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Polarography with non-mercury electrodes: A review

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This article is dedicated to the memory of
 Prof. Antonín Tockstein and Prof. Petr
 Zuman, who both had been — until their
 recent passing away — the last two Czech
 scientists experiencing personally the
 work on polarography in a team headed
 by Prof. Jaroslav Heyrovský.

Abstract

This article reviews non-mercury configurations that have hitherto been reported in the literature as the working electrodes applicable in polarographic measurements. The individual types, namely gallium, liquid amalgams, dropping electrolyte, and carbon fluid electrodes, together with a carbon paste-based assembly or even solid disc electrodes with a periodically renewable surface, are presented, discussed, and critically assessed with respect to their potential employment in the present day's electrochemistry and electroanalysis.

KEYWORDS

characterization and evaluation, non-mercury electrodes, polarography, review

1 | INTRODUCTION: POLAROGRAPHY AND THE DROPPING MERCURY ELECTRODE

If a scientist, non-chemist, sees or hears the word “polarography”, he/she probably imagines the personality of its inventor, Prof. Jaroslav Heyrovský, (see Figure 1),^[1,2] so tightly are both subjects joined together. And if a scientist, in this case, a chemist, encounters the term “polarography”, he/she would instantly recall the name “dropping mercury electrode (DME)”. Again, because these two expressions are also being tied as one.

Nevertheless, there is no equal validity of both connections mentioned above. Whereas “polarography” and “Heyrovský” is a firm and inseparable couple of meanings since the early 1920s^[3] and throughout the century up until now, the second pair, that is, “polarography” and “DME”, may not always be true; at least, not from the present-day's point of view.

This is well documented by a survey in Table 1 gathering selected definitions of polarography as the instrumental technique and taken from the literature^[3,5–7] or other sources^[4,8–14] as time went by.

In some respect, the formulations gathered in the table are very similar, in some quite different. The first definition by the inventor of polarography, Heyrovský^[3] — rather short but concise one — had more-or-less dominated in the golden years of the technique from the early 1920s up to the late 1950s when Heyrovský himself extended its meaning by adopting some new configurations of mercury electrodes,^[6] besides the classical DME with periodically renewable surface (Figure 2).

On the other hand, he and his scientific school had excluded from polarography a wide family of solid electrodes (again, see the table),^[6] which, at that time, was not so obvious in the Anglo-Saxon scientific world or in the former USSR (e.g.^[15,16] and the original titles of both reviews). This corresponds to a finding that, in the decade

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TABLE 1 Definitions of polarography through the century (1922–2022)

Original formulation ^([a–d]) see legend on bottom)	Author(s), source/year (period)	Ref.
“Electrolysis with a mercury drop cathode.”	J. Heyrovský/1922	[3]
“We can define polarography as a field of science dealing with precisely reproducible curves that illustrate the dependence of the current intensity upon the voltage applied during electrolysis.” ^{a,b}	J. Heyrovský/1930s	[4]
“In many aspects, polarography resembles spectral analysis, where the quality is given by the position of emission or absorption lines and bands on the wavelength scale, whereas polarography uses a scale of electric voltage/potential. The quantity in spectral analysis is given by the intensity of light in the optical spectra, in polarography then by the electric current intensity recorded vs. potential in the form of a polarogram, which can thus be aptly called the electrochemical spectrum. Finally, polarography also imitates spectral analysis in high sensitivity, time and material savings, or in almost perfect reproducibility of the results.” ^a	D. Ilkovič/1940	[5]
“In polarography, attention is concentrated on the current-voltage (potential) curves obtained by electrolysis with a mercury drop electrode. Recently, the field of polarography has been extended as it now includes research with other related electrodes, such as streaming (jet) mercury, hanging mercury drop, rotating and vibrating mercury electrodes, etc. However, polarography excludes measurements at solid electrodes.” ^a	J. Heyrovský, J. Kůta/1962	[6]
“Polarography is a measurement of the current-potential curves with periodically renewed test interfaces (regardless of electrode material used).”	J. Koryta, Z. Samec/1976 and 1990	[7a,b]
“Polarography is a special variant of voltammetry employing the working electrode with a non-constant surface which is renewed and its actual size gradually changing during measurement.”	L. Novotný/1997	[8]
“A measure of current as a function of potential when the working electrode is a dropping mercury (or also another liquid conductor), or any other working electrode whose surface is renewed and when unstirred solutions are used.”	IUPAC/1990s	[9]
“DC (classical) polarography: Linear scan voltammetry with the slow scan rate, in which a dropping mercury electrode is used as the working electrode.”	IUPAC /2020	[10]
“Linear-scan polarography: The first type of voltammetry to be discovered . . . , in which a dropping mercury electrode (DME) is used as the working electrode. Because there is no convection, diffusion alone controls polarographic limiting currents.” ^c	D.A. Skoog et al. (textbook)/2014	[11]
“Polarography is a type of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE) which are useful for their wide cathodic ranges and renewable surfaces.” ^c	Wikipedia.com (el. encyclopedia)/2022	[12]
“Polarography: A method of qualitative or quantitative analysis based on current-voltage curves obtained during electrolysis of a solution with a steadily increasing electromotive force.”	Merriam-Webster (el. encyclopedia)/2022	[13]
“Polarography, also called polarographic analysis or voltammetry in analytical chemistry, is an electrochemical method of analyzing solutions of reducible or oxidizable substances. In general, polarography is a technique in which the electric potential (or voltage) is varied in a regular way between two sets of electrodes (indicatory and reference) while the current is monitored.”	Britannica (el. encyclopedia)/2022	[14]

^adefinition intentionally chosen for this review, when the text used herein is a translation from Czech (and slightly edited).

^bauthentic wording from a live performance by Heyrovský taken during his lecture at Charles University in Prague.

^cshortened and/or slightly edited text.

Abbreviation: el., electronic.

1950–1960 when the related voltammetry had been coming to the fore, the Web-of-Science database reveals a nearly three-fold higher number of reports dealing with polarography compared to those found via the keyword sequence “dropping-mercury-electrode”.^[17] Yet another reason why Heyrovský’s technique was also associated with solid electrodes can be the fact that, from a historical point of view,

the term “polarography” is two-decade older than “voltammetry” (see example).^[18]

An interesting and almost unknown characterization of polarography has been made by Ilkovič who is renowned for his primacy in postulating the fundamental equation of the diffusion current in polarography. In his monograph,^[5] he had compared polarographic measurements to spectral

