On the evolution and application of the concept of electrochemical polarization

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Abstract

This paper yields an overview on the evolution of the concept of polarization applied to electrochemical systems, ranging from electrodes to cells. The historical discussion starts at the early phase of the development of electrochemistry when current-controlled measurements were possible only, and when the early definitions of *polarization*, *depolarization* and *depolarizer* were created. A number of contemporary handbooks, recommendations and other reference resources are listed in which these concepts are represented in various ways, from conservative definitions to attempts of redefining them. The traditional definitions are confronted with the everyday use of professional language, drawing attention to the fact that the widespread application of potential-controlled electrochemical measurements led to new meanings. Some suggestions are made that open room for the application of the term of polarization in accord with the modern methodologies, without compromising the traditional introduction of the term. Polarization-related phenomena in biological membranes are not dealt with in the present work.

Keywords Electrode polarization · Depolarization · Depolarizer · Current control · Potential control

The beginning: early measurements and definitions

During the early development of electrochemistry, the general method of the control of an electrochemical cell was based on the current passed through this cell. While the current was taken as the independent (technically variable)¹ parameter,

¹ Throughout the paper, the expression “independent variable” shall refer to the one that is controlled (regulated) during the experiment. The discussion will be constrained to electrodes (or cells) for which the potential and the current density are in a mutually unambiguous relationship; therefore, the controlled and measured parameter can be technically exchanged without modifying the j - E relationship. Concerning causality, the parameter whose variation results in a change of the other can be arbitrarily selected. It will be shown that the authors believe that, as an analogy to the transport process, the difference in the intensive parameters should be regarded as the driving force which causes the transport of the corresponding extensive quantity, which means the potential difference is the cause of the current. However, the reverse choice is equally possible and can lead to the same the j - E relationship, even though the j - E function is never evaluated along this line.

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the deviation of the cell voltage from its initial value was taken as the consequence (in other words, the cell voltage was the dependent variable). This contemplation is well exemplified in one of the earliest electrochemistry textbooks written by Arrhenius [1]. In his book, polarization is the very first topic. The demonstration experiment for introducing polarization is constructed from a solution (Na_2SO_4) into which two identical inert metal pieces (Pt) are immersed. When current is passed through the cell and then it is interrupted, a potential difference can be measured between the electrodes, which is taken as a consequence of the polarization of both electrodes due to the reaction products evolved thereof. Hence, electrode polarization was regarded as a potential difference due to the accumulation of specific electroactive substances on the electrodes. When the cell is short-circuited after passing the current, a current of opposite sign as compared to the externally applied one can be measured, which was called the polarization current. Although it was not claimed explicitly, polarization was elucidated as the deviation of either the electrode potential or the cell potential difference from their non-perturbed (yet not an equilibrium) value.

A step of fundamental importance was the discovery of the linear relationship between the overvoltage of a current-loaded electrode and the current density applied, known as the Tafel equation [2]:

$$\eta = A + B \log |j| \quad (1)$$

where j is the current density and η is the overvoltage (which is taken equivalent to the electrode polarization of an equilibrium electrode; see below). For the elaboration of the relationship depicted with Eq. 1, Tafel used a Hg/HgSO₄ reference electrode which made it possible to measure the potential change of the working electrode with respect to a point of fixed potential in the system, even though current control was applied. The Tafel equation is valid for a simple electrode reaction with charge transfer in the case where the concentration of the reactant can be taken unchanged in the entire current density/overvoltage range applied. It is obvious that at the time of its discovery, the current density was the primary (independent, controlled) variable, while the overvoltage was the dependent (measured) one.

As it is described in a fascinating way in the work of Bockris and Reddy [3], the current–potential relationship as the key of electrochemical kinetics just slowly coped with the equilibrium-based view of the electrochemical systems since non-equilibrium electrochemical cells had long been regarded as being “imperfect” and not worth of scientific studies. Due to the dominance of the thermodynamic approach to the field, largely influenced by the successful work of Nernst on the thermodynamic description of electrochemical equilibrium, electrochemical kinetics was just seldom studied. Additionally, the unidirectional view on the electrode potential as a variable depending on the current delayed the development in this field.

