UNIVERSAL REFERENCE ELECTRODE SYSTEM FOR NON-IDEAL MEDIA

This paper is dedicated to the 75th birthday of professor Jiří Barek.

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Potentials in electrochemical experiments are referenced to a hydrogen electrode, which is set up in an ideal aqueous medium. However, most electrochemical experiments are performed in media which are far from ideal. This inevitably leads to the necessity of using a liquid junction between ideal and non-ideal solutions, or a pseudoreference electrode. The resulting undefined and irreproducible liquid junction potential can be eliminated by the Universal Reference Electrode system presented here. This consists of two electrodes: a voltammetric metallocene electrode and a potentiometric polyaniline electrode. The system is not a replacement for a Normal Hydrogen Electrode. It is only an elimination of undefined liquid junction potential, when working in a non-ideal medium.

Content

1. Introduction

The realm of electrochemistry can be represented by a triangle in which water (A), organic solvent (B) and room temperature ionic liquid (C) occupy the three corners of the triangle (Fig.1). The real conditions of any electrochemical experiment, shown as point X in Fig.1, are then an arbitrary combination of concentrations *a*, *b*, *c* of these three pure media. This seemingly trivial description becomes complicated when a standard potential of any electrochemical process in a non-ideal medium (NIM) needs to be placed on the hydrogen scale of potentials. The hydrogen scale is based on the simple Faradaic reaction:

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \tag{1}$$

which is defined in an aqueous, ideal medium which is represented by corner A in Fig.1. In practice, it is set up with a *normal hydrogen electrode* (NHE) consisting of a 'platinized/platinum electrode immersed in an aqueous acid of hydrogen ion activity $a_{H^+} = 1$, under 1 atm pressure of H_2'

$$Pt/H_2\,(a=1)/H^+(a=1) \qquad \pi_0 = 0.000\ V \tag{2}$$

The standard potential of this electrode has been arbitrarily assigned zero value[1]. Therefore, any electrochemical experiment $X_{a,b,c}$, performed in a *non-ideal* medium is referenced to the standard state defined in the aqueous *ideal* medium.

Any electrochemical experiment requires a minimum of two electrodes, because a single electrode potential is not experimentally accessible. Only the difference between the potentials of two electrodes, the *cell voltage* E_{cell}, can be measured:

$$E_{cell} = \pi_W - \pi_{ref} \tag{3}$$

The reference electrode in that measurement is constructed in such a way that its potential (π_{ref}) is stable, reproducible, and repeatable, when specific construction details are reproduced exactly (π_W – working electrode potential). Such an electrode is called a *secondary*
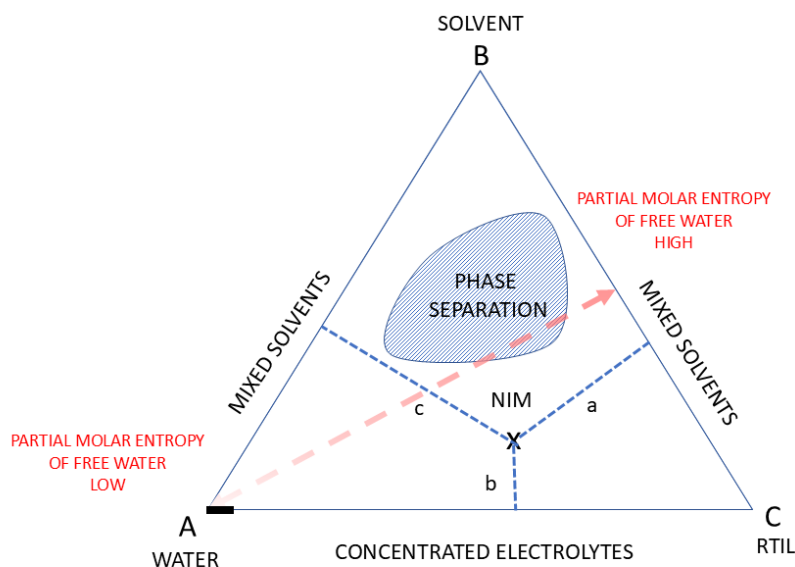
Fig. 1. **Realm of Electrochemistry. Water with dilute salt is the ideal medium (black bar at point A)**. Any other point inside the triangle must be considered as a 'non-ideal medium' (NIM). Phase separation happens in immiscible liquids at certain concentrations. The entropy of free water (dashed red arrow) increases from point A to line BC.