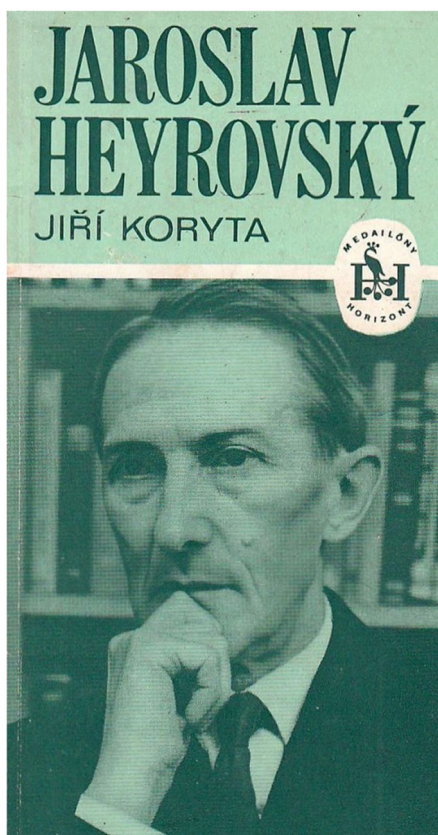


FIGURE 1 Front cover of the first monograph about the inventor of polarography, Heyrovský^[1]

analysis as documented in Table 1. Some newer definitions have further expanded the scope of polarography toward some non-mercury electrodes or even liquid electrolyte: (1) liquid electrolyte, (2) interfaces; see the rows with cit.^[7–9]; however, by respecting the ultimate condition that such assemblies must be characterized by periodically renewable surface during the measurements. Regarding traditional mercury-based electrodes, that is DME, the hanging mercury drop electrode (HMDE), and mercury film electrode — solely the first one obeys the above-stated criterion whereas the remaining two already fall into voltammetry.

Finally, the examples of information sources for students and wider audience are represented by Skoog's Analytical Chemistry, apparently the most popular textbook of a kind worldwide,^[11] and by a trio of encyclopedias^[12–14] that classify and define the term “polarography” in a more extended way.

Nevertheless, as can be seen, the respective formulations do not fully reflect the last recommendation by the IUPAC or are even partially erratic, which is the case of Wikipedia^[12] that does not respect the above-stated current position of the HMDE.

Here, one would expect that a section with the presented table and briefly commented journey through the

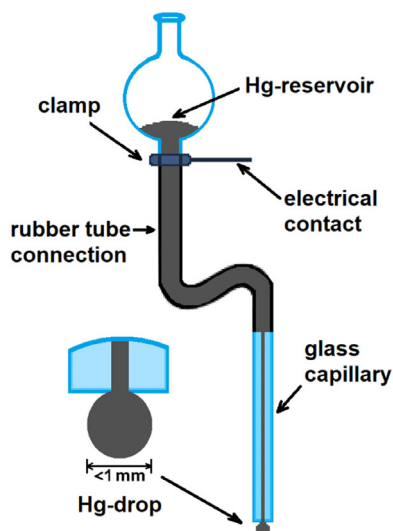


FIGURE 2 Dropping mercury electrode. A simplified scheme of the electrode proper whose set-up remains practically the same through the century

century of polarography could be completed by an ultimate definition of polarography valid in the present days. When considering the authority in the field, the latest recommendation by IUPAC should be the formulation of choice^[10]; however, if one prefers a definition with a very general meaning; then, a formulation with a “periodically renewed test interface”^[7a,b] would be more appropriate. The authors of this article do not dare to decide which point of view is the right one, but they are convinced that — from historical reasons — such an ultimate definition for the present should include both “polarography” and “DME”, when the latter may represent an alternative or an example within the respective formulation.

In the new millennium, classical polarography and especially the DME as the working electrode face both the still growing aversion from various ecologically oriented institutions or authorities because of the use of mercury as unacceptable material of high toxicity. Regarding this, one can be advised to refer to a special article that concerns this controversial theme in very detail^[19] and from various angles of view. Despite these difficulties, polarography is consensually one of the most significant achievements of electrochemists and electroanalysts in the last century, which can best be documented by the grand total number of scientific papers of around 20,000 items that had been published within the early 1920s and mid-1960s (according to the data given),^[20] when the valuable contributions are coming in solid number up until now.^[17] Hence, polarography is vital also today and still has some promise for the future, which has been repeatedly emphasized by special reports published recently and mostly reflecting the last anniversaries of polarography.^[21–24]

In this review, the authors would like to present a less well-known face of polarography – its combination with alternative working electrodes or related structures that fulfill the recently recommended definitions emphasizing the periodical renewability during the experiment.^[10] Such substitutes of the DME are represented by unique constructions and systems of non-mercury nature, including a small family of liquid amalgam-based configurations (The last named can be considered as non-mercury electrodes as well if one accepts a principle that an amalgam is not the elemental mercury.) Finally, there are some new and highly sophisticated approaches that demonstrate seemingly unlikely eventualities allowing one to employ also common solid disc electrodes.

In the following sections, all above-mentioned electrodes or related structures are of interest when being introduced and concisely described with respect to functioning or construction specifics. The presentation of the individual items is given in chronological order and each type is critically assessed if not stated otherwise.

2 | GALLIUM-BASED ELECTRODES

2.1 | Basic characteristics of gallium as the element and metal

Gallium has a melting point of 29.8°C so it requires only a slight heating and subsequent tempering to be kept in the liquid state in common laboratories.^[25] Gallium in this form exhibits a somewhat worse fluidity due to a relatively low atomic weight (69.7 g mol⁻¹), which is a 3-fold lesser value compared to that of mercury (200.6 g mol⁻¹).

Furthermore, the elemental gallium is very susceptible to passivation due to instantaneous oxidation to Ga₂O₃ or related hydrated forms, by which the surface characteristics of gallium may be changed unfavorably with respect to electrochemical behavior, including a lower hydrogen overvoltage. Regarding other features of this element, one should consider also the expensiveness of very pure gallium inevitably needed for its use as the electrode material. And similarly to mercury, there is an unfriendly toxicological profile of gallium; in particular, as waste and in some compounds.

2.2 | Dropping gallium electrode

This type was the first alternative to the DME having been reported yet during the above-mentioned golden era of polarography – in the mid-1950s.^[26] The respective configuration is schematized in Figure 3.

According to the authors of this pioneering report on the dropping gallium electrode (DGaE), rather complex construction of their DGaE had been determined by extraordinary properties of gallium. They had to ensure the liquidity of this metal by continuously tempering the electrode cell with sample solution at 30°C, which was further supported by electrical warming of the capillary by a resistance wire wound around. Also, the capillary had to be completed with a special bulb and the entire set-up with a second leveling reservoir (for both adaptations, see again Figure 3 and the corresponding parts in the scheme). All these adjustments had naturally made the construction of DGaE substantially more complex than much simpler assembly of the DME (Figure 2) and despite all these efforts, the functioning of DGaE was unsatisfactory and the authors of this initial study frankly admitted that their construction had failed.^[26]

Thus, retrospectively, when considering all the facts and findings commented above, it is maybe even surprising that the configurations based on liquid gallium and related fluids have been of continuing interest.^[27–33] Perhaps, it was believed that there is a proper construction of a liquid gallium-based working electrode. In the first two cases,^[27,28] the authors had finally come to a similar conclusion like their predecessors; the main problems of their DGaEs having been associated again with rapid oxidation of gallium in aqueous solutions and both constructions had therefore been evaluated as unsuccessful.

In the following study,^[29] a substantially simplified construction of the DGaE has been introduced, which is clearly documented by the corresponding scheme in Figure 4 when comparing it with the previous one. Here, a new approach was tried to attain the regular dropping of liquid gallium and, at the same, at preventing its undesirable passivation.

