HIGH-FREQUENCY POLAROGRAPH

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UDC 543.253

The application of a modulated signal to an unsymmetrical nonlinear cell may give a signal with a potential or current which varies with the frequency of the modulated signal (rectification) depending on the wiring diagram [1, 2]. In the region of the potentials of an electrochemical reaction the electrode processes exhibit the properties of an unsymmetrical nonlinear cell [3]. High-frequency polarography is based on this principle (Faraday rectification).

In the radio-frequency method developed by Barker [4] the cell is polarized by a high-frequency current which is modulated by a low-frequency square-wave signal, which comes from the polarograph. The low-frequency square-wave signal obtained from the cell after a low-pass filter is recorded on a square-wave polarograph.

An important merit of the method for obtaining high-frequency polarograms is the almost complete absence of capacity current in the measuring circuit, which considerably improves the signal-noise ratio and simplifies the polarograph circuit. The slight capacity component in the signal, which arises from the low nonlinear capacity of the double layer for simple polarographs, occurs at the level of the instrumental noise.

The polarograms obtained have the form of the second derivative of a classical polarogram. If the electrode process is conditioned by diffusion they pass through the zero line at the half-wave potential. However, the electrode processes, which in classical and in low-frequency polarography are strictly reversible, in high-frequency polarography frequently become more and more irreversible with increase in the carrier frequency.

Figure 1 shows the curves obtained on a radiopolarograph for cadmium and nickel ions. With a supporting electrolyte of 1 N potassium chloride the reduction process for cadmium ions is reversible, and the transfer coefficient α is close to 0.5 (curve 1); with an ammonium-ammoniacal supporting electrolyte the reduction process is not reversible, and $\alpha \neq 0.5$ (curve 2). The rates of the direct and reverse reactions with nickel ions in a supporting electrolyte of 1 N potassium chloride differ strongly, and therefore also $\alpha \neq 0.5$ (curve 3).

Accordingly, when the transfer coefficient α differs from 0.5, the form of the polarogram with increased carrier frequency approaches that of that of the first derivative of a classical polarogram, with a maximum at the half-wave potential. The polarity of the "peaks" is determined by the value of the coefficient α.

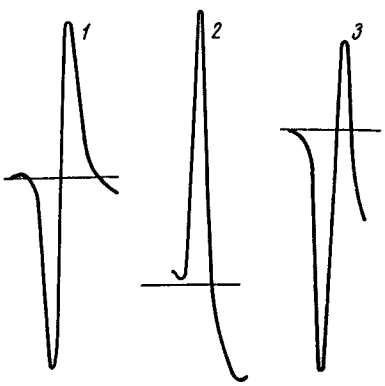

Fig. 1. Radio frequency polarograms for cadmium and nickel.

With high-frequency polarograms the resolving power of polarography can be increased, and new possibilities are opened up in the study of the kinetic parameters of electrochemical reactions.

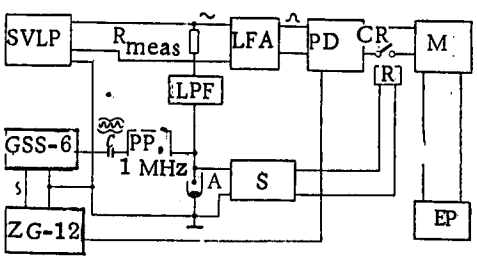

Fig. 2. Circuit diagram of radio frequency polarograph. R, relay; EP, electronic potentiometer; PP, phase plate; CR, control relay.

Special Design Office for Automation in Nonferrous Metals Industry, Institute of Chemistry and Laboratory of Measuring Techniques, Academy of Sciences of the Moldavian SSR. Translated from Zavodskaya Laboratoriya, Vol. 34, No. 12, pp. 1542-1543, December, 1968. Original article submitted November 29, 1967.

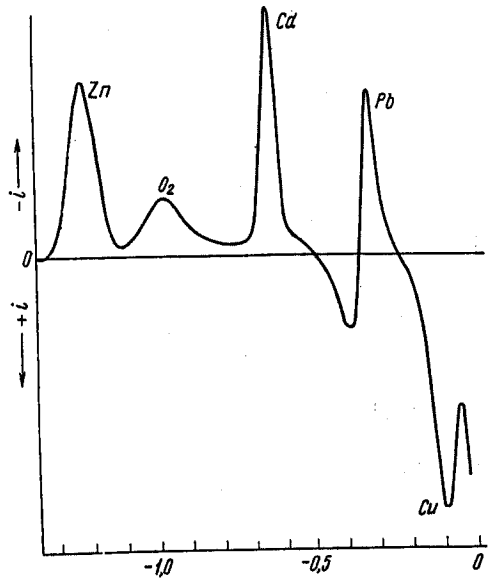

Fig. 3. Radiofrequency polarogram for solution containing $5 \cdot 10^{-7}$ mole/liter Cd^{2+} and $3 \cdot 10^{-6}$ mole/liter each Zn^{2+}, Pb^{2+}, and Cu^{2+}. The modulation frequency was 400 Hz.