reference electrode. Its potential π_{ref} is always referenced to the NHE. Aqueous silver/silver chloride or calomel electrodes are examples of such secondary reference electrodes. Their potential is defined by the activity of a chloride ion in the aqueous *inner* compartment of the reference electrode. The necessity to close the electrical circuit requires that electrical connection is made between the inner compartment and the working electrode compartment in the electrochemical cell. This is accomplished with an *ionically conducting liquid junction*, which introduces its own *liquid junction potential π_{LJ}*. Thus, the liquid junction is an ionically conducting physical barrier that separates the *inner* compartment of the reference electrode from the outer *working* compartment, where the actual electrochemical experiment is performed. If the media in the outer and the inner compartment are identical, the junction potential is zero. At zero net current and constant temperature and pressure, such a system is in thermodynamic equilibrium. In reality, it never is, because the solutions in the inner and in the working compartments are never identical. This seemingly trivial condition is very important for the Universal Reference Electrode (URE) system presented in this paper.

In common practice, the media in the two compartments are different, yet they electrically communicate with each other through the liquid junction. Therefore, the chemical potential ($\mu_i = (\partial G/\partial n_i)_{j,T}$) of all species in the two compartments must equalize. This condition is true for both ionic and electrically neutral species. If the media are not identical, the liquid junction always leads to the formation of the undefined and

variable liquid junction potential π_{LJ}. Because an NHE is defined in an aqueous medium, water plays a dominant role in all electrochemistry, from bioelectrochemistry, to batteries, to organic electrosynthesis.

In bulk water, only a small fraction of water exists in the form of free single molecules. It is called 'free water'. The rest is coordinated by hydrogen bonds into a complex water structure. However, it is the *free water* that dominates the interaction with other species, in solvation. Thus, species H_2 and H^+ in Eq. 1 do not exist in water. They always interact with other water molecules, they are solvated. If another miscible component is present, *mixed solvation* occurs. Therefore, by performing and comparing electrochemical experiments in different media, the solvation energies of individual species need to be included in the overall energy balance. Because an NHE (Eq. 2) is defined in an ideal aqueous medium, the energy of solvation for any point outside that region needs to be included. That comparison is based on the *free energy of transfer* between the ideal and non-ideal media, for all species. The farther away the point X is from point A (Fig. 1), in any direction, the more severe this problem becomes. The organization of water in any medium, *i.e.* the entropy of free water, is the most important thermodynamic parameter in any electrochemical experiment. It is shown as the red gradient arrow in Fig.1. The free water entropy is lowest in a purely aqueous solution, and highest in media containing a low fraction of water (line BC in Fig. 1).

The use of a conventional aqueous secondary reference electrode in NIM always leads to the formation of an undefined and irreproducible liquid junction

potential. In this paper, we present a reference electrode system in which the undefined liquid junction potential in NIM is eliminated and describe the procedure for calibrating it. The system consists of three electrodes: a Universal Reference Electrode (URE), a metallocene reference electrode PtMc, and a secondary reference electrode, such as a silver-silver chloride or calomel electrode, which relates the potentials in NIM to the hydrogen electrode scale. The solvation energies of the metallocene reference are assumed to be constant in all NIM. This assumption is based on non-thermodynamic considerations[2]. Therefore, the universal reference electrode system for non-ideal media links the URE to NHE, but it is not a replacement for it. It merely eliminates the undefined liquid junction potential.

2. Components of the Universal Reference System for NIM

The elimination of unwanted liquid junction potential in any NIM is done in an ordinary three-electrode voltammetric experiment (Fig. 2) in which a URE, metallocene working electrode (PtMc) and an auxiliary electrode (Aux) are used. The liquid junction (LJ) is an ionically conducting physical barrier between the inner compartment of the URE and the compartment of the working electrode. These two compartments need to contain identical medium. The purpose of the liquid junction is to prevent the electroactive species (depolarizer) in the working compartment from entering the inner compartment of the URE.
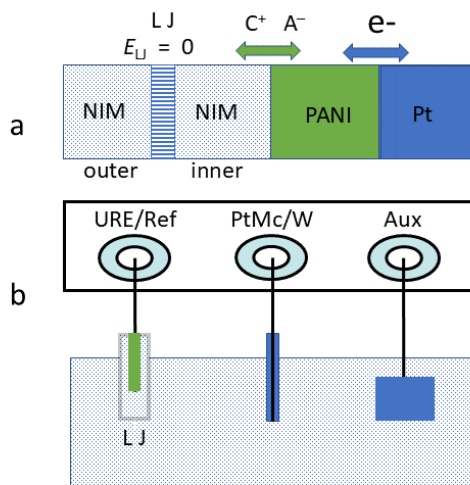

Fig. 2. **(a) Schematic diagram of Universal Reference Electrode. (b) Voltammetric cell for electrochemistry in non-ideal media.** Metallocene electrode (PtMc) is connected to the working electrode terminal for URE calibration. In the actual electrochemical experiment, the URE is replaced with the working electrode (W) and is connected to the reference electrode input.