It had utilized a stream of nitrogen blown into the reservoir, from where the liquid metal was pushed into the capillary and then outward in the form of large droplets. The second role of the inert gas was then the above-mentioned protection against oxidation by the formation of inert atmosphere in the bulb. Rather unique was also the employment of this new type of DGaE. Being aware of bad experience with the previous configurations and their failure in aqueous solutions, the authors examined their electrode for measurements in non-aqueous media of fused salts in the molten state, that is, at a higher temperature (of about 180°C^[29]) and hence under completely atypical conditions for common polarography.

In the period from the mid-1960s up to the early 1980s, about twenty studies with DGaEs had appeared elaborated by the scientists from the former Eastern Bloc. Herein, it is represented by a trio of reports^[30–32] only, when such

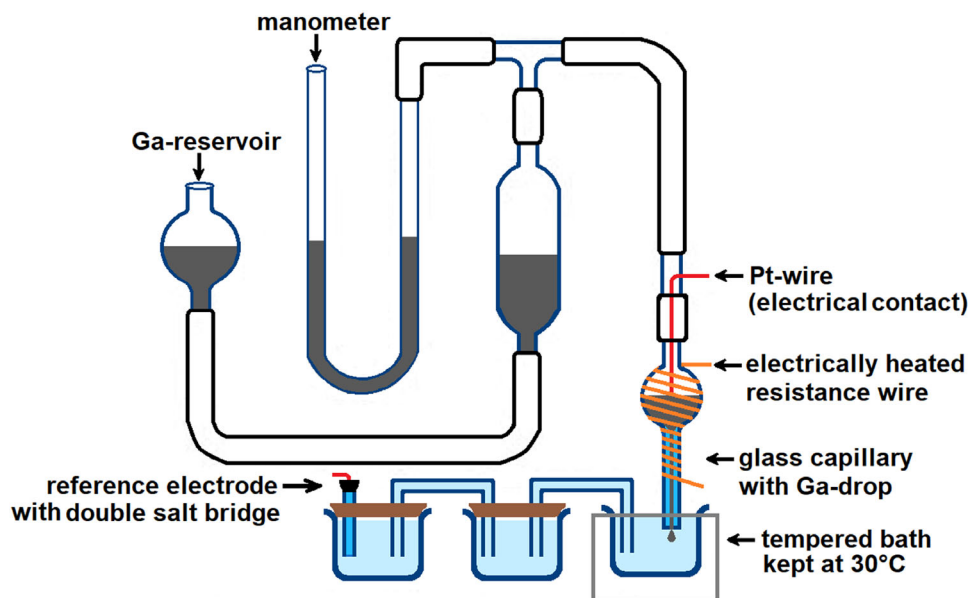


FIGURE 3 Dropping gallium electrode: The first proposal. Overall scheme (redrawn and rearranged^[26])

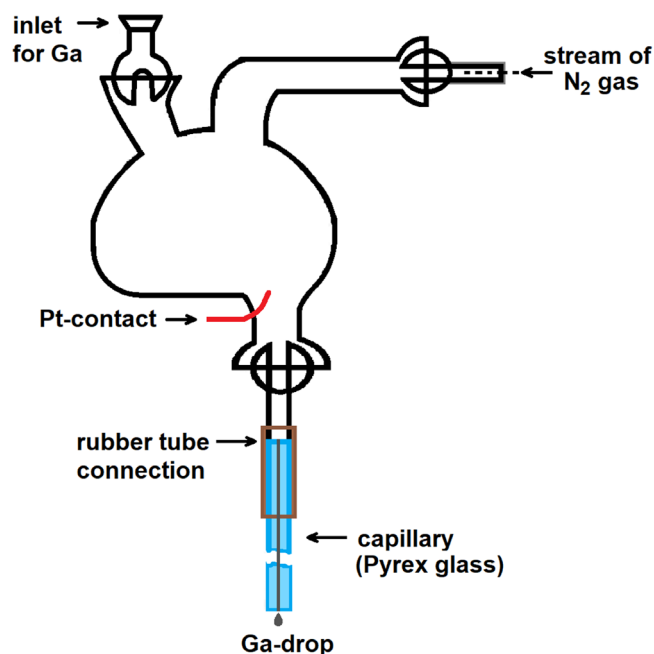


FIGURE 4 Dropping gallium electrode: Construction for measurements in molten salts. Overall scheme (redrawn and rearranged^[29])

a truncated selection reflects the fact that these papers had been published in hardly accessible regional and local journals.

Then, the topics of the individual publications could be deduced solely from the titles, which was, in fact, the only information available in databases like Web-of-Science.^[17] Apparently, the respective studies — arranged as a series of consecutive reports — had concerned a systematic

characterization of the DGaE of own construction, having covered thematic studies on the effect of key experimental parameters, such as hydrogen overvoltage^[30] or pH-value of the supporting electrolyte.^[31] Besides this, it can also be noticed that the latest contribution^[32] has already been dealing with a modified variant of the electrode that had employed a liquid alloy from gallium and thallium. Once more, there have been no details about such configuration, as well as no information on the benefit of thallium in the alloy.

Yet another attempt to resurrect the concept of the dropping gallium electrode was made in the mid-1980s by a research team of Italian authors.^[33] The respective construction incorporated a thin tube from polyethylene, which was another attempt how to overcome problems with the oxidation of gallium. It was confirmed that the inner walls of highly hydrophobic polymer repelled effectively somewhat sticky surface of passivated liquid gallium, thus enabling a better flowing through the capillary and also hindering its clogging. An obvious precaution to keep gallium finely liquid and properly dropping was a thorough tempering of the reservoir with gallium, as well as the electrode cell with the sample solution, both at about 32°C. Under such conditions, typical drop times of Ga-droplets were 1–3 s and the electrode assembly could be operated for 2 h with reproducibility of $\pm 2\%$ rel. and the configuration of DGaE was found to be working quite satisfactorily. Most of the experiments have been done in parallel with the DME to reveal and evaluate the individual differences and nuances in their behavior. Of particular interest were capacitance characteristics and electrode kinetics, both reflecting the actual structure of the double layer.

Hitherto the last contribution reporting on a gallium-based liquid electrode — in this case, eutectic Ga-In alloy — has been presented a few years ago by Japanese authors^[34] who were also interested in capacitance and surface-tension measurements at the interface between the Ga-In alloy and ionic liquids, namely, dialkylimidazolium tetrafluoroborate and *bis*(nonafluorobutane-sulphonylamide). It is interesting to notice that the selection of gallium-based electrode material had been inspired by some of the already mentioned studies by electrochemists from the former USSR who had been experimenting with such a kind of alloys in the early 1970s when publishing their results in regional electrochemical journals.

2.3 | Galistan drop electrode

This promising alternative to liquid gallium has been presented at the dawn of the new millennium,^[35] when two German authors introduced galistan as a new kind of electrode material. It is the eutectic mixture of gallium, indium, and tin with a melting point of -19°C , which is deeply below that for gallium alone. According to the authors, the galistan-based electrode had exhibited satisfactory mechanical, physicochemical, and electrochemical properties and — in some respect — almost comparable to those of mercury counterpart.

