

Polarography—past, present, and future

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Abstract Polarography was first developed as an automated method of voltage-controlled electrolysis with dropping mercury electrode. The spontaneously renewed pure electrode surface provided reproducible electrochemical results which enabled scientists to work out adequate theory and rich analytical applications. The original method was then instrumentally modified in various ways. Later, hanging mercury drop was added as an alternative indicator electrode—in this way, polarography turned formally into voltammetry with mercury drop electrodes. Beside, in potential-controlled electrolysis, the mercury drop electrodes have been also used in current-controlled electrolysis (chronopotentiometry)—there, it has provided new experimental effects. Polarography has thus gradually covered a wide field of electrolytic methods

based on the use of mercury electrodes, in which it continues developing.

Keywords Dropping mercury electrode · Potential-controlled electrolysis · Current-controlled electrolysis · Hanging mercury drop electrode · Voltammetry · Chronopotentiometry

Introduction

Nowadays, almost 90 years after its introduction, the word “polarography” does not have the original meaning of a single electrochemical method—it denotes whole branch of electrochemistry. In the present review, the complex historical development of the term is outlined with references to some of the pertaining papers.

Past

Polarographic prehistory

Polarization curves

After electrolysis was established as a physical process, several scientists studied the phenomena occurring at various electrodes by applying certain potentials/currents to electrolytic cells and measuring the corresponding currents/potentials. The then plotted current–potential or potential–current dependences have been known as electrochemical polarization curves [1]; as a rule, the precision and reproducibility of the first polarization curves were for the scientists not satisfactory.

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Mercury electrode

Gabriel Lippmann [2] introduced mercury in research for exact measurement of surface tension of polarized electrodes.

Dropping mercury electrode

In order to improve precision of Lippmann's method, Bohumil Kučera [3] determined the surface tension by weighing mercury drops falling from polarized dropping mercury electrode.

Polarographic history

Birth of polarography

By weighing mercury drops, Kučera's postgraduate student Jaroslav Heyrovský tried to find reason for anomaly occurring on some drop weight–potential curves. Apart from drop weight measurements, he tried on Friday, 10th February 1922 afternoon, to measure also current in potential-controlled electrolysis with dropping mercury electrode, and found that the corresponding current–potential curves were precisely reproducible [4]. In the presence of electroactive substances in the electrolysed solution, on the curves appeared wave-shaped increases of current at definite potentials with their heights depending on concentration [5, 6].

Classical polarography

The new way of electrolysis became especially attractive when Heyrovský and Shikata (Fig. 1) included in the voltage-controlled circuit an instrument for automatic photorecording of the polarization curves by means of mirror galvanometer [7]. The apparatus was called “polarograph” and that gave the method its name. Polarography became the main subject of research at the



Fig. 1 Masuzo Shikata and J. Heyrovský in London, December 12th 1923

Department of Physical Chemistry at Charles University in Prague under the heading of Professor Jaroslav Heyrovský. In the Czechoslovak team of polarographic researchers were invariably foreign participants. After the journal *Collection of Czechoslovak Chemical Communications* was started in 1929 under the editorship of J. Heyrovský and E. Votoček, it became newsletter of the Prague polarographic school.

Systematic study of polarographic curves led to distinction of different types of polarographic currents according to different respective electrode processes; exact formulations of equations for the basic currents were the beginning of polarographic theory. Thus, gradually appeared quantitative discussions of the polarographic “waves” due to catalytic [8–10], migration [11], diffusion [12], charging [13], kinetic [14, 15], and adsorption [16, 17] currents; in addition, an interpretation was given to the anomalous current maxima “of the first kind” [18, 19] and “of the second kind” [20]. For characterizing the quality of polarographically active substances, the term “half-wave potential” was introduced [21]. In polarography was started research on the degree of reversibility of the reactions involved in the electrolytic process [22]. After the Second World War, polarography was found to have been among the five most frequently used analytical methods—e.g., in the “Manhattan project”, it helped to analyze transuranium elements.

In the 1950s, polarography was an experimentally as well as theoretically fully developed method, in its original simple form it has been referred to as “classical polarography”. That stage of polarography has been thoroughly treated in textbooks (e.g., [23, 24]), instructions for practical applications of polarography were published separately (e.g., [25, 26]). Figure 2 shows v. Stackelberg, Breyer, and Semerano, who contributed to polarography in the post-war period.

Derived polarographic methods

The general acceptance of classical polarography spurred attempts to modify it instrumentally in various ways in order to specify it for different purposes.

The intention to increase the rapidity of the method introduced the cathode ray oscilloscope to polarography. The first attempt by Matheson and Nichols [27] was later improved by Randles [28] and Ševčík [29]—the theoretically formulated current–potential curves were readily shown on the screen of the cathode-ray tube. A different approach was chosen by Heyrovský and Forejt [30]: they polarized the dropping mercury electrode by alternating current and on the oscilloscope they observed potential–time curves or curves displaying time derivative of electrode potential as function of potential. Analytical



Fig. 2 Mark von Stackelberg (Bonn, Germany), Bruno Breyer (Sydney, Australia), and Giovanni Semerano (Padua, Italy) (from left to right) at the International Symposium on Polarography in Dresden, Germany, in 1957

applications of polarography were in that way considerably accelerated and widened [31]. The oscillographic curves provided information about electrode processes and electroactive compounds additional to that obtained from classical polarography [32, 33].