2.1. Universal Reference Electrode (URE)

Any reference electrode must satisfy the following requirements: its construction must be reproducible, and it must be suitable for any medium depicted in the triangle (Fig. 1). It must also be stable for the expected duration of the experiment, typically for 24 hours. Details of the URE for NIM and its placement in the electrochemical cell are shown in Fig. 2. The system consists of an *inner electrode, inner NIM* and *liquid junction,* which physically separates the inner and the outer compartments. The depolarizer in the working compartment is always present at a much lower concentration than that of any other electrolyte, typically $< 10^{-4}$ M. Therefore, its effect on the liquid junction potential can be neglected. Because the media on both sides of this junction are otherwise identical, $\pi_{LJ} = 0$ V. The elimination of the π_{LJ} from the measured cell voltage is true for any NIM and any junction. The actual construction and materials used for the junction are not critical. Glass frit, asbestos fibre, teflon capillary, etc. can be used. The impedance of the junction is not critical either, since the electrode is connected to a high-impedance input of the potentiostat, and the input bias current is always zero.

The inner electrode in a URE is a Pt electrode coated with a thin layer of conducting polymer, *e.g.* polyaniline (PANI). The purpose of this layer is to serve as a *mixed electronic/ionic* conductor. It facilitates a purely *electronic* communication between the conducting polymer and the platinum, and a purely *ionic* communication between the polymer and the electrolyte in the inner compartment of the electrode. In other words, the inner electrode is an electronically conducting ion exchanger. In the absence of any redox species in the inner compartment, the interfacial potential between the PANI and NIM is purely determined by the ion exchange at the polymer/medium interface. In principle, any stable, conjugated conducting polymer can be used, such as polypyrrole, polythiophene, etc. PANI serves here only as an example[3].

The polymer/metal interface is ohmic, which means that electrons are the charge carriers. As a result, a *contact potential* forms at the PANI/Pt interface and as such, it cancels out in the overall measured cell voltage. When conditioned in any medium, PANI is stable at zero current. The deposition of PANI onto Pt can be done by solvent casting[4], or electrochemically by deposition at constant potential[5]. The electrochemical properties of PANI are illustrated in cyclic voltammograms shown in Fig. 3. Its electrochemical behaviour depends on the medium. In strong acids, the redox transformation at ~ 0.7 V is accompanied by an exchange of anions, while that at ~ 0.2 V by proton exchange (Fig. 3). The *open cell potential*, $\pi_{OCP} = \pi_{URE}$ (Fig. 3, arrows) is the potential of the PANI/electrolyte interface at zero net current ($J = 0$). Because multiple ions freely participate in the ion exchange between PANI and the medium, π_{OCP} is by definition a *mixed potential.* It is determined by the magnitude of the individual partial exchange current
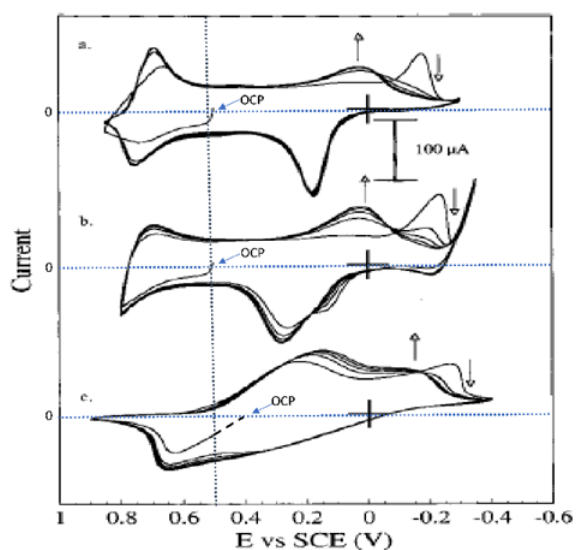
Fig. 3. **Cyclic voltammograms of PANI cast at Pt electrode from formic acid and cycled in 2 M:** (a) HBF_4, (b) H_2SO_4, and (c) CH_3COOH (adopted from Ref. 4). The open cell potential (OCP) is indicated by arrows. The peak at –0.3V on the first scan and the isosbestic point at –0.2 V are characteristic of the solvent exchange from the casting to cycling in a, b, c.