The kinetic description of the electrode reaction as formulated by Erdey-Grúz and Volmer [4] opened a new era in the study of electrode kinetics. From their study concerning the overvoltage of the hydrogen evolution reaction on mercury in aqueous solutions, they concluded the relationship that was soon generalized for essentially all electrochemical processes in which charge transfer is a rate-determining step. With the terms applied nowadays, the Erdey-Grúz–Volmer equation [5] (often also cited as Butler–Volmer equation [6]) for a one-step reaction involving a single electron transfer, $\text{Ox} + e^- \rightleftharpoons \text{Red}$ is as follows:

$$j = k_A F c_R \exp\left(\frac{\alpha_A F (E - E_0)}{RT}\right) - k_C F c_O \exp\left(-\frac{\alpha_C F (E - E_0)}{RT}\right) \quad (2)$$

The k parameters are the rate coefficients, c is the concentration of the species marked in the lower index, and the dimensionless α parameters are the so-called charge transfer coefficients for each partial reaction.

In the light of the description of an electrode reaction with the above equation, it is straightforward that the Tafel equation is a good approximation of the $j(E)$ relationship if the electrode potential is far enough from the equilibrium value so that either the anodic or the cathodic partial reaction is

sufficiently suppressed. This makes it possible to give a quantitative meaning for the constants A and B in the Tafel equation. In spite of the kinetic description given by Eq. 2 in which the electrode potential (or the overvoltage) plays the role of the driving force, electrochemical kinetic measurements remained for a long time a current-regulated technique, which necessitated different views for theoretical and practical approaches.

The book of Vetter on electrochemical kinetics [7] summarized the knowledge achieved in this field until about 1960. Vetter offers a definition for the overvoltage η of an equilibrium electrode that is still feasible nowadays ($\eta = E - E_0$ where E_0 is the equilibrium potential). Then, he makes an attempt to define polarization as well, taking into account electrodes on which several electrode reactions take place simultaneously and hence, they exhibit a mixed potential (non-equilibrium case). The definition of the polarization is given for the mixed electrode only by an equation similar to that applied for the overvoltage and taking E_0 as the “zero current potential” of the electrode. By admitting that differentiation between overvoltage and polarization was not very explicit in the electrochemical literature, Vetter indicates that the two concepts are essentially the same for an equilibrium electrode. It is just collaterally mentioned that polarization can be a function of the current density, indicating that various reasons may stand behind the variation of E_0 of a mixed electrode. The question remains if a zero-current state can be achieved for a mixed electrode at different conditions, which of them may yield the “true” E_0 value as compared to which polarization can be calculated.

The change in methodology: transitions from current to potential control

Vetter’s book was the last comprehensive work whose concept was based on the impact of the current as a primary technical variable and in which the overvoltage was taken as a result. At the same time, all kinetic equations were formulated in a manner by taking the electrode potential (or overvoltage) as the part of the driving force of the reaction. However, in a contradictory manner, the overvoltage of the electrode was carefully discussed concerning the origin of the difference as compared to the equilibrium state. In this sense, Vetter’s monograph crowned an era that declined with the widespread accessibility of potential-controlled electrochemical techniques.

The far-reaching impact of the contemplation to regard the electrode potential as the real driving force could manifest itself when potentiostatic (or potential-controlled) measurement was made possible. The first potentiostat was described by Hickling [8]. Commercial potentiostats with analogue input/output and data acquisition were available only until about the late 1980s, and the 2000s brought the age when any possible operation of programmable conditions, performed with either current or potential control, could be made

with a single instrument completed with digital data acquisition.

In parallel with the above listed changes, “polarization” with the ordinary meaning lost its importance since the electrode potential became the technically controlled parameter. In some sense, the world was stood to feet from its upside-down situation caused by the current control in which the widely admitted driving force (i.e., the electrode potential) had to be treated as a consequence. This led to that the setting of the potential of the working electrode was also called shortly polarization, hence avoiding a complicated phrasing of the action of the experimenter. This is what necessitates the reconsideration of the terminology.

