

On the interpretation of the potentiometric response of the inert solid electrodes in the monitoring of the oscillatory processes involving hydrogen peroxide

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Abstract Solid inert electrodes are frequently used in potentiometry. However, potentiometric responses may significantly depend on the inert electrode material, a fact which may manifest itself particularly distinctly for the dynamical chemical systems—oscillating processes. We found that for the homogeneous oscillators involving hydrogen peroxide and either thiocyanates or thiosulfates, the periodic variations of the platinum and palladium indicator electrode potential are both not in phase with the variations of the potential of the gold and glassy carbon electrodes, the latter two exhibiting in turn concordant, in-phase responses. Potentiometric responses were compared with the impedance characteristics of the electrodes during the oscillations. In spite of high mechanistic complexity of the studied homogeneous oscillatory systems, we explain different responses of inert electrodes in terms of the concept of the mixed electrode potential, i.e., determined by more than one redox couple of different kinetic characteristics (exchange current densities). In our model explanation, two coupled Ox_1/Red_1 and Ox_2/Red_2 redox systems are considered. It is suggested that for Au or glassy carbon electrodes, the mixed potential is largely determined by the Ox_1/Red_1 couple. For Pt or Pd electrodes, due to the catalytic effect of their surfaces on the Ox_2/Red_2 couple, its exchange current largely controls the measured mixed potential. Our concept is supported by numerical calculations involving the classical Brusselator as the model generator of chemical oscillations. The proper interpretation

of potentiometric kinetic data is crucial for the diagnosis of the correct reaction mechanism.

Keywords Oscillatory reaction · Potentiometry · Redox electrode · Electrochemical impedance spectroscopy · Mixed Potentials · Exchange current · Brusselator · Hydrogen peroxide

Introduction

Oscillatory chemical processes remain the subject of intensive experimental and theoretical research [1–3]. The oscillatory course of homogeneous redox reactions is frequently monitored potentiometrically, using, in most cases, the platinum electrode assumed to be chemically inert. Comparisons of Pt response with other theoretically inert electrodes are very rare. For example, in [4], there are described potentiometric responses of the graphite, platinum, and glassy carbon (GC) electrodes for the oscillatory Belousov–Zhabotinsky (BZ) reaction catalyzed with various redox couples: Ce(IV)/Ce(III), Mn(III)/Mn(II), or Ferrin/Ferriin. Some differences between the reported oscillatory responses, including certain phase shift, were explained in terms of various thermodynamic (standard electrode potential E°) and kinetic (exchange current density i^0 , proportional to the standard rate constant of the electron transfer) properties of these catalytic redox couples at different electrodes. For some organic compounds (like vanillin), the predominant role in the oscillatory changes of the Pt electrode potential was ascribed to the Br_2/Br^- redox couple.

During our recent studies [5] of the Cu^{2+} -catalyzed oscillatory oxidation of thiocyanates with hydrogen peroxide in alkaline media [6, 7] we found differences between the responses of the Pt, Pd, Au, and GC electrodes that were

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much more remarkable than for the BZ system. In the present paper, we report representative results of our potentiometric studies, compare them with the electrochemical impedance measurements, and propose the semiquantitative model explanation of observed discrepancies. The understanding of such phenomena is important for the comparison of the experimental and theoretical variations of the inert electrode potential as a source for the diagnosis of the correct reaction mechanisms.

Experimental

All reagents: Pure for analysis (p.a.) NaSCN (Fluka), p.a. NaOH (Merck, Germany), p.a. $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (ChemPur, Poland), p.a. 95% (w/w) H_2SO_4 (Chempur), p.a. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Chempur), p.a. 30% H_2O_2 (Chempur) were used without further purification.