In the otherwise inspiring report,^[35] it is not unfortunately explained why the galistan electrode had been employed merely in the hanging-drop arrangement, that is, in the voltammetric regime. Thus, its performance and potential applicability in polarographic measurements are not known, which can be challenging for eventual examination.

3 | DROPPING AMALGAM ELECTRODES

3.1 | Dropping bismuth amalgam electrode

It has for the first time been reported in a study by a couple of Soviet scientists^[36] who investigated some electrode reactions in dependence of pH, for example, in the perchloric acid-based supporting electrolytes. Of interest was also the stability of bismuth amalgam and its possible dissolution in such media.^[37]

Another configuration of dropping bismuth amalgam electrode ($\text{DBi}[\text{Hg}]_x\text{E}$) has been employed as an indicator electrode for amperometric titrations of some metal ions based on complex formation in the presence of a large concentration excess of halides.^[38] When using normal pulse

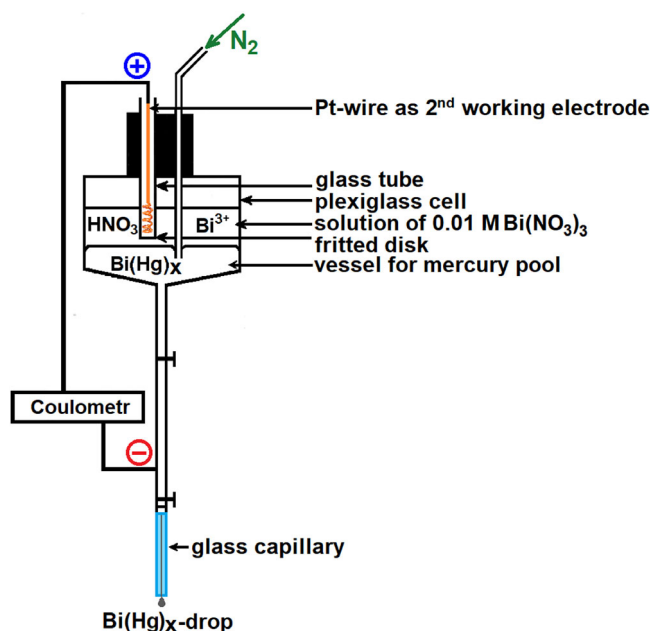


FIGURE 5 Dropping $\text{Bi}(\text{Hg})_x$ amalgam electrode: Construction schematized in a cross-section (redrawn and rearranged^[38])

polarography as the technique of choice, the liquid bismuth amalgam was chosen to prevent the unwanted formation of insoluble Hg^{I} halides and Hg^{II} halide complexes interfering with an indication at the conventional DME. As shown by the scheme in Figure 5, the construction of $\text{DBi}(\text{Hg})_x\text{E}$ resembles that of a common DME.

The liquid amalgam was prepared by electrolysis of 0.01 M $\text{Bi}(\text{NO}_3)_3$ in 1 M HNO_3 , when the resultant concentration of bismuth in the amalgam was *ca.* 0.001 mol L^{-1} , that is, very low. The method itself had then been examined with various metal ions, when Pb^{2+} , Fe^{3+} , and Th^{4+} gave the best results in both direct- and back-titration arrangements.

3.2 | Dropping lead amalgam electrode

The respective configuration proposed by the same research team^[39] is very close to the previous one^[38] and served also as a newly tested amalgam-based indicator electrode for amperometric titrations. In this case, however, the amalgam for the dropping electrode had been prepared by dissolving the elemental lead in mercury. (Prior to this, the metallic lead was rinsed with acetone and kept in 1 M HClO_4 in order to remove lead oxides.) And, again, the resultant concentration of lead in the amalgam was chosen *ca.* 0.001 mol L^{-1} . During characterization of the behavior of the dropping lead amalgam electrode ($\text{DPb}[\text{Hg}]_x\text{E}$), of interest were the I-E curves recorded at varying con-

centrations of the halide ions, namely 0.001–1 M Cl^- , Br^- , and I^- , where the effects of the respective precipitates and halide-complexes were studied. Regarding amperometric titrations, they had represented instrumentally indicated chelatometry (with ethylenediaminetetraacetic acid) performed in the presence of halide ions and tested as both direct and back titrations for determination of Zn^{2+} , Ga^{3+} and VO^{2+} ions.

3.3 | Bismuth amalgam electrode (vs. DME)

Hitherto last paper from the category of reports on liquid-amalgam based electrodes is a study from Spain,^[40] focused on the development and testing of chronoamperometric and polarographic methods for the determination of phosphate in the form of HPO_4^{2-} and throughout the work optimizing the electroanalytical performance of $\text{DBi(Hg)}_x\text{E}$ in parallel with the DME.

4 | CARBON-BASED ELECTRODES WITH PERIODICALLY RENEWABLE SURFACE

4.1 | Basic characteristics of the respective carbonaceous materials

Carbon is undoubtedly one of the most frequent electrode materials used in electrochemical measurements.^[41,42] This statement concerns almost equally natural and synthetic graphites in the compact state, their milled and powdered variants, as well as the new forms of carbon, such as fullerenes, nanotubes, or graphene.^[42,43]

In electrochemistry and electroanalysis, graphite is appreciated for its excellent conductivity, very good mechanical properties, and favorable polarisation capabilities, especially in the anodic direction. Furthermore, it is also a high chemical inertness although resistivity against oxidation may have certain limits. Besides this, the specific structure of some synthetic forms results in enhanced compactness, whereas new modifications of carbon possess very large surfaces exhibiting effective catalytic capabilities. Last but not least, almost all carbons and graphites are non-toxic and environmentally friendly.^[42,43]

Most of the above-surveyed valuable features are typical also for powdered forms; however, if these materials are used in heterogeneous mixtures with a binder (e.g., carbon pastes or various composites) they may manifest less predictable behavior in the resultant electrode configuration compared to homogeneous solid counterparts.^[41,42]

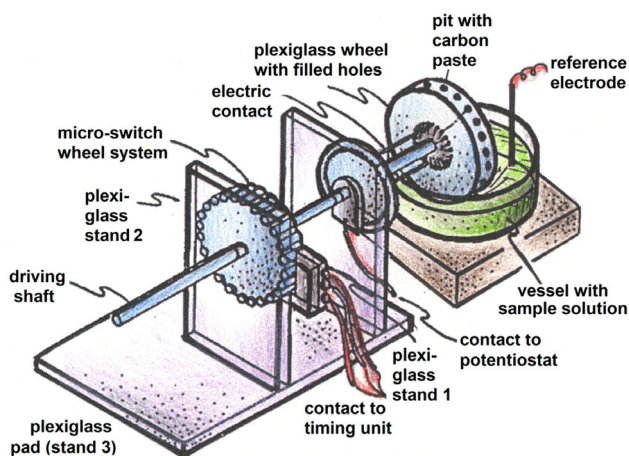


FIGURE 6 Revolving wheel electrode: Construction in an overall scheme with a detailed description of all the components (redrawn and rearranged^[44])

Regarding the configurations presented in this review and surveyed below, only spectroscopic graphite powders were the constituents of choice in the respective electrode materials and, so far, no new forms of carbon have been tested.

