ADVANCES IN POLAROGRAPHY ON SOLID ELECTRODES (REVIEW)

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Most polarographic investigations are conducted with mercury capillary electrodes; due to the continuous or periodic renewal of the surface, these electrodes give high reproducibility and stability in the results. However, the use of a mercury electrode is limited by the solution potential of mercury, which is inconvenient for anodic polarography, and also the boiling point of mercury, which is important in the polarography of melts. Furthermore, the use of polarography to study the kinetics of electrode processes cannot be limited only by processes on the mercury electrode. Methods of polarography using solid electrodes have therefore been given considerable development. In many cases, work with these electrodes is simpler than polarography with a dropping electrode.

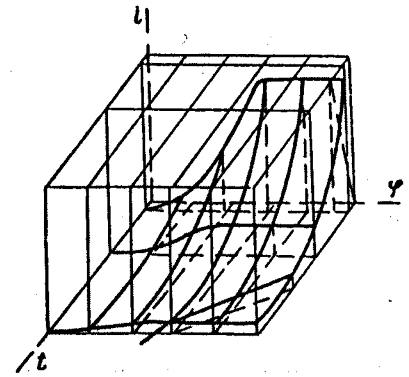

Diagram of "current – potential – time."

The principles for the use of solid electrodes in polarography were developed in the investigations of Laitinen and Kolthoff [1], and also Skobets [2].

Gerasimenko [3] used ten indicator electrodes, of which only one was polarized alternately, and the remainder "recovered" or were depolarized by short circuiting. This principle has been used in other work [4].

Theory of Polarography on Solid Electrodes

The electrochemical processes which occur when a direct current passes through an electrode are determined by three variables: the current i, the potential φ, and the time t from the start of electrolysis. These processes can be represented in the form of a certain function $F(i, \varphi, t)$ [5-7], which can be obtained by arranging in the coordinates i, φ, t the curves i and t experimentally plotted for different values of φ or (see figure), curves of φ and t experimentally plotted for different values of i. By using the function $F(i, \varphi, t)$, we can explain polarographic and related methods and methods for polarography on various electrodes.

On a mercury drop electrode with slow increase of the drops, each new drop returns the process to the plane $t = 0$, i.e., it stops the increase in the variable t and starts it all over again. The mean value of the current which is recorded by an inertia galvanometer corresponds to the cross section of the surface $F(i, \varphi, t)$ by a certain plane $t = \text{const}$. It is practically the same with rapid growth of the drops, although here the strength of the momentary current increases due to an increase in the electrode surface. The polarograms obtained with a mercury drop electrode are therefore time-independent relationships.

The mechanism of drop formation therefore ensures the observation of two criteria of reproducibility [5]: 1) Successively taken polarograms coincide; 2) the polarograms are independent of the rate and direction of exposure. Each point of the polarogram can be obtained regardless of from which side of the surface $F(i, \varphi, t)$ it is appraoched. It therefore makes no difference which of the two quantities (i or φ) is the measured variable.

If measurements are made on stationary electrodes (solid or liquid), then the process will change with time. To obtain reproducible data, a strict allowance should be made for the variable t. This condition is stipulated in polarography methods using solid electrodes.

The process on the electrode reaches an almost stationary state on the passage of a certain time τ. The quantities i or φ taken at $t > \tau$ do not vary with time. This formed the basis of the method suggested in 1891 by Leblan; this was the method of prolonged waiting; it corresponded to the cross section of surface $F(i, \varphi, t)$ by the plane $t = \text{const} > \tau$.

The cross section of surface $F(i, \varphi, t)$ by any plane $t = \text{const}$ gives time-independent values. For each value of φ in [2] they suggested recording the so-called surge currents, recorded by a current galvanometer when a potential φ was applied to the electrode, since the time of deflection of the galvanometer coil from zero to the maximum value is independent of the size of the current and is determined by the ballistical data of the galvanometer.

If the electrolysis process proceeding at a certain potential φ is stopped and then renewed at another potential, this will be equivalent to returning the process to the plane $t = 0$.