Potentiometric experiments were performed with a three-channel Hewlett Packard 7090A measurement plotting system (USA). The round platinum plate ($A=0.6 \text{ cm}^2$), the 1-cm-long gold wire ($A=0.22 \text{ cm}^2$), the 1.2-cm-long Pd wire ($A=0.19 \text{ cm}^2$), and a glassy carbon disk electrode ($A=0.096 \text{ cm}^2$) fixed in Teflon casing served as the respective indicator electrodes. Prior to these experiments, the electrodes were cleaned by immersion into a concentrated solution of either NaOH or $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$ solution for 5 min, and the GC electrode was additionally polished with Al_2O_3 (grain size $\varphi=0.3 \mu\text{m}$). These procedures were followed by careful rinsing of the electrodes with distilled water. The potential of every indicator electrode was measured against the $\text{Ag}|\text{AgSCN}|0.1 \text{ M NaSCN}$ reference electrode, separated from the studied solution with a salt bridge filled with 0.1 M NaSCN. The potential of this electrode was found to be for 123.5 mV more positive than the potential of the standard hydrogen electrode.

Chronoamperometric and electrochemical impedance spectroscopy measurements were performed under open circuit conditions with the CH Workstation mod. 660 (CH Instruments). In both techniques, the potential of the working electrodes was monitored vs. the $\text{Ag}|\text{AgSCN}|0.1 \text{ M NaSCN}$ reference electrode. For the impedance measurements, the frequency range 0.1–10 kHz or 10–10 kHz and ac amplitude 5 mV were used. Prior to measurements, the Pt and Au electrodes were washed with acetone, then cleaned with the acidified (H_2SO_4) solution of H_2O_2 , and finally rinsed with distilled water.

For the studies of the oscillations, both the glass batch reactor ($V=25 \text{ cm}^3$) and the flow reactor of the same volume were used. The latter reactor was connected to the three-channel peristaltic pump ISMATEC SA MS REGLO (Switzerland), with the stepwise adjustment of the flow rate. The contents of both reactors were homogenized with

the use of a magnetic stirrer PM TYPE MM 6 (Poland), and measurements were made at an ambient temperature maintained within the range 292–300 K.

Results

Potentiometric measurements

The $\text{H}_2\text{O}_2\text{--OH}^-\text{--SCN}^-\text{--Cu}^{2+}$ oscillator [6] was prepared by mixing NaSCN, NaOH, and H_2O_2 solutions (in the indicated order), and oscillations were induced by injection of an appropriate portion of CuSO_4 solution. The crucial observation was that monitoring of these oscillations using three electrodes, Pt (as in [6] and [5]), Au, and GC, led to remarkably different responses, shown in Fig. 1a: When the Pt potential increases, the potential of the other two electrodes decreases, with the values of the potential closest to each other only at the peak values. One should note that the direction of the Pt potential changes was concordant with that reported in the previous papers [6, 7]. Similar discrepancies were observed by us also for the flow conditions (Fig. 1b).

Furthermore, Fig. 1c proves that the response of the palladium electrode was similar to that of the Pt electrode (only with a bit smaller amplitude of oscillations) whose observation is generally not surprising, taking into account the well-known chemical similarity of both metals.

In turn, Fig. 2 proves that also for another H_2O_2 -based oscillator, $\text{H}_2\text{O}_2\text{--H}^+\text{--S}_2\text{O}_3^{2-}\text{--Cu}^{2+}$, the potential of Pt electrode increases when the potential of Au electrode decreases, so again, the minima of Pt electrode potential correlate with the maxima for the Au electrodes.

These potentiometric measurements suggest that the studied H_2O_2 -based oscillatory systems, with any two different, e.g., Pt and Au electrodes immersed, form a galvanic cell of the electromotive force oscillating as a function of time and thus causing the flow of the oscillating electric current through the circuit (Fig. 3). As the impedance measurements for the same system proved, this current was controlled by the charge transfer resistance R_{ct} (approximately $2 \text{ k}\Omega \text{ cm}^2$) rather than by the relatively low solution resistance $R_s=51 \pm 1 \Omega \text{ cm}^2$ which would explain only a significantly higher current.