Recommendations and definitions

The primary source of the relevant definitions is the IUPAC recommendation which is a reference work comprising the consensus of international scientific bodies. As it can be seen from [9], “Polarization is the difference of the electrode potential from the corrosion potential”, which is very much in accord with Vetter’s definition. This is the only recommendation and the single one mentioning the term of polarization in the IUPAC recommendations. For depolarizer, the IUPAC recommendation is that “The term ‘electroactive substance’ should be used in preference to ‘depolarizer’” [10]. Since the corrosion potential is never an equilibrium one, it can be questioned whether this definition provides an exact reference for a quantity to be measured since the reference conditions are ill-defined.

Another reference work is the Dictionary of Electrochemistry [11] which is a very comprehensive collection of definitions that strives to comply with both the officially accepted definitions and the consensus of the electrochemical community. For polarization, the definition [12] refers to both electrodes and cells, telling that “for a cell or an electrode that has a defined equilibrium potential (...), a departure of the electrode (or cell) potential (E) from its equilibrium value (E_{eq}) is called polarization”. Here, equilibrium of the cell obviously refers to the *electrochemical equilibrium* [13] which refers to the homogeneity of the phases, equality of the electrochemical potential of all components across the interfaces that they are allowed to pass and hence, a zero net current, while chemical equilibrium of the cell reaction would lead to $E_{MF} = 0$.

The conflict between Refs. [9, 12] is obvious. On the one hand, the former has a rather restrictive approach by claiming the necessity of the equilibrium, which obviously cannot be the case for a corroding electrode referred to in Ref [9]. On the other hand, however, Ref. [12] extends the application of the term polarization from electrodes to cells.

Treatment of the notions: how do we speak and write about them?

Polarization used with its traditional meaning

The current-based definition of the polarization is useful with no doubt still nowadays when the passage of a fixed current is either a directly controlled or a measured parameter. This is the case when a reference electrode is rated for the application in three-electrode cells [14]. Here, the potential response of the reference electrode to a burden of current due to the imperfect cell construction and, more importantly, to the limited (i.e., not infinitely large) input impedance of the reference connection of the instrument is the parameter of topmost interest. Since the reference electrode is assumed to be one of a constant potential, its *polarizability* is to be kept at the minimum. Although electrochemical polarizability has no definition in the sources available to the authors, it may be our intuitive feeling that the polarization resistance is a candidate for its proper quantitative measure. At least, polarizability of an *electrode* is to be distinguished from that applied for chemical substances and species in electric field (where polarizability is the ratio of the induced dipole moment and the electric field causing it). Where electrode polarizability (as well as non-polarizability) is discussed, it is noted that no absolute meaning can be attributed to this term, whereas it is admitted to be time- and load-dependent [14, 15] when a long-term application of an electrode is discussed. While the long-term application of an electrode is characterized with an integral (macroscopic) term referring to polarizability, the polarization resistance as a differential quantity can characterize the actual state of an electrode.

Another field where the current-based definition of the polarization is useful is the study of batteries and other electrochemical power sources (e.g., fuel cells). These devices contain two electrodes by default, without an internal potential reference that is independent of the load. The electrical performance of these devices is rated at various currents passing. For these devices, it is particularly true that the current is the independent (regulated) parameter, while the deviation of the cell voltage from its equilibrium value is the dependent one (i.e., a consequence of the current flow). This is well indicated by the structure of the polarization diagram of such devices in which the current (density) is displayed at the abscissa of the graph. The classical terms related to the *origin of the polarization* are highly relevant in this case. Namely, activation, ohmic and diffusion polarization are usually distinguished as the cell load increases, identifying the phenomenon related to the potential drop in various parts of the battery/fuel cell.