The mean current recorded by the galvanometer, as on the drop electrode, will correspond to the cross section of the surface $F(i, \varphi, t)$ by the plane $t = \text{const}$, and will give stationary polarograms with the observation of both criteria of reproducibility. This is achieved by sharply moving the electrode into the electrolyte (jumping electrode), periodically removing the electrolyte from the electrode by a gas bubble (dipping electrode), periodically dipping the electrode in mercury and breaking the electrolysis circuit (linearly moving electrode), periodic electrochemical depolarization of the electrode, and periodic breaking of the electrolysis circuit.

With automatic plotting of the polarograms, one of the variables ($\underline{i}$ or φ) is given linearly in time. This corresponds to the section of surface $F(i, \varphi, t)$ by a plane passing through the axis of the currents (the method with a specified potential – galvanometric polarography) or through the axis of the potentials (method with specified current – potentiometric polarography). With the same rate of plotting and conditions for diffusion of the depolarizer to the electrode, automatic plotting ensures reproducibility in the curves. However, the second criterion of reproducibility is not observed, since the process depends on the time.

Galvanometric plotting gives curves with a maximum, since the current rises from zero to unsteady values with potential and then falls to steady values with time. For quantitative determinations we can use the current of the maximum, as shown theoretically [8] and in practice [2], or steady values of the limiting current, which are independent of the rate of plotting.

In potentiometric plotting the polarograms do not have a maximum, since the electrode potential is continually increasing.

When the electrolyte and electrode are moved relative to one another, the diffusion layer is considerably shortened and the current on the electrode becomes practically constant with time when there is a sufficient rate of mixing. In the case of a rotating electrode this is expressed in the fact that with faster rotation the steady current approaches the surge current, and even very rapid plotting gives polarograms without maxima. This corresponds to compression of the $F(i, \varphi, t)$ surface along the time axis and an increase in the value of the steady current. The movement of the electrolyte and electrode relative to one another in polarography is achieved by stirring the electrolyte, by making the electrolyte flow by the electrode, by rotation, vibration, or movement of the electrode.

Among these types we can also include the stationary point electrode of Lydersen [9]. For a spherical electrode the ratio of the unsteady current to the steady current approaches unity with reduction in the electrode radius; by reducing the radius to the smallest possible value (the point electrode), we can therefore obtain stationary polarograms.

The $F(i, \varphi, t)$ surface also classifies certain methods related to polarography – chronopotentiometric and chronogalvanometric methods. The first are obtained for a section of the $F(i, \varphi, t)$ surface by the planes $i = \text{const}$, the second by the planes $\varphi = \text{const}$. The $F(i, \varphi, t)$ surface explains phenomena connected with the layer of electrolyte next to the electrode and the diffusion of the depolarizer to the electrode. For reproducibility an important part is also played by the renewal of the electrode itself. It can be done between plottings or during plotting by chemical, electrochemical, and mechanical treatment, short circuiting to the other electrode, or by breaking the electrolysis circuit. In the last case the electrolysis products are removed under the action of local microcells.

Periodic short circuiting of the electrodes during the plotting is the most effective [2]. By regulating the period of polarization and depolarization it is possible to achieve complete renewal of the electrode surface. The faults in the method are the large capacitance currents which form when the electrode is overcharged.

The renewal of the electrodes between the plottings during slow plotting is less effective; during the plotting the electrode may be subjected to nonperiodic irreversible changes. Very reproducible and stable data are given by rapid plotting of the polarograms in 5-10 sec with automatic depolarization of the electrodes between the plottings.

Various methods for using solid electrodes are considered in review and general articles [10-18].

Use of Solid Electrodes in Investigations into Electrochemical Kinetics

The polarographic method has been used to study the kinetics of many electrode reactions. This includes the mechanism of reduction of hexavalent chromium on a rotating gold electrode [19] and on platinum [20], the behavior of triiodide, iodide, and iodine on a rotating platinum disc [21, 22], the oxidation of the sulfite, nitrite, and hydrogen peroxide, the ionization of hydrogen on platinum [23], iridium, rhodium, palladium, and gold [24], the oxidation of tetravalent uranium salts on platinum [25], the reduction of oxygen and hydrogen perioxide on various electrodes [26], the oxidation of chloride and hypochlorite on vibrating graphite and platinum electrodes [27], the electrochemical behavior of organic substances [28-30].