Electrochemical impedance studies

The course of spontaneous oscillations was further monitored using electrochemical impedance spectroscopy under open circuit conditions. Figure 4 collects the impedance parameters for the Pt and Au electrodes calculated from the measurements at single frequency $f=100 \text{ Hz}$. Within the sharp oscillatory peak, the real (Z') and the imaginary (Z'')

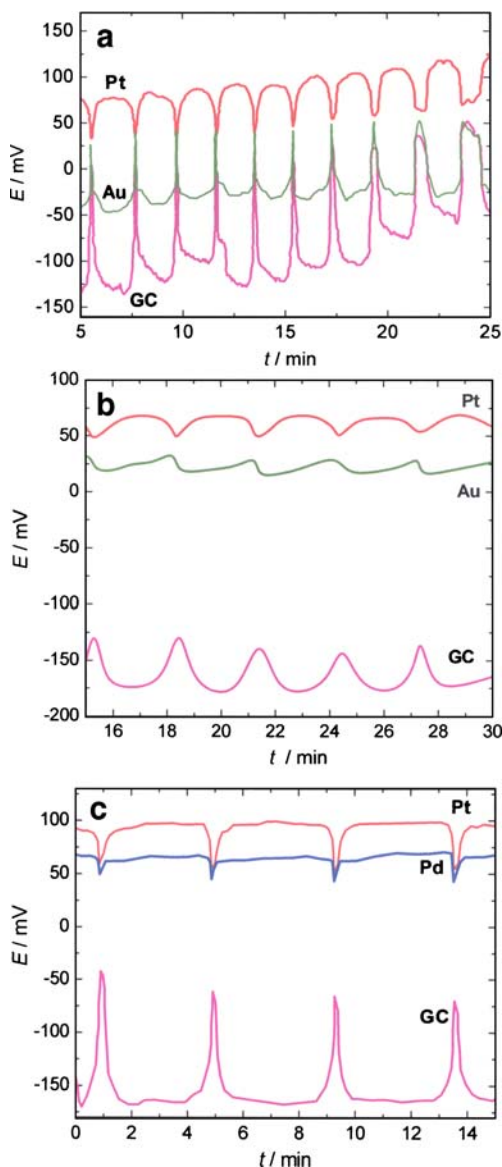


Fig. 1 Oscillatory variations of the electric potential of various indicator electrodes as a function of time for the Cu^{2+} -catalyzed oxidation of SCN^- with H_2O_2 . **a** GC, Au, and Pt electrodes; stirred batch reactor. Initial concentrations (M): $[\text{H}_2\text{O}_2]_0 = 0.38$; $[\text{NaSCN}]_0 = 0.056$; $[\text{NaOH}]_0 = 0.038$; $[\text{CuSO}_4]_0 = 2.46 \times 10^{-4}$. **b** GC, Au, and Pt electrodes, continuously stirred tank reactor (CSTR), initial concentrations in the streams feeding the reactor (M): $[\text{H}_2\text{O}_2]_0 = 0.50$; $[\text{NaSCN}]_0 = 0.10$; $[\text{NaOH}]_0 = 0.10$; $[\text{CuSO}_4]_0 = 2.0 \times 10^{-4}$. The kinetic parameter related to the summary flow of all streams $k_0 = 6.16 \times 10^{-3} \text{ s}^{-1}$. **c** GC, Pd, and Pt electrodes; stirred batch reactor. Initial concentrations (M): $[\text{H}_2\text{O}_2]_0 = 0.34$; $[\text{NaSCN}]_0 = 0.051$; $[\text{NaOH}]_0 = 0.045$; $[\text{CuSO}_4]_0 = 2.1 \times 10^{-4}$. Temperature, 299.2 K. The intensity of the pale yellow color of the solution was slightly increasing at high Pt (or Pd) potentials

parts of the impedance change in the same direction for the Au electrode and in the opposite directions for the Pt electrode. In consequence, the variations of the phase angle are also opposite. The analysis of impedance response in terms of the appropriate equivalent circuit showed that for