4.2 | Revolving wheel electrode

Undoubtedly, one of the most peculiar constructions of an electrode that has ever been proposed is a revolving wheel electrode (RWE^[44]) or also carbon-paste rotating wheel electrode (CP-RWE^[45]). Perhaps, its development and realization had been associated with the rapidly growing popularity of carbon paste-based electrodes invented in the late 1950s^[46] and, since then, still more often appearing in electrochemical labs.^[41,47] Or it could also be another attempt to devise a new electrode assembly applicable in polarographic oxidations of organic compounds (for a time-period context, see the next chapter).

No matter what is true, the latter has been achieved and the RWE represents an example of the electrode whose surface is more-or-less solid in nature, but capable of periodic renewal, thus obeying the principal criterion for a polarographic working electrode.

As seen in Figure 6, the function of this sophisticated construction relies on a large plexiglass wheel containing 24 holes drilled around periphery and each filled up with (the same) carbon paste mixture.

During the measurement, the wheel is slowly turned by electromotor and the construction ensures that its small part is always immersed in a vessel with the solution, thus representing the active electrode surface, which is controlled by a timer with a switching unit enabling the

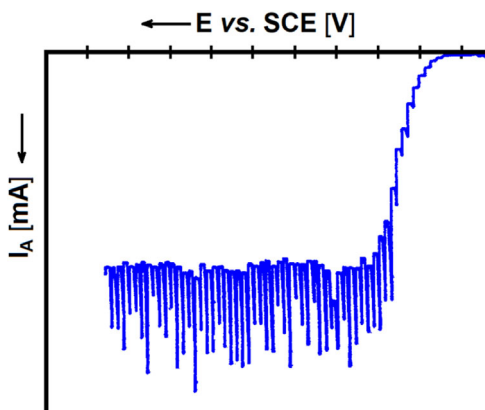


FIGURE 7 Typical polarogram obtained at the revolving wheel electrode after anodic oxidation of 0.005 M 3,3-dimethoxybenzidine in 1 M H_2SO_4 (taken^[44] and redrawn)

inevitable electric contact. Finally, the slow turning of the wheel allows one to manually regenerate the carbon paste surface during the experiment in the holes that are not actually dipped in the solution. This can readily be accomplished by careful smoothing with a clean tissue (e.g., filter paper), further eased by the soft consistency of carbon paste (made of graphite powder and paraffin oil).

That the authors had indeed succeeded in constructing a functional alternative to the DME for anodic oxidations, it can be documented by Figure 7 and finely drawn polarographic wave, including typical oscillations, herein, reflecting the course of periodical replacement of one hole by another in the solution whilst revolving the wheel. Somewhat unsteady limiting current evident also on the polarogram can be attributed to possibly not fully quiescent solution nearby the mechanically moving wheel.

Despite the above-stated, the initial study with the RWE^[44] remained alone and no one else continued in further investigations nor followed this concept with a similarly functioning device. The reason for such a statement seems to be rather complex construction, as well as overall large dimensions, which is incompatible with the oncoming trends of simplification and miniaturization of electrochemical instrumentation.

4.3 | Dropping carbon fluid electrodes

Original Concept by Adams et al. (after^[41,45–48]). Already in the 1950s, when the popularity and practical applicability of Heyrovský's polarography had apparently culminated, some electrochemists interested in the investigation of organic compounds have been thinking about an alternative to the DME that could be applicable for anodic oxidations, where mercury-based electrodes are inapplicable. One of the leaders of such efforts was Adams, worldwide

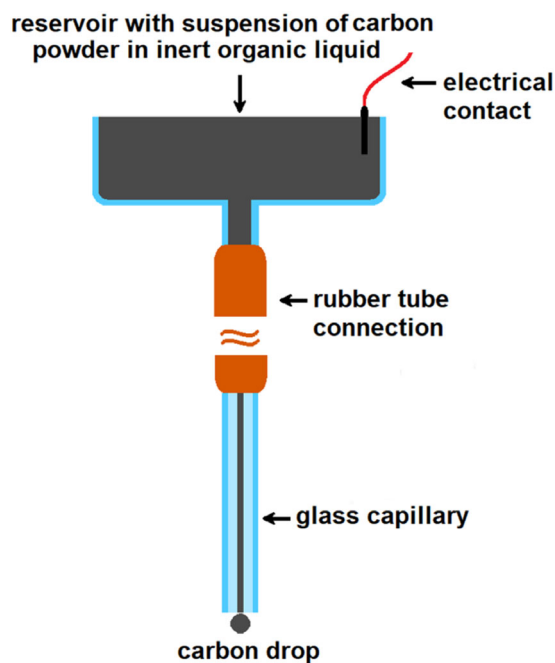


FIGURE 8 Unrealised concept of the dropping carbon electrode by Adams. Schematic view of a possible construction (after^[48] and redrawn^[49])

known as a propagator of voltammetry at solid electrodes and the author of highly acclaimed monograph dealing with this topic.^[41]

Adams had for the first time mentioned a “dropping carbon electrode (DCE)” as a new type of electrode already in his very first paper on CPEs,^[46] having also promised, “a detailed report in the near future”. However, it had never happened and Adams did not reveal more about the DCE until the edition of his book^[41] where could be read that he, himself, and his group had been hardly working on the development of a DCE. He had admitted that the chosen concept with a carbon suspension as the renewable electrode material “was far from ideal” and therefore, their attention had turned to a “thicker paste... (that) would be much more advantageous”.^{[41],[45]}

Further details, for a long time hidden to a wider auditorium, were unearthed relatively recently by one of the former Adams's student, Kuwana,^[48] during the preparation of his own text for a special foreword in the monograph mentioned above.^[45]

In Kuwana's own words, he was a “voluntary slave” who had been carrying out most of the experiments with the original DCE; see Figure 8. Although initial measurements with a suspension of carbon powder had shown some promise, the whole concept failed mainly on a finding that “the liquid binder started to separate from the carbon particles when the composition was sufficiently fluid to flow through and out of the capillary, thus leading to