Polarographic investigations using solid electrodes have also been used to study catalytic waves [31], to determine transfer numbers [32], exchange currents [24, 33], rate constants of electrochemical reactions [34], and dissociation constants [29]. A number of papers have dealt with the main kinetic regularities in polarography on solid electrodes [35, 36].

A large amount of work has been done on polarographic investigations into diffusion kinetics, especially investigations on a rotating disc electrode. In accordance with the Levich theory [37], determinations have been made of the diffusion coefficients of triiodide [38, 39], silver [40], quinone and hydroquinone [41], cadmium, thallium, lead, zinc [42], the chloroaurate [39, 43], oxygen, chloroplatinate, chloropalladate [39], in aqueous solutions, silver in a chloride melt [44]. A rotating disc was also used to determine migration currents [45] and to calculate the rate constants of chemical reactions [46]. Other rotating electrodes have been used as well as the rotating disc.

The theory of this problem has been studied by Japanese electrochemists [47]. Using rotating wire electrodes, determinations have been made of the diffusion coefficients of iron, copper, silver, thallium, lead, ferri- and ferrocyanides [48]; studies have been made of the rate constants of chemical reactions [49].

With very intensive mixing of the electrolyte the thickness of the diffusion layer decreases to molecular dimensions. The limiting current then no longer depends on the diffusion coefficient; it is determined entirely by convection. A linear relationship is preserved between the limiting current and concentration [50].

Stationary electrodes have also been used to determine diffusion coefficients and to study electrochemical kinetics. However, they have mainly been used for chronogalvanometric [51] and chronopotentiometric [52] measurements.

Use of Solid Electrodes for Analytical Determinations

The use of solid electrodes in polarography for analytical purposes is especially important. In amperometric titrations solid electrodes are used almost as frequently as the mercury drop electrode.

Most papers have dealt with the polarographic behavior of individual inorganic depolarizers: bromine and bromides [4, 9], bismuth [53], iron, ferri- and ferrocyanides [1, 9], gold [54], cobalt, manganese, copper, nickel, lead, thallium, zinc, and indium [55], cadmium, iodine, and iodides [56], oxygen, ozone, and peroxides [57], nitrite [58], palladium and platinum [59], thiocyanate [60], mercury [52, 54], silver [1], thiosulfate [58], and chloride [61].

Several papers have dealt with the polarographic behavior of organic depolarizers [9, 29, 62, 63]. Interesting work has been conducted on the polarographic behavior of inorganic ions in nonaqueous solvents [64], polarographic investigations of suspensions of insoluble substances [65], the exaltation of limiting currents [66], and polarography at high pressures [67].

New solid electrodes have recently been developed for polarography: carbon and graphite [67, 68], from boron carbide [69], platinized platinum [70], high-boron [62], and cylindrical platinum electrodes [71], and nickel for the polarography of fluorides [72].

As well as these papers, investigations on the polarographic analysis of natural, technical products, and mixtures of substances are of special interest. Methods have been described for determining tannin in tanbark [72], manganese in copper alloys [73] and steels [74], iodine and bromine in mineral waters [75], copper, zinc, cadmium, and manganese in the air of industrial buildings [76], silver in silverplating baths [77], hydrogen sulfide and sulfur dioxide in technical gases [68], copper in ores and steels [78], copper, lead, and cadmium in concentrates of natural waters [79].

Methods have been developed for determining silver in concentrates from ion exchangers [80], hydrogen [81], chromium [82], lead and mercury, mercury and copper when present together [83], chloroiridate in the presence of rhodium, platinum, palladium, copper, nickel, zinc, lead, tellurium, and selenium [84], dissolved oxygen [85], mixtures of hydrogen and oxygen [86].