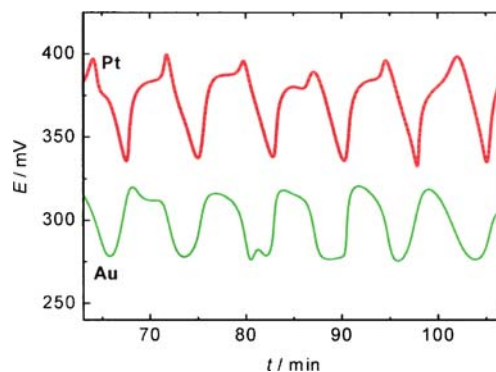


Fig. 2 Oscillatory variations of the potential of the Au and Pt electrodes as a function of time for the Cu^{2+} -catalyzed oxidation of $\text{S}_2\text{O}_3^{2-}$ with H_2O_2 in the continuously stirred tank reactor (CSTR). The reactor was simultaneously fed with three streams (A, B, C) with the following concentrations of the reactant in the given stream (M) A: $[\text{Na}_2\text{S}_2\text{O}_3]_0 = 0.03$; B: $[\text{H}_2\text{O}_2]_0 = 0.3$, C: $[\text{CuSO}_4]_0 = 7.5 \times 10^{-5}$, $[\text{H}_2\text{SO}_4]_0 = 0.003$. The kinetic parameter related to the summary flow of all streams $k_0 = 0.010 \text{ s}^{-1}$. Temperature, 299.2 K

both electrodes, the serial resistance, R_s , neither significantly changed during the oscillations nor exhibited any periodical fluctuations. One can conclude that the oscillations are not associated with the periodical formation/destruction of a new solid phase at the electrode surface. In turn, differential double-layer capacities, C_d , as expected from the variation of the imaginary part of impedance, in principle exhibited periodical small amplitude oscillations with opposite phases for Au and Pt, but this effect can be explained in terms of the trivial dependence of the double-layer capacity on the periodically varying interfacial potential drop.

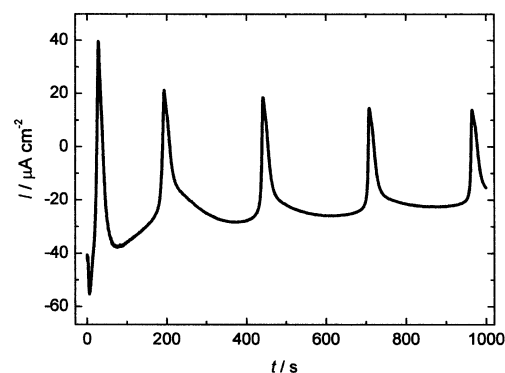


Fig. 3 Oscillatory current–time dependence measured for the Pt| H_2O_2 , OH^- , SCN^- , Cu^{2+} |Au cell upon zero external polarization with Pt as the working and Au as the counter-electrode of the same surface area $A = 0.6 \text{ cm}^2$. Initial composition of the solution (M): $[\text{NaOH}]_0 = 0.045$; $[\text{NaSCN}]_0 = 0.051$; $[\text{H}_2\text{O}_2]_0 = 0.34$; oscillations induced after injection of $2.1 \times 10^{-4} \text{ M}$ CuSO_4 (batch stirred reactor). Inter-electrode distance, 0.4 cm. Temperature, 295.2 K