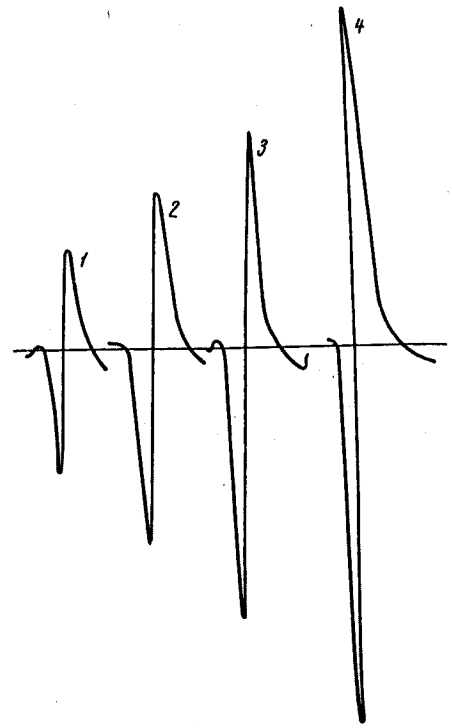

Fig. 4. Dependence of polarogram height on concentration of Cd^{2+} ions: 1) 6 mg/liter; 2) 10 mg/liter; 3) 14 mg/liter; 4) 20 mg/liter.

At the Special Design Office for Automation in the Nonferrous Metals Industry and at the Laboratory of Measuring Techniques in conjunction with the Institute of Chemistry of the Academy of Sciences of the Moldavian SSR, laboratory installations have been set up for the production of high-frequency polarograms, and preliminary work has been carried out on high-frequency polarography.

A high-frequency signal modulated by a low-frequency signal of sinusoidal form was used. The general form of the circuit is shown in Fig. 2.

Industrial oscillators GSS-6 and ZG-12 are used to produce a modulated high-frequency. The low-frequency signal from the cell (A) is selected by the low-pass filter (LPF) and after amplification by a selective amplifier is detected by the phase detector (PD). An amplifier with 100% negative feedback is used to apply the slowly changing potential to the cell. This compensates for the potential drop at the measuring resistance. The input potential of the amplifier is set both manually and from a slowly varying linear potential generator (SVLP). The signal is only recorded at a particular moment in the life of the drop in the course of 100 μ/sec, for which a synchronizer (S) is incorporated in the apparatus. After removal of the drop the synchronizer provides a delay calculated so that the recorder is switched off at the necessary moment towards the end of the life of the drop [5].

The sensitivity of the measuring part of the instrument allows a potential of up to 10 μV to be recorded at the measuring resistance, which means that a concentration of 10^{-7} mole/liter Cd^{2+} can be recorded against a supporting electrolyte of 1 N potassium chloride.

A memory (M) is employed to maintain the signal level when the recorder is disconnected.

Figure 3 shows a high-frequency polarogram for a multicomponent solution containing Zn^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+} ions at concentrations of 10^{-4} g/liter or $\sim 10^{-4}$ to 10^{-5} mole/liter. The cadmium ion is reduced reversibly, while the zinc, lead, and copper ions are reduced irreversibly. The zinc and lead peaks are on opposite sides. The waves of all four elements are fairly easily distinguished.

A 1 N solution of potassium chloride was used as supporting electrolyte. This polarogram is similar to the polarogram obtained by Barker [4] on a radiofrequency polarograph.

In view of the fact that we did not encounter any methods for measuring the peaks on radiopolarographs in the literature, it was of interest to investigate the dependence of the peak heights on the concentration. Radiofrequency peaks can be divided into positive (+h), negative (−h), and combined (h_c) (Fig. 4). The variation of +h, −h, and h_c with concentration is linear, and it is therefore possible to plot a calibration curve both for each individual peak and for the combined peaks.

Of organic compounds furfurol gives good radiofrequency polarograms with a supporting electrolyte of 1 N KCl, and the peak heights again vary linearly with concentration.

All the polarograms were recorded with a mercury dropping electrode in a cell with a mercury pool.

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