Solid electrodes are very convenient for analyzing streams of materials [87]. Stationary convection [50], rotating and vibrating electrodes [88] in a laminary stream of electrolyte have been used for this purpose.

Silicon and germanium electrodes have been used to study semiconductor properties [89].

Solid electrodes are irreplaceable for the polarographic determination of oxygen in living tissues. Krog and Johansen [90] used a coaxial platinum cathode and silver anode (total diameter 1 mm) with a teflon membrane on the end for this purpose. Rice [91] used similar electrodes (tin anode) with a total diameter of 70μ.

Polaroscopy and Other Methods of Investigation on Solid Electrodes

In oscillographic (polaroscopic) methods of investigation the main difference between the mercury drop and solid electrodes disappears, since the surface of both types of electrode is unchanged during the rapid plotting.

Heyrovsky was the first to try to use solid electrodes for polaroscopic investigations; however, this was unsuccessful, presumably due to the large capacitance currents caused by the roughness of the electrode surface. Randles [92], using a plotting time of 1-2 sec for the polarization of a stationary platinum cathode with subsequent "resting" of 7-10 sec, obtained reproducible oscillograms of lead and thallium. Bersuns and Delahay [8] polarized a stationary platinum cathode by using a 5- to 10-sec time of plotting. The obtained oscillogram of cadmium was insufficiently reproducible, presumably due to the low duty ratio between the pulses of the polarizing voltage.

Nigmatullin [93] and Tsapiv [94] short circuited the electrodes between the plottings for the depolarization. The electrodes were polarized by linear and sine pulses with a frequency of 50 Hz. A similar method was used by Gordievskii and Zotov [95].

Shain and Grittenden [96] used a rotating electrode in oscillographic investigations. Gokhshtein also obtained oscillograms on solid electrodes [97].

Gorodyskii [98] and Hills [99] conducted oscillographic investigations into fused electrolytes. Mine used a modification of the oscillographic method for solid electrodes [100].

A method with a specified sine current was used for a silver amalgamated electrode by Papousek [101], Micka [102], Skobets and Shapoval [103]. The latter suggested arrangements for an investigation with solid electrodes, a method of difference oscillographic polarography, and observed the discharge of complex ions on solid electrodes.

Leont'ev and Fedot'ev used rapid polarization (14 sec) and an automatic recording potentiometer with a vibrating solid electrode [104].

As well as oscillographic investigations, solid electrodes have been used for differentiated [105] and differential polarography [106], pulse polarography [107], and polarography with anodic dissolving [108, 109].

Solid Electrodes and the Polarography of Melts

For polarographic investigations in fused electrolytes, solid electrodes often represent the only solution. The polarography of melts has been discussed in review articles and monographs [5, 110-113]. About a hundred papers have been published on electrochemical kinetics in melts and the behavior of various depolarizers. Investigations have been conducted using supporting electrolytes of fused nitrates [114, 115], chlorides [98], pyrosulfates [116], silicates [117], borates [118], metaphosphates [119], and sulfates [120].

Many of these articles dealt with the development of analytical methods for the appropriate supporting electrolytes.

Ranges of Application and Possibilities in the Use of Solid Electrodes

The use of solid electrodes together with mercury drop electrodes considerably extends the experimental and theoretical possibilities of the polarographic method. In the anodic polarography of difficultly oxidizable substances, and in the polarography of melts, the use of solid electrodes is the result of practical necessity. In amperometric titration, where the most important factor is the stability of the limiting current, solid electrodes are also a convenient substitute. The use of solid electrodes is therefore connected with these three fields, and also with investigations into electrochemical kinetics. They will no doubt find application in the analysis of streams of materials and in oscillographic polarography.

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THE PULSE POLAROGRAPHIC METHOD OF ANALYSIS
(REVIEW)

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Pulse polarography is one of the new developments in polarographic analysis. This expression [1] is taken to mean polarography using a pulsating polarization voltage.

Pulse polarography is more sensitive; it can be used to increase the degree of separation of neighboring polarographic waves and to reduce the interfering action of certain impurities. The possibility of determining