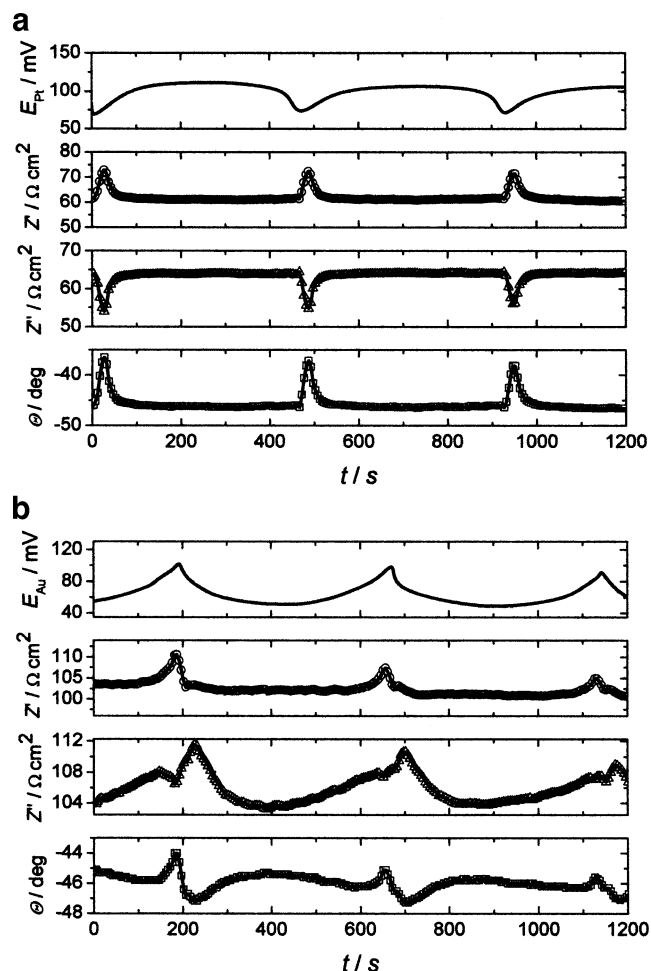


Fig. 4 Correlation between the oscillating electrode potential (—) and simultaneously determined (for $f=100$ Hz) ac characteristics: real Z' (—○—), imaginary Z'' (—△—) parts of impedance and the phase angle θ (—□—) for the Pt (**a**) and Au electrode (**b**), respectively. The circuits consisted of **a** Pt working electrode ($A=0.60$ cm²), Pt quasi-reference electrode ($A=1.00$ cm²), Au counter-electrode ($A=0.92$ cm²) and **b** Au working electrode ($A=0.95$ cm²), Au quasi-reference electrode ($A=0.95$ cm²) and Pt counter-electrode ($A=1.00$ cm²). Composition of the solution (M): [NaSCN]=0.1, [NaOH]=0.1, [H₂O₂]=0.5, [CuSO₄]= 2×10^{-4} , kinetic parameter for CSTR, related to the summary flow of all streams $k_0=2.46 \times 10^{-2}$ s⁻¹. Temperature, 296.2 K

Additional SERS studies

We also attempted to make a series of experiments using surface-enhanced Raman spectroscopy (SERS) involving roughened Au electrode, as well as the Au electrode on which the Pt monolayer was deposited [8], with the intention to detect eventual different states of these surfaces in contact with H₂O₂-containing media. However, for the oscillating H₂O₂-SCN⁻-OH⁻-Cu²⁺ system, the SERS response for both electrodes became very complex, noisy, and poorly reproducible, presumably only partly because of continuously evolving bubbles of oxygen that disturbed the pathway of a laser beam.

Thus, using the SERS technique, it is difficult to get a clear information about the differences in the state of Pt and Au electrodes in the oscillatory H₂O₂-SCN⁻-OH⁻-Cu²⁺ system. From the literature studies [9], one can conclude that although thiocyanate ions adsorb specifically on Pt electrode, with possible potential- and pH-dependent dissociation into S_{ads} and CN⁻, the amplitude of oscillations observed in our experiments is too small to cause such decomposition, so one may suppose that SCN⁻ ions are non-electroactive and remain adsorbed on Pt surface.

In view of the above results, the different potentiometric responses of various inert electrodes in H₂O₂-containing media will now be discussed in terms of the thermodynamic and kinetic characteristics of the redox couples in the solution in contact with the given electrode.

Discussion

Application of the concept of the mixed potential

We postulate that a source of differences between the responses of various inert electrodes for the H₂O₂-based oscillators is the complexity of those systems containing several redox couples [the catalytic Cu(II)/Cu(I) couple being only one of them]. In such a case, the measured electric potential of the inert electrode is a mixed potential, dependent on the relative magnitudes of the exchange currents of the coexisting redox couples [10]. For instance, for the simplest case of the two one-step, one-electron processes with cathodic (α) and anodic (β) transfer coefficients equal to 1/2 (symmetrical activation barrier):