Another modification of polarography consisted in superposition of alternating voltage of small amplitude upon the d.c. voltage applied to the electrodes and in recording the ensuing alternating current—d.c. voltage curves; this, the so-called a.c. polarography, proved sensitive to adsorption processes at the dropping electrode [34]. A.c. polarography specified in studying electrochemical surface phenomena was called tensammetry [35].

The knowledge that of all polarographic currents the charging current decreases fastest with time was the main idea of fast polarography (current sampled polarography, from the German word “tasten”—to touch) [36] in which the instantaneous current at the dropping electrode was measured only in the last phases of the drop life—thus, the sensitivity of polarography to electrolytic current was increased.

Similar principle combined with a.c. polarography, but with right angle course of alternating voltage was utilized in highly sensitive square-wave polarography [37, 38]. Here, in order to decrease the charging current component, the total instantaneous current was measured at the end of each pulse.

In pulse polarography, a single constant voltage pulse was applied to each mercury drop and the corresponding current, practically without the charging current component, was measured before the drop fell off—that was the normal pulse polarography [39, 40]. If the difference of currents before and after the pulse was measured, the resulting current–voltage curve had the shape of a derivative, and that modification was called differential pulse polarography (for general theory see, e.g., [41]).

There were many more modifications of polarography described in the literature, those above mentioned ones have been the most widely utilized methods.

Voltammetry with hanging mercury drop electrode

The term “voltammetry”, accepted officially by the IUPAC Nomenclature Committee in the 1960s, was originally coined in 1940 by Kolthoff (Fig. 3) and Laitinen [42] for voltage-controlled electrolytical methods. According to that terminology, polarography has become voltammetry with dropping mercury electrode, and when mercury stops dropping, the method should not be called polarography any more—it is voltammetry with hanging mercury drop electrode (HMDE). HMDE has been used in polarography since the 1950s [43, 44] and there also appeared papers on stationary electrode polarography [45, 46]. Compared with dropping electrode, the stationary electrode has the advantage of the possibility of accumulation of an electrode reaction product for some time at constant potential before the potential scan is applied for “stripping” off the accumulated substance—that leads to considerable increase of analytical sensitivity. Besides, by cyclic voltammetry the cathodic and anodic reactions of an electrode process are recorded on one curve and thus can be compared under various scan rates on the one hanging mercury drop. The official terminology had not been strictly followed, basi-



Fig. 3 IM Kolthoff and J Heyrovsky in front of Chemical Institute of Charles University, Prague, in 1948

cally it was maintained that polarography and mercury drop electrode belong together.

Chronopotentiometry with HMDE

From the 1960s, the electroanalysts turned their interest to current-controlled electrolysis or chronopotentiometry [47, 48], in which HMDE played important role [49]; for analytical purposes, derivative chronopotentiometry appeared as its particularly attractive modification [50, 51]. When in bioelectrochemistry, the attention concentrated on electrochemical behavior of biopolymers, the derivative constant current chronopotentiometric stripping analysis became a favored method [52, 53], especially after discovery of the sensitive signal of the often occurring catalytic evolution of hydrogen, called “peak H” [54, 55].

Present

Nowadays with the generally used computer-controlled instrumentation, the various modifications of polarography can be usually carried out with one special apparatus, and the experiments can be automatically evaluated on the computer screen according to the appropriate software. The advantageous properties of mercury can be modified according to needs by using different amalgams as electrode material [56, 57]. The unsubstantiated fear of liquid mercury as poison inspires introduction of many electrodes composed of various materials, however, the unique natural advantages of mercury electrodes remain unchallenged. Although “voltammetry” and “chronopotentiometry” have become common words in electrochemical language, it is subconsciously understood that they originate from the common polarographic ground.

Future

It can be expected that the methods developed from polarography will have growing general acceptance in fundamental and applied research and in analysis because of their theoretical base, precision, sensitivity, specificity, relative simplicity, and low cost.

Conclusion

Thanks to objective favorable conditions, polarography first became an experimentally simple, reproducible electrochemical method with gradually built up appropriate exact theory. The positive acceptance of polarography spurred introduction of its various instrumental modifications

having specific advantages in certain directions; each modification got its own more or less fitting theory. In this way, polarography, originally a single method, had become a wide experimental and theoretical approach to problems of chemistry in general, based on the advantageous properties of a choice of methods of electrolysis with dropping mercury electrode. Further major widening of the scope of polarography has been brought about by introduction of the hanging mercury drop as an alternate indicator electrode - polarography has thus become partly “voltammetry”. In that way the word “polarography”, originally denoting “electrolysis with dropping mercury electrode” became unofficially the term expressing an approach to problems soluble by the specific properties of potential-controlled electrolysis with mercury drop electrodes, hanging or dropping. Another fundamental modification occurred when the dropping or hanging mercury electrodes were applied in current-controlled electrolysis. Thus again, various new phenomena enriched electrochemical experience and spurred development of new theoretical approaches. At the present stage, more than 90 years after its introduction, polarography covers a field of experimental and theoretical electrochemistry based on electrolysis with mercury drop electrodes in general, and it can be expected that with progress in research this trend will develop further.

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