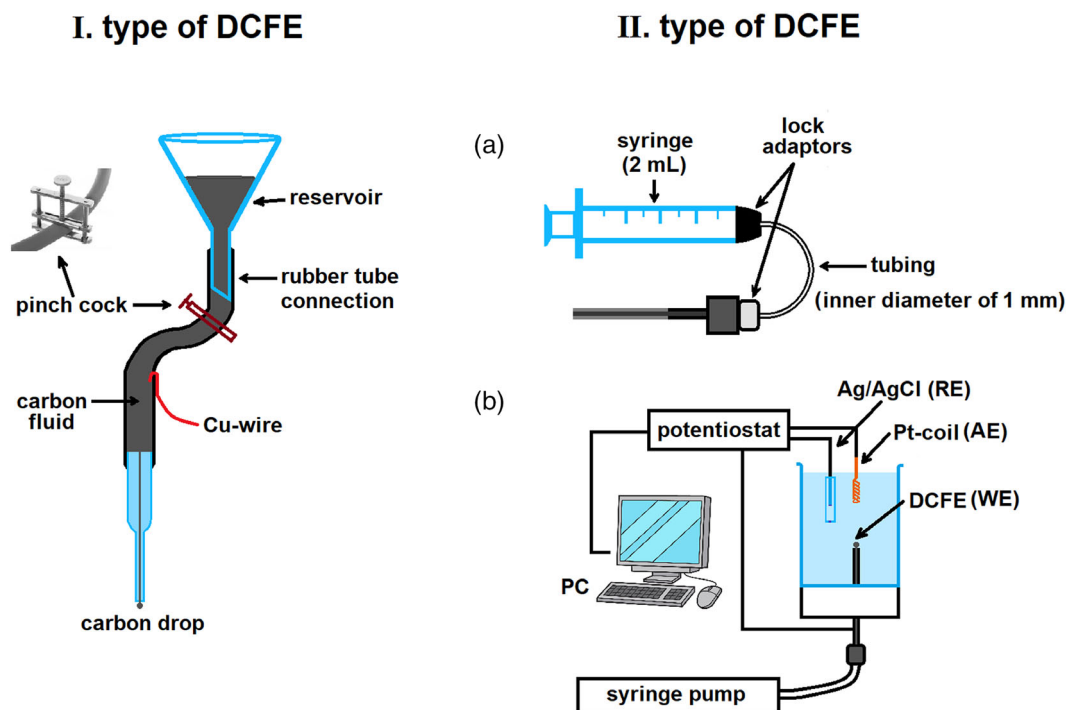


FIGURE 9 Realized concept of the dropping carbon fluid electrode (DCFE) proposed by Tatsumi et al and constructed in two variants. Legend: (I) the first prototype, overall scheme; (II) second improved variant, (a) detail of DCFE with the injection system, (b) overall scheme depicting the reverse arrangement with up-side-down dropping. (Redrawn and rearranged^[50,52,53])

a gradual loss of the conductivity up to a total electrical disconnect”.^[45]

Thus, as already stated, the work on the DCE in Adams’s labs was abandoned in favor of carbon paste with a thicker consistency that became soon a very popular electrode material.^[41,47] Apart from a few remarks about the DCE in later literature,^[45,49] there were no further activities associated with this type of electrode till the end of the 2000s.

Realized Concept(s) by Tatsumi et al.: The idea of a dropping carbon electrode has been resurrected by a team of Japanese scientists in 2012, coming with their own models based on new types of carbon fluids.^[50–55] In a series of systematic studies with the respective configurations, they have originally proposed, in fact, two different formulas that were examined in consecutively improved constructions; see Figure 9.

The modifications in progress have comprised the arrangements operated either as a dropping carbon fluid^[50–55] or also as the stationary carbon drop,^[50] in the linear scan,^[50–53,55] or differential pulse mode,^[54] with the forced (pushed) dropping^[51–53,55] via a delivery system or, finally, in a reverse arrangement, when the carbon drops were extruded from a capillary upward (^[52–54]; scheme II B).

The first configuration – DCE^[50,51,53]: In contrast to Adams’s unsuccessful DCE, Tatsumi and Shiba chose a completely different medium to bind the graphite parti-

cles represented by a mixture of dioctyl phthalate and diiodomethane; the resultant mixture containing *ca.* 20 g C and 50 ml DOP + CH₂I₂ (1:1).

Reportedly, the initial mixture was only binary, without CH₂I₂, but it had been too light, the droplets irregular and not properly falling from the capillary.^[51,53] Thus, a liquid molecule of CH₂I₂ with a very high density (>3 g cm⁻³) was admixed and both fluidity and the dropping thus bettered. Originally, it had been believed that the DCE would have been operated via the natural gravity,^[50] but the configuration had to be eventually devised with a subsidiary delivery system employing a syringe pump.^[51,53]

So improved DCE could then be tested on its performance in selected polarographic measurements; namely, for anodic oxidations of ferrocenyl carboxylate, FcCOO⁻, at the micromolar concentration level in aqueous solutions of 0.1 M KCl. A set of nice polarograms manifesting also characteristic oscillations (due to the periodical dropping) have documented well the functioning of DCE in its revised form and possible applications of “carbon polarography”^[51] could thus be discussed with respect to electrochemical, capacitance, and kinetic studies performed.

The second configuration – DCFE: Despite the evident progress in the original construction described in the second contribution,^[51] the authors have been continuing in further development of their concept.^[52–54]

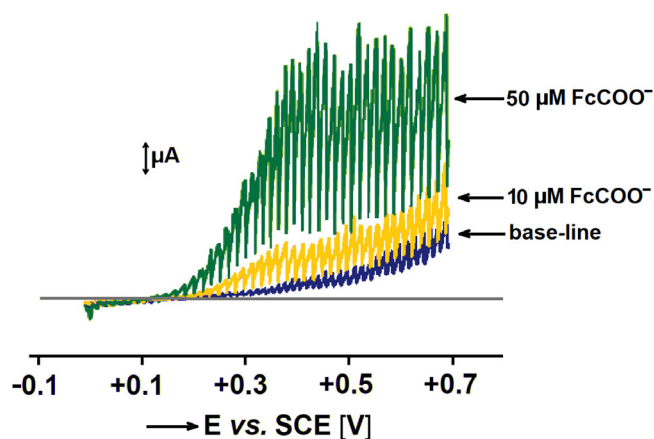


FIGURE 10 A set of polarograms obtained with the dropping carbon fluid electrode and illustrating anodic oxidation of the ferrocenyl derivative at two different concentrations at the micromolar level (redrawn and rearranged from^[52])

At first, the presence of highly dense diiodomethane was ascertained as rather problematic (due to possible oxidation at higher anodic potentials) and the following type, renamed to DCFE, has already omitted the use of this highly toxic substance.^[51] Thus, the authors went back to a binary carbon fluid making it — perhaps coincidentally, but quite surprisingly — very similar to the original Adams's mixture because the newly proposed fluid consisted of graphite powder and paraffin oil at a ratio of C:PO = 4:11. However, also, in this case, the configuration of DCFE required a forced dropping via a delivery system; moreover, in a reverse arrangement with the capillary outlet directed upward (depicted in scheme II B). Furthermore, whereas the first design had employed a glass capillary or small plastic tip, the second construction was devised with the stainless tube.

Finally, for adaptation in differential pulse polarography,^[54] the so far last construction of DCFE was yet equipped with a mechanical pipette, nozzle, and a couple of actuators; all these components being incorporated in a special knocking mechanism that enabled fine and strictly regular dropping.

The electroanalytical performance of DCFE has been studied on a series of experiments when the model compound of choice was again and always FcCOO^- at the low and middle micromolar level. For the up-side-down arrangement used, the appropriate supporting electrolyte was saturated solution of CsCl tested under both air-saturated and air oxygen-free atmosphere. A set of polarograms obtained for the latter case is then shown in Figure 10.

Otherwise, as with the first type of DCE, of interest were some electrochemical and kinetic characteristics, when the experimental data from measurements at DCFE were

confronted with those calculated by means of formulas known from polarographic theory, including the Ilkovič equation for the actual diffusion current, here, in a slightly adapted form.^[52]

Last, but not least, the carbon fluid drop has also been tested in the stationary arrangement in cyclic voltammetry^[50] and in the construction with knocker for differential pulse voltammetry,^[52] where a solution of diluted KCl could be used instead of atypical saturated CsCl recommended before.