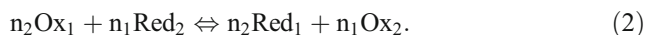
$$E_{\text{mixed}} = \frac{RT}{F} \ln \frac{[|i_{0,1}| \exp(\frac{FE_1}{2RT}) + |i_{0,2}| \exp(\frac{FE_2}{2RT})]}{[|i_{0,1}| \exp(\frac{-FE_1}{2RT}) + |i_{0,2}| \exp(\frac{-FE_2}{2RT})]} \quad (1)$$

where $|i_{0,1}|$ and $|i_{0,2}|$ mean the absolute values of exchange current densities, while E_1 and E_2 denote the equilibrium potentials for the separated Ox₁/Red₁ and Ox₂/Red₂ couples, respectively. An analogous concept was used in [4] for the explanation of the (relatively slight) discrepancies of various inert electrodes for the Belousov-Zhabotinsky system.

However, in our case of the H₂O₂-based oscillators, it is not sufficient to stop the explanation at this stage, since one has to understand also the reversed directions of the changes of the (Pt or Pd) and (Au or GC) electrode potentials in the areas of the peaks as well as different average potentials attained by every of these electrodes.

Let us keep, for simplicity, the model assumption of only two, Ox₁/Red₁ and Ox₂/Red₂, redox couples present in the system considered. Let us assume further that for both Au and GC electrodes, the exchange current density of the Ox₁/

Red₁ system is much higher than that for the Ox₂/Red₂ couple. As a consequence, the oscillating mixed potential attained by these electrodes is largely due to oscillations in the [Ox₁]/[Red₁] ratio. Then, the reversed direction of the oscillatory peaks reported for the Pt and Pd electrodes means that in contact with the surface of these metals, the electron transfer rate (or the exchange current density) for the [Ox₂]/[Red₂] couple significantly overcomes that for the Ox₁/Red₁ couple, but with the [Ox₂]/[Red₂] concentration ratio increasing when [Ox₁]/[Red₁] ratio decreases, and vice versa. This, in turn, means that Ox₁/Red₁ and Ox₂/Red₂ redox systems are coupled through the following interaction:



These equilibria are schematically depicted in Fig. 5. In reality, this reaction may not necessarily (and probably is not) a single-step process, but it may consist of several steps summarizing into the schematic coupling expressed by Eq. 2.

In terms of this explanation, let us compare further the shape of oscillations shown in Fig. 1. The maximum amplitude occurs for the GC electrode which presumably reflects mainly the oscillations of the [Ox₁]/[Red₁] ratio. For the Au electrode, the same direction of oscillations is still observed, but their amplitude is smaller and the average potential is more positive than for GC whose changes are understandable in terms of a bit greater exchange current of the Ox₂/Red₂ system. For Pd electrode, the average potential is even more positive and the oscillations are already reversed, with their amplitude a bit smaller than for

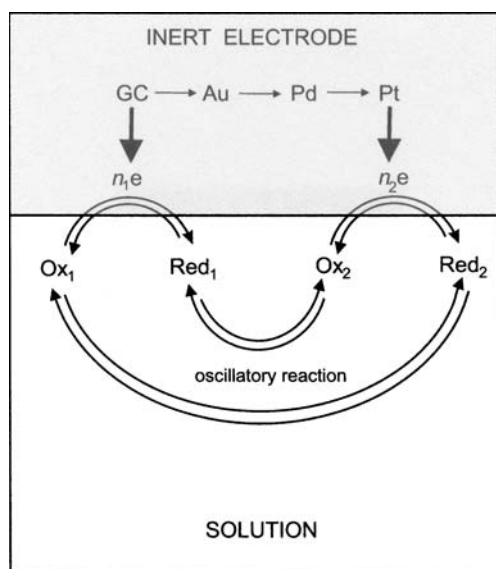


Fig. 5 Schematic representation of, involved in oscillations, coupled Ox₁/Red₁ and Ox₂/Red₂ redox systems for which the individual heterogeneous standard rate constants of the electron transfer at the inert electrode|electrolyte interface depend on the electrode material. Thick vertical arrows indicate the redox couple of the standard rate constant (or exchange current density) predominating for a given electrode material (GC or Pt)

the Pt electrode. It is understandable in terms of so enhanced exchange current of Ox₂/Red₂ couple, compared to Ox₁/Red₁ system, that the latter couple does not decide the direction of oscillations any more. Ox₁/Red₁ is only able to make the net amplitude of oscillations moderate. For the Pt electrode, the exchange current for Ox₂/Red₂ is already so high that the average potential is most positive and the amplitude of reversed oscillations is the highest.