Polarization in experiments where the working electrode is under potential control

In contrast to current-controlled measurements, polarization apparently obtained a new meaning when potential-controlled

experiments are performed in three-electrode cells to study the working electrode (reaction) only. A search for the term “potentiostatic polarization” yields hundreds of papers. One can often encounter phrasings such as *the electrode is polarized to/at a particular potential* in recent papers (a few examples selected from various fields can be found in Refs [16–24]). In the description of experiments performed with the control of potential, anodic/cathodic polarization is extensively mentioned as the indication of either the potential sweep direction, the potential range studied as compared to the rest potential of the electrode or the sign of the current hence produced [25, 26]. It also occurs that a polarization regime is given for indicating the stability range of some electroactive substance, which clearly refers to a potential interval instead of any current [27]. These terminologies occur regardless of whether or not either the manipulation with the electrode potential results in the permanent flow of a particular current or the source of the electrochemically active species can maintain a *constant* current.

When one has either an electrode with no substance electrochemically active in the potential window applied (this is often termed as the ideally polarizable electrode [28]) or an electrode with fixed redox capacity, the potential setting operation can be achieved by passing a limited *charge* through the cell. In either of the above cases, the deviation of the potential of the electrode of interest from its rest potential (that is not even necessarily an equilibrium potential) is not regarded as a result of a permanent current. For such systems, polarization is naturally elucidated as either setting or sweeping the electrode potential in a suitable interval [29, 30].

For experiments with potential control, the current is taken as the consequence of the potential setting of the electrode. In such cases, the classification of the means of polarization (activation, diffusion etc.) loses its significance. Rather, one can speak about the means of control (or limitation) of the resulting reaction: activation or mixed control, diffusion-limited process etc.

The change in terminology has another aspect, too. While polarization in a current-controlled experiment is the *reaction* or the *response* of the electrode (or that of the cell) to the current passed, it becomes a *deliberate action* of the experimenter when conducting potential-controlled operations. This duality makes polarization a Janus-faced term in modern electrochemical terminology. The second definition of the polarization also leads to the loss of the meaning of depolarization since a potential setting applied externally to an electrode presumably cannot be counteracted by a chemical reaction at the electrode, provided that a power source of sufficiently large capacity is applied.

Polarization of electrified interfaces that are not electrodes: the ITIES

Interface of two immiscible electrolyte solutions (ITIES) is an interface across which charge transfer is possible at

appropriate conditions; therefore, it makes a two-phase electrochemical system with ionic conductors at both sides of the interfaces. This is why ITIES is not an electrode, having no electron-conducting phase involved in the two-phase system.

As compared to current-controlled two-electrode cells and three-electrode cells with potential-controlled working electrodes, the study of ITIES usually requires a near-symmetric four-electrode cell without a working electrode. The potential difference across the interface is measured between two reference electrodes that are connected to each side of the interface by using a Luggin capillary in order to minimize the ohmic drop if current flows across the interface. The current can be applied by using two auxiliary electrodes that are not close to the interface of the two liquids. For micro-ITIES, the measurement can be performed in two-electrode configuration, provided that the auxiliary electrodes are sufficiently large as compared to the ITIES surface area. This case is fully analogous to the potential-controlled experiments with a microelectrode as working electrode and a macroscopic electrode as combined counter and reference electrode.

Since the early age of the electrochemical studies of ITIES, the terminology used has been very much parallel to that applied for electrodes [31]. The criteria for both “non-polarized” (i.e., non-polarizable or ideally depolarized) and “ideally polarized” (i.e., ideally polarizable) interfaces are similar to the electrodes concerning the commonality of the components of varying oxidation state.

ITIES is generally considered as a polarizable interface in the scientific literature nowadays [32–40]. However, we can find no traditional root of the ITIES polarization related to current control but experiments are carried out with the control of the potential difference of the reference electrodes quite exclusively. This sounds very natural if we consider that the birth of the field is dated after the spread out of the potentiostat.