The third configuration: Inkjet polarography with DCFE^[55]: The latest improvement of the entire assembly has been attained by choosing a novel carbon fluid, or carbon ink, respectively, prepared from graphite beads and oil of the perfluoroalkane type (in a ratio of ca. 6: 9 gr.) whose favorable consistency allowed the authors to return back to a normal position of the capillary (with outlet downward), but still with forced extrusion of the droplets by a specially devised piezo-electrically driven actuator.^[55] Also measurements with this innovative setup have been tested on the redox transformations of the FcCOO^- species.

5 | OTHER CONFIGURATIONS OPERATED AT POLAROGRAPHIC PRINCIPLES

5.1 | Interface with dropping electrolyte

Rather an unusual approach on how to obtain a dropping electrode with periodical renewal has been shown by a trio of Czech electrochemists^[7a] who introduced a special set-up based on two immiscible electrolytes where one had acted as a working electrode – the so-called electrolyte dropping electrode (EDE). The respective assembly is depicted in Figure 11.

It loosely resembles Heyrovský's DME with the capillary outlet situated reversely – up-side-down and operated in the three-electrode configuration although the whole system incorporates, in fact, five electrodes. Besides the electrolyte drop, there is a mini-reference of the Ag/AgBr type (hidden inside glass capillary), the spiral auxiliary (immersed in the reservoir), and another Pt-electrode as a pair (in this construction with oppositely charged Pt-poles imitating a reference for non-aqueous medium). The aqueous electrolyte was represented by a solution of 0.5 M NaBr and continually dropped upward from capillary which was in direct contact with non-aqueous electrolyte, 0.05 M $\text{N}(\text{C}_4\text{H}_9)_4^+\text{B}(\text{C}_6\text{H}_5)_4^-$ in pure nitrobenzene. Under such conditions, an interface between the two immiscible liquids had been formed at the surface of each drop and immediately polarized.

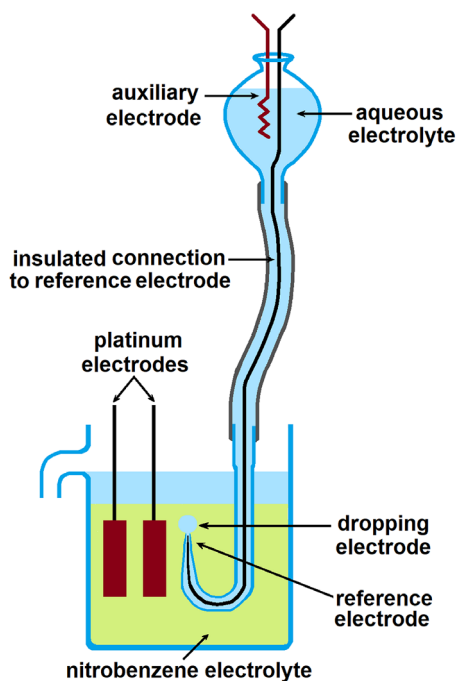


FIGURE 11 Set-up for experimenting with electrolyte dropping electrode. Overall scheme, cross-section (redrawn and rearranged from [7a])

The whole system “pumped” the current flow of positive charge from the solution of bromide across the interface into the nitrobenzene solution, giving rise to flat polarographic waves corresponding to the oxidation of the tetrabutylammonium ion. And if this test analyte was added at the increasing concentrations, the oxidation waves increased proportionally, too. Although the results with EDE had shown still some limitations, the study demonstrated that polarographic principles could be obeyed even with an “electrodeless” working electrode.

A similar liquid-liquid interface for polarographic experiments has been described a decade and a half later by Samec and Papoff.[7b] In their significantly simpler set-up, the electrolyte dropping electrode was used for the study of the ion transition across the interface formed between aqueous solutions of alkali metal ions, Me^+ , and either nitrobenzene or 1,2-dichloroethane, transported through both immiscible liquid phases by means of three model dibenzo-crown ethers and the respective complexes known for their circular structure intercalating the Me^+ ions in the central cavity. In an interesting study, the authors utilized the proposed set-up for evaluating the stability constants of the individual crown complexes with all the alkali-metal ions, that is Li^+ , K^+ , Na^+ , Rb^+ , and Cs^+ having found that organic media chosen had been able to bind the Me^+ species manifold stronger (from 10^5 x to 10^{12} x) than the aqueous environment. Maybe the experiments presented could have been completed with a study

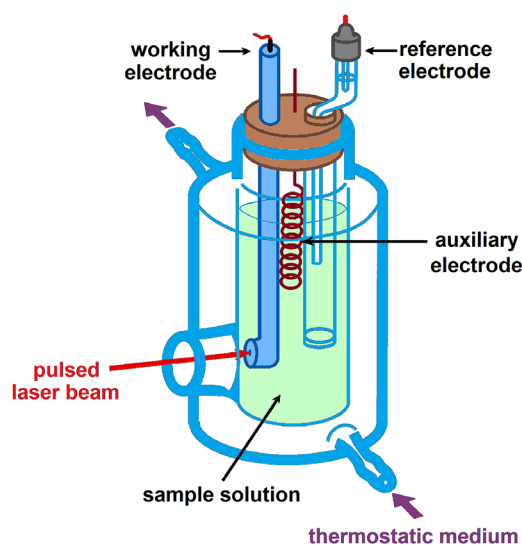


FIGURE 12 Electrode cell with pulsed laser for periodical renewal of working electrode with the solid disc surface. Overall scheme (redrawn and rearranged [57])

on the ammonium ion because of its similar ionic diameter with K^+ , which is a known feature being behind serious interfering effects of ammonium in the determination of potassium at ion-selective electrodes, including the crown-ether modified carbon paste-based variants (see example [45] and the references therein).

5.2 | New concepts with renewable solid surfaces

Periodical renewal of solid electrodes with the aid of laser ablation: A couple of recent reports by Hinoue et al. [56,57] is a proof that the use of highly energetic laser beams ceases to be a domain of spectral techniques and can be useful also in electrochemistry and electroanalysis. The first applications of laser ablation (LA) from the 1980s were proposed for the regeneration of solid electrodes and modifications of some electrode reactions (see example [56] and the references therein).

If the laser is applied in the form of regularly replicated pulses that are targeted directly to the active area of an electrode from compact materials, such as precious metals, then, one can achieve the effective periodical renewal of the surface. Such a configuration with the working disc electrode is shown in Figure 12.

The entire assembly is relatively simple, nevertheless requiring certain shielding due to the after-effects of laser beam stroke (intense emission of light, together with sound and heat blast), which is accomplished by a thermostat with cooling medium; see again the scheme.

Although the authors have called the respective measurements with such a set-up as LA voltammetry (LAV), a close relation with polarography is evident from the principle, as well as on the current-to-potential curves recorded – they resemble traditional polarograms, including typical oscillations given by the laser pulsation. After the inevitable “taming” of rather an aggressive laser and its too intense impact on the microstructure of the electrode surface, as admitted by the authors themselves, it is believed that LAV would find wider use in electrochemical laboratories, especially those dealing with deeper research of electrode kinetics.