The model

In order to confirm at least semiquantitatively the presented explanation, we constructed the model which explains the dependence of potentiometric oscillations on the kinetic properties of the Ox₁/Red₁ and Ox₂/Red₂ couples. The following assumptions were made:

- Since the detailed reaction mechanism in the H₂O₂–SCN[–]–OH[–]–Cu²⁺ system is not entirely known in spite of advanced efforts [7], the oscillatory concentration changes of the species involved in reaction 2 may be simulated by any reasonable model mechanism which produces the concentration oscillations of two species with a significant phase shift, and not related to bistability, as it is the case for the H₂O₂–SCN[–]–OH[–]–Cu²⁺ system [6].
- The classical two-variable Brusselator model [11] was arbitrarily chosen as the generator of model oscillations of the intermediate X and Y species:



One should add that any other model with autocatalytic steps, producing oscillations with the phase shift, could also be used instead of Brusselator.

- In scheme 3, X species was identified as Ox₁, while Y species was assumed to be identical with Ox₂ in Eq. 2; in this way, when [Ox₁] attains maximum during the oscillations, the [Ox₂] value is close to its minimum, just like for reaction 2;
- Since Brusselator is only a two-variable model, it is further assumed that the oscillating concentrations of Red₁ and Red₂ species are the complements to the constant summary concentrations: [Ox₁] + [Red₁] and [Ox₂] + [Red₂]; during the oscillations, only the relative proportions [Ox₁]/[Red₁] and [Ox₂]/[Red₂] are changing. This means of course that the Brusselator cannot be considered a part of a real mechanism of the oscillatory process considered. It is only a model tool for the direct generation of oscillatory changes of Ox₁ and Ox₂ concentrations. If this approach seems

questionable, it is useful to add here that instead of Brusselator or any other two-variable autocatalytic reaction scheme, one could use even two abstract sinusoidal dependences: $[Ox_1]/[Red_1]=a \times \sin(t)$, $[Ox_2]/[Red_2]=b \times \sin(t+\pi)$ and prove the essential validity of the whole model, but the oscillatory potential changes would then have the shapes markedly different from those observed experimentally.

- (e) The concentrations of Red₁ and Red₂ species adjust instantaneously to the Ox₁ and Ox₂ concentrations generated by Brusselator;
- (f) The number of electrons exchanged for Ox₁/Red₁ and Ox₂/Red₂, respectively, $n_1=n_2=1$ was assumed;
- (g) The kinetics of the electron transfer for Ox₁/Red₁ and Ox₂/Red₂ at the electrode|electrolyte interface, defined by the standard heterogeneous rate constants $k_{s,1}$ and $k_{s,2}$, respectively, are considered the only factors affecting the response of the given electrode; thermodynamic parameters characterizing the redox couples in the solution bulk are kept constant during the simulations.

Based on the above assumptions, for every discrete time step Δt , the following numerical procedure was employed:

- (a) Calculation of the actual instantaneous Ox₁ and Ox₂ concentrations from the numerical integration (using Runge–Kutta method) of the differential equations corresponding to the Brusselator model; the assumed constant values $[A]=1$ and $[B]=2.5$ met the condition for the sustained oscillations: $[B]>[A]^2+1$; the initial values $[X]_0=[Ox_1]_0=0.3$ and $[Y]_0=[Ox_2]_0=0.1$ were chosen.
- (b) Calculation of the corresponding actual concentrations: $[Red_1]=2.8-[Ox_1]$, $[Red_2]=3.8-[Ox_2]$ where the numbers mean (exemplary) total concentrations of (Ox₁+Red₁) and (Ox₂+Red₂), respectively.
- (c) Calculation of the corresponding equilibrium potentials E_1 and E_2 :

$$E_1 = E_1^{0'} + \frac{RT}{F} \ln \frac{[Ox_1]}{[Red_1]} \quad (4a)$$

$$E_2 = E_2^{0'} + \frac{RT}{F} \ln \frac{[Ox_2]}{[Red_2]} \quad (4b)$$

with $E_1^{0'} = -0.085$ V and $E_2^{0'} = 0.050$ V denoting the formal potentials of the Ox₁/Red₁ and Ox₂/Red₂ couples, respectively, estimated based on the experimental courses from Fig. 1.