Depolarization: the application range of a term not recommended anymore

Similarly to the term of polarization, depolarization has also undergone some meaning change, though it is relatively minor. The recent terminology often speaks about oxygen depolarized cathodes in aqueous electrolysis cells [41–43]. This terminology simply means that the cathode reaction is oxygen reduction instead of hydrogen evolution, which results in a diminished cell voltage due to the difference in the potential regime of O_2 and H^+ reduction. For the reactant at the anode, the term “anode depolarizer” also occurs [44]. In both cases, depolarizer is the synonym of the electroactive substance, which is much alike the identification of the species to be reduced in a corrosion process [45] (nevertheless, the term of “hydrogen depolarization” can be heavily criticized since H^+ is reduced and hydrogen $/H_2/$ is the *product* of the

reaction). Depolarization is also used as a term to indicate that by using a certain electron conducting metal for one of the electrodes, an electrolysis process requires lower cell voltage than with another metal [46]. Similarly, depolarization is mentioned when an overvoltage-diminishing additive is applied to facilitate a process [47, 48], even if it is not a reactant but rather a catalyst. For the literature of solar cells, depolarization is used as a term indicating the decay of the potential of an electrode, comparing illuminated and dark conditions [49]. The latter example is an exception in the above list in the sense that it is not related to the application of external current for a cell or for an electrode. Somewhat differently from the above listed papers, “charge depolarization” was used to indicate that the surface charge of a semiconductor electrode could be reduced in the presence of a suitable adsorbate [50]. Some authors attempt to make their findings understood in terms of depolarization and depolarizer, noting at the same time that these concepts are not only old but “obsolete” [51].

Handbooks: what do we teach nowadays?

Handbooks that give a definition for electrode polarization

Koryta, Dvořák and Kavan [52] offer a definition for electrode polarization that is much in accord with that given later in [12]. Their definition for electrode polarization is based on an equilibrium cell, simply by telling that the electrode potential change due to the current passed as compared to the equilibrium state is the electrode polarization. The definition of overvoltage for electrodes having a single equilibrium reaction is the same as given earlier in Vetter’s monograph [7]. Although the concept of electrode polarization could be easily extended for electrodes that are not in electrochemical equilibrium, it was not applied in the abovementioned work [52]. In the discussion of the electrode kinetics, the j - η dependence is termed the polarization curve, and the latter term is not extended to a j - E relationship of an electrode not in electrochemical equilibrium at the rest potential, although it was obviously used throughout the work. Interestingly, the authors also use the expression “polarization voltage” for potential-controlled experiment, indicating the extension of the term polarization to the set-up of the electrode potential instead of applying a certain current. Similar terms related to the potential control, such as the polarization rate as the analogy of the sweep rate, occur in various part of this work [52].

The highly controversial application of the term polarization can be seen in Chapter 2.4.5 of Ref. [52] dealing with conductometry. On the one hand, it is stated that alternating current is applied for conductometric measurements and the electrodes are covered with platinum black “to avoid electrode polarization”. On the other hand, however, it is also indicated

that perturbation amplitude of a few millivolts is used. Hence, a concept coming from current-controlled experiments is transferred to potential-controlled experiments without a proper explanation, and the two contemplations are applied in parallel, which can be misleading for the reader.

In one of the most cited textbooks of electrochemistry and electroanalysis, Bard and Faulkner [53] define polarization in accord with the definition given in Ref. [12], telling that: “If a cell has a defined equilibrium potential (...), that potential is an important reference point of the system. The departure of the electrode potential (or cell potential) from the equilibrium value upon passage of faradaic current is termed *polarization*. The extent of polarization is measured by the *overpotential*, η ” (Page 22 of Ref. [53]). In other parts of the same work, however, the authors do not adhere very strictly to the definition cited above. In many cases when the primary controlled experimental variable is the electrode potential, polarization is used as an equivalent expression for the setting of potential (see, e.g., Chapter 13.3 of Ref. [53] on the double-layer structure). Also, the expression of *concentration polarization* is used in many cases where the experiments are run exclusively with potential control.

Polarization is by far not consequently used even in textbook where it appears at all. Bockris, Reddy and Gamboa-Aldeco speak about polarization in a footnote only as a cloudy and ill-defined term used only at engineering fields for the quantization of all overpotentials occurring in a cell (page 1279 of Ref. [54]). In spite of the lack of a definition specified for electrodes, they use various expressions with polarization (anodic polarization, concentration polarization, polarization curve, constant current/potential polarization).