Mechanically renewable pencil electrode utilizing a special cutting device: During the revision of this article, Tatsumi et al have published a new paper^[58] indicating a certain sidestep from the so-far consistently pursued route with carbon dropping fluids and inks toward the solid electrodes whose surface can be renewed mechanically by an online-controlled cutter with zirconia blade capable of reliable and reproducible cutting a very thin layer of a pencil lead that forms the electrode material.

Otherwise, the functioning of such device has been tested in the already established way in the polarographic mode by using $[\text{Fe}(\text{CN})_6]^{3/4-}$ and $\text{FcCOO} / \text{FcCOO}^-$ redox pairs. Also here, polarograms exhibited distinct pulsations; however, with noticeable wider signals.

6 | SUMMARY AND OUTLOOK

The previous chapters have introduced and briefly described all hitherto reported non-mercury electrodes that could be traced up in the accessible literature as the configurations with periodically renewable surfaces and thus applicable in polarographic measurements.

Whereas the individual types of such electrodes have been described mainly via their specific design and the most important physicochemical properties, the following survey is made in a more general way as a critical assessment of their positive and negative features with respect to possible employment in the contemporary electrochemical research, compatibility with modern instrumentation, as well as characterization via their actual toxicological and ecological profiles.

6.1 | The pros and cons of the individual configurations

Particular groups and types of non-mercury electrodes with a periodically renewable surface that have been of interest in the above text can be evaluated as follows:

- *Gallium-based electrodes:* Although the corresponding configurations had been examined in numerous studies coming in several waves (see example^[26–31] and the reference therein, ^[32–34]), the results were mostly inconclusive or even negative. The main reasons were, in fact, two: (i) unfavorable mechanics and physical properties of liquid gallium and (ii) its strong inclination to rapid passivation. To eliminate or, at least, to minimize the undesirable effect of both these features, the authors had tried to adapt their constructions, but the attained improvement was only partial, and the overall performance remained questionable.

Thus, in perspective, the liquid gallium-based configurations seem to be no way as the new working electrode for modern polarographic research. A certain promise can be deemed from the attempt with the electrode from galistan alloy^[35]; however, its performance in polarography must be first examined as the realized prototype has been tested merely in the (stationary) hanging drop arrangement.

- *Dropping amalgam electrodes:* Herein, some special studies with bismuth amalgam-based configurations^{[36,37],[40]} cannot be evaluated because of the inaccessibility of the original papers and the corresponding details. Consequently, the two remaining variants, $\text{DBi}(\text{Hg})_x\text{E}$ ^[38] and $\text{DPb}(\text{Hg})_x\text{E}$,^[39] can be taken into account. Despite that both have been proved as fully functioning, one can legitimately doubt whether such electrodes represent indeed the alternatives to the traditional DME. Due to the very low content of the respective metal in mercury (after recalculation, *ca.* 0,2 % w/w), these two electrodes are rather bulk-modified DMEs than dropping bismuth and lead amalgams as they have been presented in the original publications.^[38,39]
- *Carbon fluid- and carbon paste-based electrodes:* From the present day's of view with still increasing accent on ecological aspects, the configurations based on carbon fluids or periodically renewable carbon paste appear to be the proper choice if one seriously thinks of the non-mercury dropping electrode for anodic oxidations in the polarographic mode.

This has been shown by Tatsumi et al. in the last decade on a series of studies.^[50–55] However, there are some “buts” that can be deduced from the reported results and observations. In brief, the final electrode assembly employing a carbon suspension would apparently be more complex requiring (i) special units to deliver lightish carbon fluids through the capillary^[52,53,55] or even (ii) additional knocking mechanism,^[54] and the final assembly would probably

suffer from (iii) lesser conductivity due to the inevitable presence of a binder to keep the array of graphite particles in the flowing state, which may be reflected, among others, in lower sensitivity of measurements.

Regarding carbon-based mixtures, there is also the CP-RWE^[44] that does not employ the carbon fluid and therefore does not require the above-stated adaptations; nevertheless, it is quite improbable that one would prefer this type of working electrode with renewable (carbon paste) surface due to its rather complicated and sizable construction which is scarcely imaginable in modern electrochemical laboratories.

- *Dropping electrolyte electrodes*: Unusual configurations of electrolyte drops with specific liquid-liquid interface^[7a,b] — or else, working electrodes without electrode in the traditional sense — can certainly be useful for occasional electrochemical studies on transport phenomena or phase and chemical equilibria, but hardly will find wider use. And this can be predicted not only because of a rather gentle experimental set-up but also due to the use of organic solvents often problematic from an ecological and toxicological point of view.
- *Periodically renewed solid electrodes*: In contrast to the rather skeptical conclusion made in the previous paragraph, the newest activities associated with the development of systems for renewal of solid electrodes — including the most ordinary ones — seems to be a way of preserving or even strengthening the position of polarographic principles in modern electrochemistry and electroanalysis. And if one imagines a great diversity of solid electrodes and the effectiveness of their modifications, the horizon is wide open...

6.2 | Future prospects

It can be concluded that non-mercury electrodes with periodically renewable surfaces reviewed in this article represent a practical realization of other working electrodes for polarographic measurements, some of them being quite attractive for eventual applicability in anodic oxidations of organic compounds.

Nevertheless, in consequence of numerous technical and experimental specifics commented throughout this text, the individual configurations would apparently remain rather as interesting items in literature databases or, eventually, as an inspiration for the future than the electrodes more widely used in electrochemical research.

At the very end, the authors of this evaluation cannot omit certain associations with one significant achievement in the latest electrochemistry and electroanalysis. It is the area of bismuth film electrodes (BiFEs) and related

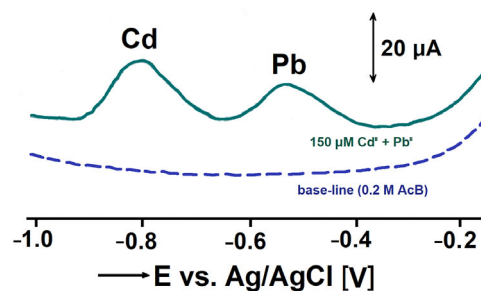


FIGURE 13 Model experiment with a bismuth paste electrode in the square-wave anodic voltammetric mode using a model mixture of Cd^{2+} and Pb^{2+} ions in a diluted acetate buffer. (taken and redrawn^[60])

configurations^[59] as, consensually, the most successful attempt to replace mercury-based electrodes with more environmentally friendly alternatives. Within a still growing number of various kinds and types of BiFEs, there has also been a single experiment with a thick bismuth paste and the respective electrode.^[60] The paste itself, representing a curious example of the carbonless mixture of fine bismuth powder with silicone oil, has been found to be functional (see Figure 13). Thus, it can be deemed as the already existing predecessor of a bismuth fluid.

So far, an electrode assembly based on properly dropping bismuth fluid is an idea only, but when finding a suitable liquid binder — represented, for instance, by some of the well-conducting ionic liquid — and after performing the inevitable tests, a new type of the working electrode for polarography, fulfilling today's strict ecological demands, may become a reality.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

DATA AVAILABILITY STATEMENT

Not applicable.

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