-a - K\Delta I_0}{2} = r \rightarrow Im(\text{Au}) = Y$$

3)
$$\frac{a - K\Delta I_0}{2} - \frac{-a - K\Delta I_0}{2} = a \rightarrow (Re\,\text{Au}) = G$$

bellow 20 Hz; error of the complex conductance: better than 3% for tg δ from 0·1 to 10; potential stability: ±0·5 mV; error of polarizing current measurement 1%; both digital and analog data output; dimensions 480 × 120 × 440 mm; weight 12 kg.

The block diagram of the polarograph-impedancemeter for frequency range from 20 Hz to 200 kHz[7] is shown in Fig. 3. As can be seen the voltage E of the polarizing source PS and the potential difference between the working WE and the reference RE electrode of the electrochemical cell C are substracted by the summing amplifier A_1 and the difference is converted to the current by means of the measuring convertor MC_2. The resulting current flowing between the polarizing PE and the working electrodes creates the voltage difference $\varphi = E$. The alternating current component is sensed by the measuring convertor MC_1, to the input of which is fed the harmonic voltage U_0 from a sine-wave oscillator *via* the reference voltage stabilizer RVS. This current component is independent of the cell impedance and yields a voltage directly proportional to the impedance. This voltage is amplified by the measuring amplifier MA and is passed to the block of a two-channel phase sensitive detector. One channel is used for measurement of the real impedance component (ReZ) and the other one for determination of the imaginary component (ImZ) of the electrochemical cell impedance (Z).
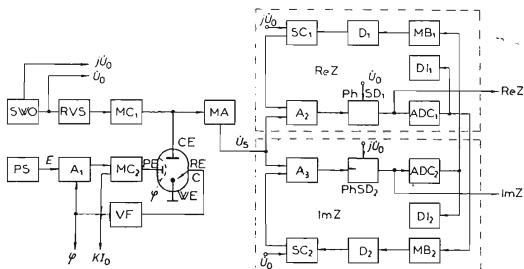

FIG. 3

Block-diagram of polarograph-impedancemeter. SWO sine-wave oscillator delivering two signals $\dot{U}_0$ and $j\dot{U}_0$; PS polarizing source; RVS reference voltage stabilizer; A_1, A_3 summing amplifiers; MC_1, MC_2 measurement convertors voltage-current; VF voltage follower; C electrochemical cell; CE, RE, PE and WE counter, reference, polarizing and working electrodes; MA measuring amplifier; SC_1, SC_2 scale convertors; D_1, D_2 decoders; $PhSD_1$, $PhSD_2$ phase-sensitive detectors; MB_1, MB_2 memory blocks; DI_1, DI_2 digital indicators; ADC_1, ADC_2 analog-to-digital convertors

In order to exclude unmeasured quadrature component at the input of the phase-
-sensitive detector PhSD each of the channels contains an analog-to-digital convertor
ADC, a digital memory block MB, a decoder D and a scale convertor SC of
quadrature component code. Output voltages of the SC_1 and SC_2 are substracted
from voltage $\dot{U}_s$ of the measuring amplifier in the summing amplifier $A_2(A_3)$ of the
cannel ReZ(ImZ). Thus, in each of two channels, unmeasured quadrature component
is excluded from the input signal of PhSD.

The polarograph-impedancemeter X-206 described above allows to choose the
following measuring regimes: $\varphi = f(I)$; φ, X, R $= f(I)$; φ, X, R $= f(\omega)$; φ, X, R $=$
$= f(t)$; $I = f(\varphi)$; I, X, R $= f(\varphi)$; I, X, R $= f(\omega)$; I, X, R $= f(t)$.

The instrument X-206 is characterised by the following basic specifications:
working frequency range 20 Hz to 200 kHz; range of measured impedance $1 - 10^6 \Omega$
with subranges of 10, 10^2, 10^3, 10^4, 10^5, $10^6 \Omega$; alternating voltage level for subranges
10, 10^2, 10^3, 10^4, $10^5 \Omega$ less than 5 mV; for a subrange of $10^6 \Omega$ less than 50 mV;
maximum error of complex resistance 2%; potential range ± 3 V; potential stability
and voltage errors less than ± 2 mV; polarizing current measurement error 1%;
input resistance of potential measuring circuit $10^9 \Omega$; measuring time 0·1 or 1·0 s;
digital and analog data output; power consumption 20 W; dimensions 480 × 120 ×
× 440 mm, weight 10 kg.

The above-described instruments are widely used in practice of scientific electro-
chemical analysis.

In particular, these instruments were applied for studying the following problems
listed bellow: *a*) The dependence of the double layer capacitance on the potential
of a silver electrode[8] using the fixed frequency mode and linear potential scanning
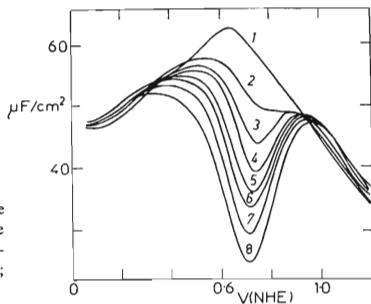(Fig. 4). A diffuse minimum of the capacitance observed at 0·7 V indicates the zero

Fig. 4

Dependence of the double layer capacitance
vs the potential of silver electrode in the
solution of NaF (pH = 4) of various con-
centrations (mol/l): *1* 0·5; *2* 0·2; *3* 0·1; *4* 0·05;
5 0·03; *6* 0·02; *7* 0·01; *8* 0·005.

charge point of polycrystalline silver at this potentials. *b*) The zero charge potentials of oxide-free iron in diluted solutions of potassium fluoride and sodium sulphate were found to be -0.7 V and -0.73 V respectively. *c*) Various other applications for elucidation of electrochemical processes are given in ref.[9].

In conclusion it should be mentioned that designed instruments could be effectively used also in electrotechnics, radio-engineering, semiconductor-technics, medicine, biology and other fields where polarographic and/or impendace methods are applicable.

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