The dual meaning of polarization in the everyday language of electrochemists was sensitively observed by Bagotsky [55]. While he adheres to the ordinary definition of the electrode polarization based on the current flow and potential response (Page 29 of [55]), later, he refines it. With a minor logical rearrangement of his definitions (Page 80 of [55]), he says that the electrode polarization can be:

1. The phenomenon of change in electrode potential under current flow, and, as its quantitative measure, the change of the electrode potential relative to its equilibrium value
2. An operation performed by the experimenter at obtaining a potential change by passing current of a suitable strength and direction

Even though the second definition of Bagotsky is very close to the everyday terminology, it still bears the contemplation that the primary (i.e., controlled) variable is the current that causes a potential change, not vice versa.

The concept of Sato [56] is quite similar to that of Bagotsky. He defines the term of polarization in electrochemistry as the deviation in the electrode potential from a specific

potential; namely, from the rest (zero-current) potential, whether or not it is a well-defined equilibrium one. In Sato's definition, the potential deviation is not even connected to the flow of current. The meaning of the verb "to polarize" is associated by Sato with the shift of the electrode potential, regardless of the source of the phenomenon (either internal to the system or external). Non-polarizable electrodes are classified as those with the equilibrium of an electrochemical reaction, while the lack of any chemical reaction is given as an inherent feature of a polarizable electrode.

Works that do not deal with the definition of the polarization of either electrodes, cells or ITIES

Apparently, the introduction to electrochemistry is well possible without mentioning polarization itself but relying in a definition concerning the polarizability of an electrified interface. Although it is not known whether the lack of the definition of electrode polarization means that the authors find it either useless or unnecessary, it is worthwhile of summarizing the examples found.

With such an approach, Gileadi [57] offers a rather qualitative verbal definition to the polarizability of an electrochemical interface and loosely connects this definition with the reversibility of the chemical reaction occurring at that interface (Chapter 1.2.1 of [57]). In this definition, the interrelation of the current passed and the potential difference achieved are taken as being independent of which of them was a controlled parameter by restricting the perturbation to a near-equilibrium linear region. Throughout his work, Gileadi avoids the term polarization but overpotential is used wherever needed and even polarization resistance related to electrochemical impedance measurements is called faradaic resistance. Similarly to Gileadi, Lasia [58] also avoided the definition of both polarization itself and polarization curves, although he classified the electrodes as ideally polarized or non-polarized ones on the basis of their response to external perturbation. Unlike Gileadi, Lasia still called the $j(E)$ function the polarization curve.

A similar concept is offered in the work of Hamann, Hamnett and Vielstich [59]. They define neither polarization nor do they call the $j(E)$ dependence polarization curve but the term *current–potential characteristics* is applied throughout their book. Electrode as a *polarizable* object is referred to at the discussion of the behaviour of the electrical double layer (Page 115 of [59]). Electrodes with chemical equilibrium are distinguished from those at which the species are all non-reactive in the sense of the current response to an external potential perturbation, equilibrium electrodes exhibiting a current response and non-reactive electrode characterized with a double-layer rearrangement consuming a little charge only without developing a permanent current. Electrodes with non-reactive species are called *polarizable*. Since it is related

to a potential perturbation, it is clear that the instinctive elucidation of the polarizability is quite far from the current-based definition of the potential change, not to mention the lack of equilibrium on an electrode with non-reactive species only.

The term of ideally *polarizable* electrode as opposed to an ideally *polarized* electrode may appear as a very subtle and even negligible difference. However, it indicates that one speaks about the feature of an electrode itself, regardless of any external impact whose application makes the electrode indeed polarized in a particular way.

A treatment similar to that applied in Ref. [59] can be found in some older literature, too [60]. Here, electrodes permeable for at least one kind of species that maintain equilibrium are called *ideally reversible electrode*, while those having no such species are termed as *blocking* or *ideally polarizable* electrodes. Polarization itself is not defined in the abovementioned work, and the $j(E)$ relationship is alternately called either current–potential curve or polarization curve.