densities (j_i) of all ions passing through the PANI/ electrolyte interface at net zero current:

$$J = \sum_i j_i = 0 \qquad (4)$$

Mixed potential is dominated by the ion with the highest exchange current density. It is called the primary ion, whose activity is a_x. Other ions contributing smaller exchange current density are secondary ions and are usually present at lower activities a_j. In ion-selective electrodes, the domination of the primary ion is the measure of selectivity of the primary ion with respect to the secondary ions. In potentiometric measurement, it is described by the Nikolskij-Eisenmann equation:

$$\prod\nolimits_{\mathrm{URE}} = \frac{2{,}3RT}{z_xF}\log\left(a_x + \sum_{ji} K_{x,j} a_j^{z_x/z_j}\right) \qquad (5)$$

π_{URE} is the potential of the universal reference electrode. The primary (a_x) and the secondary (a_j) ions have charges z_x and z_j, respectively. Multiple ions pass freely through this interface (Eq. 4), with individual charge exchange densities (j_i) greater than 10^{-3} A cm^{-2}. The constant $K_{x,j}$ is the selectivity coefficient, which normalizes the exchange current of the primary and the secondary ions[6]. The shapes of the CVs in Fig. 3 indicate that the overall ion exchange accompanying redox transformations is fast, which indicates that this interface is *non-polarizable*. As far as

we know, this is true for PANI in all electrolytes. In summary, the π_{URE} of PANI/ NIM is stable, but its value is different in different media. Therefore, it must be calibrated against the constant potential of the metallocene reference electrode.

2.2. Metallocene electrode

The effects of solvent on the electrochemical behaviour of various metallocenes (Mc) have been studied in detail[7]. They have been proposed and approved by IUPAC as a universal standard for the free energy of transfer. Ferrocene and cobaltocene have been used as a standard for the electrochemical definition of Hammett acidity functions[8–10]. In those measurements, polarograms of dissolved metallocenes were recorded at a dropping mercury electrode. The experiments were plagued by unpredictable adsorption of the Mc onto the mercury (Fig. 4).

In NIM, the Stokes radius of Mc and Mc$^+$ is likely to change, causing errors in the determination of $E_{1/2}$ from voltammetric measurements. To avoid these adverse effects, metallocene needs to be covalently attached to the surface of the Pt electrode[11–13]. A well-developed CVs of immobilized Mc can be obtained. However, the Faradaic current is obscured by a large capacitive current, therefore pulsed voltammetric techniques must be used instead of normal CV[14]. With this caveat, the PtMc electrode becomes the reference, which can be calibrated against aqueous secondary reference electrodes. Such calibration links it to the hydrogen potential scale.
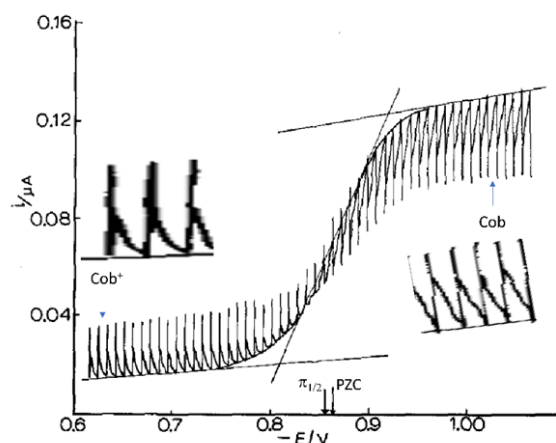

Fig. 4. **Normal polarogram of 10^{-4} M cobaltocenium acetate in 0.965 M aqueous ethylene diamine, recorded on dropping mercury electrode.** Segments of *i-t* curves are shown for Cob$^+$ (E < PZC) and Cob (E > PZC, rotated 180 dg.) for comparison of the shapes of the *i-t* curves. The half-wave potential and potential of zero charge are indicated by arrows. Adopted from ref.[9]
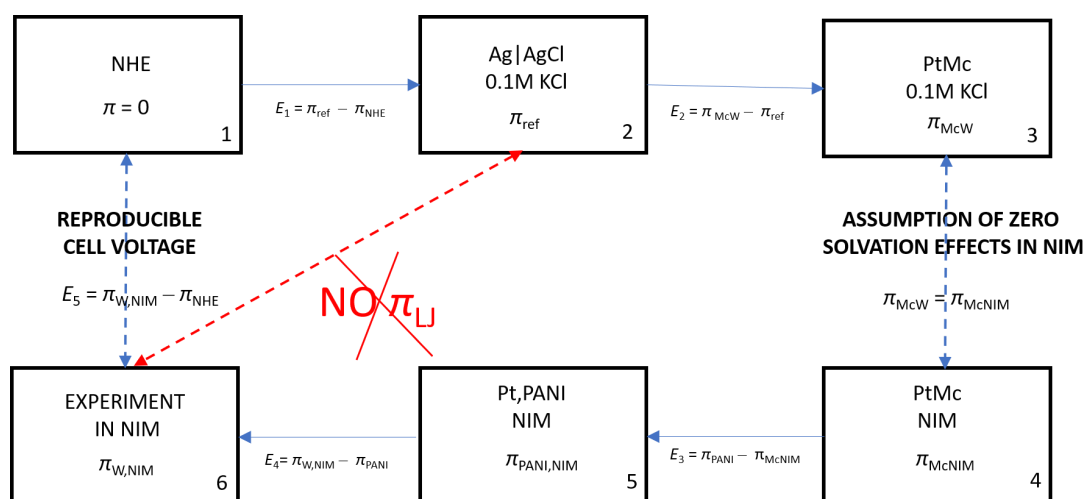
Fig. 5. **Process of elimination of liquid junction potential and calibration against Mc/Mc$^+$ redox standard.** See text for explanation.

2.3. Procedure for the elimination of π_{LJ} by the URE system

Liquid junction potential can be cancelled out by making the media on both sides of the junction equal. The mixed potential of the inner electrode is then calibrated against the potential of the PtMc electrode in the same NIM. The procedure is summarized in Fig. 5. The six panels depict the states of the electrodes. The transitions from panel to panel represent the measurements of the cell voltages.

Panel 1 is the *normal hydrogen electrode.* Panel 2 is the *secondary reference electrode*, i.e. Ag|AgCl in KCl. The measurement of cell voltage in the 1–2 transition is the calibration of that secondary reference electrode against NHE. This yields a known value of the potential of the secondary reference electrode *vs.* NHE. For Ag|AgCl in 0.1 M KCl, this cell voltage is + 0.288 V *vs.* NHE at 25 °C.

$$E_1 = \pi_{ref} - \pi_{NHE} = 0.288 \text{ V} \qquad (6)$$

Panel 3 is the platinum electrode with covalently attached metallocene. Measurement 2–3 in aqueous KCl is the calibration of the PtMc electrode against the secondary reference electrode using cyclic voltammetry. In order to eliminate a high capacitive current, differential pulse voltammetry can be used. The determined values of Mc/Mc$^+$ potential links the potential of the PtMc electrode to the hydrogen electrode scale of potentials.

$$E_2 = \pi_{McW} - \pi_{ref} \qquad (7)$$

Panel 4 is the same electrode but immersed in the non-ideal medium (NIM) used in the experiment. This transition is based on the *assumption of zero medium effect of metallocene* on the potential of the PtMc. In other words, it is assumed that the potential of the metallocene electrode is the same in water and in the NIM.

$$E_2 = \pi_{McW} - \pi_{McNIM} = 0 \text{ V} \qquad (8)$$

Panel 5 is the URE, which consists of Pt coated with polyaniline, immersed in the NIM. The potential of the URE is variable and depends solely on the NIM used. Measurement 4–5 calibrates the URE against the PtMc electrode in that particular NIM.

$$E_3 = \pi_{PANI} - \pi_{McNIM} \qquad (9)$$

Panel 6 is the actual electrochemical experiment in the NIM, with the depolarizer under study. In measurement 5–6, the URE is connected to the high-input impedance input ($I_{bias} = 0.000$ A) of the potentiostat. The electrochemical experiment of interest is done at the working electrode required for the experiment. The working and the inner compartments of the URE are separated by a liquid junction, which prevents contamination of the inner compartment with the depolarizer under study. Because the medium is the same on both sides of the junction, the liquid junction is zero by definition

$$E_4 = \pi_{PANI} - \pi_{W,NIM} \qquad (10)$$

The potential of the working electrode in the NIM on the hydrogen scale of potentials is then obtained by solving equations 7 through 10.