The polarizability of electrodes in the book of Schmickler and Santos [61] is dealt with in relation to electrodes at which no electrochemical reaction takes place in the potential window of the solvent. The notion of the ideally polarizable electrode is introduced without either telling any definition of polarization or referring to what kind of current–potential (or vice versa) relationship makes the polarizability ideal. The definition of the electrode polarization is completely missing from the work of Brett and Oliveira Brett [62] who mention the term of polarization in relation with membrane processes only.

As books written by either a single or at most a few authors often rely on intuitive understanding of the reader on the electrode polarization, this is particularly true for edited books. The introductory chapter of the book of Zoski [63] defines the ideal polarizable and ideal non-polarizable electrodes without the definition of polarization itself (and, sadly, connects these definitions with the role of the electrodes in a three-electrode cell as if the former were the consequence of the latter). The authors of other chapters apply the term of electrochemical polarization as the analogy of electrochemical treatment by passing some currents through, or applying a particular electrode potential for, the electrode of interest (see Chapter 5 of [63]). Various other books edited by a few authors but written by a wider team (e.g., [64–66]) have a similar character in the sense that polarization remains an undefined term while it is widely used by the authors of various chapters in accord with their own understanding.

Do we have to refine traditional definitions?

When speaking about polarization with general meaning, we often associate polarization with the generation of poles; i.e., with charge separation and increase of field strength, should

they originate from any specific interaction. The decrease in the electric field strength can be understood as depolarization, and the susceptibility of a system towards external impacts affecting the field strength can be called polarizability. At the same time, it is to be noted that no field of science defines two terms for the positive and negative result of the same effect but gives the appropriate sign to a quantity (we speak about acceleration only and do not define deceleration separately, we give sign to the magnetic susceptibility etc.). Hence, speaking about polarization and depolarization in electrochemistry depending on the direction of a change seems to violate this rule.

By refraining from extreme vulgarization which may suggest that in electrochemistry, polarization is what the potentiostat does, it is thought that polarization should be acknowledged as a term with multiple meanings, depending on the control mode of either a cell or an electrode. Potential-controlled operations should no longer be called polarization merely in the lab slang but it could be recognized that it gained a new meaning as a result of the improvement of the available instrumentation. It is also thought that, for the sake of the usage of the term *polarization curve* as the compact and smooth description of the current–potential relationship of the electrode behaviour as well as the application of *polarizability characteristics* of an electrode, it is necessary to give *polarization* an up-to-date definition.

Therefore, the following multiple definitions of polarization are suggested to resolve terminology problems as well as to ease everyday speech on electrochemical experiments:

1. For an equilibrium electrode, polarization is the deviation of the potential of this electrode from its equilibrium value as current is passed through the electrode from an external power source.
2. For any electrode, polarization is the manipulation of the electrode during which a particular electrode potential or current (or a pre-defined time function thereof) is applied externally.
3. For an electrochemical cell with a defined electrochemical equilibrium, polarization is the deviation of the cell voltage from the electromotive force of the same cell as a result of the current passed through this cell.
4. For the interface of two immiscible electrolyte solutions, polarization is either the change of the potential difference across this interface as a result of the current passed from an external source or the setting of this potential difference.

The current–potential relationship (in particular, a steady-state one) can hence be called polarization curve for any of the above cases. The above suggestions make it possible to extend the term of polarization for potential-controlled experiments, in accord with the everyday terms, although it would not be

possible with the traditional definition. Version (ii) of the above definition list allows the match of the electrode classification of electrode polarizability to the polarization curves, regardless of the mode of electrode control (current or potential control) since a constant current is not a requirement of polarization. It is also to be recognized that there is no convenient way to use polarization as a current perturbation-related term for non-equilibrium cells because of the lack of any well-defined fixed point in the scale of the cell voltage.

When we strive for correct and easily applicable definitions of the basic concepts of electrochemistry, we have to bear in mind that this pursuit is not self-contained. Experienced electrochemists would certainly adopt the attitude to understand the view of other researchers, but students can be much discouraged if they encounter any controversy that impedes their understanding.

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