$$E_5 = \pi_{W,NIM} - \pi_{NHE} \qquad (11)$$

3. Discussion

The procedures described here are assumed to be performed in a fully equilibrated state. However, every species and every interface is solvated by the medium. When the medium is abruptly changed, *e.g.* in the transition from Panel 3 to 4 (Fig. 5), the solvation sheets are changed accordingly. That exchange can be a very

slow process, sometimes lasting hours or days[9,15]. Slow kinetics of solvation and solvent exchange, and their effect on the equilibrium potentials in NIM can be dealt with in the following experiments: two identical URE electrodes are prepared in aqueous solution. The first URE_1 is kept in the given NIM for the arbitrarily chosen equilibration time of *e.g.* 24 hours. The second URE_2 is then inserted into the NIM at time $t = 0$ and the $EMF(t) = URE_1 - URE_2$ is recorded as a function of time ($E_{cell}(t) = X_3(t)$). If the kinetics of solvent exchange are fast, $X_3 = 0$, and there is no problem. However, if $X_3(t) > 0$, this is an indication of slow solvation kinetics, and the URE needs to be allowed to stabilize before it can be used as the reference in the actual experiment. The kinetics of the solvent exchange are not known *a priori*. On the other hand, such measurements could become a new tool for the electrochemical study of kinetics of solvation.

The suitability and selection of the most appropriate metallocene reference redox couple for any medium can now be discussed in terms of the Marcus Theory of the outer sphere electron transfer, without the uncertainty of the undefined liquid junction potential in the actual experiment. A comprehensive study of the electrochemical behaviour of ferrocene, pentamethyl- and decamethyl ferrocene in twenty-eight organic solvents has been done[7]. Decamethyl ferrocene proved to be superior due to its dominating hydrophobic effect. However, covalent attachment of decamethyl ferrocene to the Pt electrode would be more challenging and has not has been done yet.

4. Conclusions

There are two electrodes in the URE system. The first is the platinum coated with polyaniline. It is a mixed ionic/electronic conductor, which at zero current establishes a stable, but unknown potential in any NIM. It is always connected to the reference electrode input of a potentiostat to ensure the zero-current condition. The second is a platinum electrode with a covalently bound, medium-independent metallocene redox couple. The voltammetric experiment is then performed at this electrode. Following the workflow outlined in this hypothetical paper, we presume that the undefined liquid junction potential can be eliminated.

REFERENCES

1. Bard A. J., Faulkner L. R.: *Electrochemical Methods*, Chapter 1, 2nd Ed. J. Wiley & Sons, Inc., New York 2001.
2. Strehlow H., Wendt H.: Z. Phys. Chem. N. F. *30*, 141 (1961).
3. Garcia B., Fusalba F., Belanger D.: Can. J. Chem. *75*, 1536 (1997).
4. Hatchett D. W., Josowicz M., Janata J.: J. Phys. Chem. B *103*, 10992 (1999).
5. Jonke A. P., Josowicz M., Janata J.: J. Electrochem. Soc. *159*, 40 (2012).
6. Janata J.: *Principles of Chemical Sensors*, Chapter 6, 2nd Ed. Springer, New York 2009.
7. Noviandri I., Brown K. N., Fleming D. S., Gulyas P. T., Lay P. A., Masters A. F., Plillips L.: J. Phys. Chem. B *103*, 6713 (1999).
8. Janata J., Jansen G.: J. Chem. Soc., Faraday Trans. 1 *68*, 1656 (1972).
9. Janata J., Holtby-Brown R. D.: J. Chem. Soc., Perkin. Trans. 2 *7*, 991 (1973).
10. Janata J., Zuman P.: Collect. Czech. Chem. Commun. *74*, 1635 (2009).
11. Wrighton M. S., Austin R. G., Bocarsly A. B., Bolts J. M., Haas O., Legg K. D., Nadjo L., Palazzotto M. C.: J. Electroanal. Chem. *87*, 429 (1978).
12. Sheridan M. V., Lam K., Geiger W. E.: Angew. Chem. Int. Ed. *52*, 12897 (2013).
13. Lenhard J. R., Murray R. W.: J. Am. Chem. Soc. *100*, 7870 (1978).
14. Dorčák V., Hrbáč J., Janata J., Vacek J.: *unpublished results* (2024).
15. Moakes G., Janata J.: Acc. Chem. Res. *40*, 720 (2007).