- (d) Calculation of the individual exchange current densities [12]:

$$|i_{0,1}| = Fk_{s,1}[Ox_1] \exp \left[-\alpha F \left(E_1 - E_1^{0'} \right) / RT \right] \quad (5a)$$

$$|i_{0,2}| = Fk_{s,2}[Ox_2] \exp \left[-\alpha F \left(E_2 - E_2^{0'} \right) / RT \right] \quad (5b)$$

with the cathodic transfer coefficient α assumed to be equal to 0.5.

- (e) Calculation of the corresponding mixed potential, E_{mixed} , based on Eq. 1.

In all simulations $k_{s,1}=1 \times 10^{-4}$ m s⁻¹ was kept constant, while the rate constant $k_{s,2}$ varied from 1×10^{-6} to 1×10^{-2} m s⁻¹; in this way, the electron transfer in the Ox₂/Red₂ couple was either lower, comparable to, or faster than that for the Ox₁/Red₁ couple. Representative results of these calculations, collected in Fig. 6, clearly show that the ratio of standard rate constants determines the shape of the oscillations in the manner closely resembling those observed in our experiments. In particular, if the electron transfer for the Ox₂/Red₂ couple is relatively fast (curve 4), the minimum of the mixed potential is close to its maximum on the course for the much faster electron transfer for Ox₁/Red₁ (curve 1). Furthermore, the average potential and the shape of oscillations vary with increasing $k_{s,2}/k_{s,1}$ ratio in a way resembling the experimental dependences: The high amplitude oscillations in curve (1) turn into low amplitude ones of the same phase (2), then to the low amplitude of the reversed phase (3), and finally to the high amplitude oscillations of a reversed phase (4), with monotonously increasing average potential. Clearly, model courses (1)–(4) may be considered analogous to those recorded for the GC, Au, Pd, and Pt electrodes, respectively.

The validity of the model is confirmed also in this way that for increasing $k_{s,2}/k_{s,1}$ ratio, the oscillatory courses approach an asymptotical shape, very close to curve (4) in Fig. 6, corresponding to the situation that the mixed

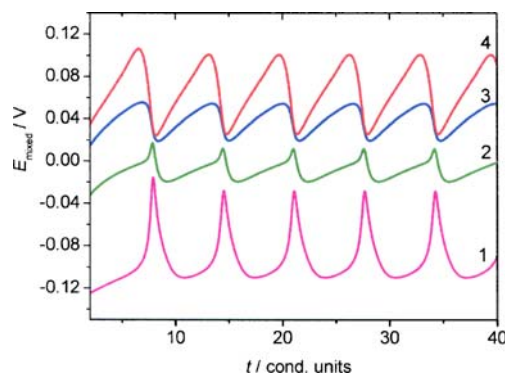


Fig. 6 Simulated time series of the mixed potential E_{mixed} , calculated with Eq. 1 for the Ox₁/Red₁ and Ox₂/Red₂ couples engaged in oscillations generated by the Brusselator model, for the constant heterogeneous standard rate constant $k_{s,1}=1 \times 10^{-4}$ m s⁻¹ and various $k_{s,2}=1 \times 10^{-6}$ (1), 1×10^{-4} (2), 1×10^{-3} (3), 1×10^{-2} m s⁻¹ (4) (see text for more detailed description). Courses (1), (2), (3), and (4) resemble experimental courses for the GC, Au, Pd, and Pt electrodes, respectively, shown in Fig. 1a. $T=298.15$ K

potential is determined practically only by the Ox_2/Red_2 couple. On the contrary, for increasing $k_{s,1}/k_{s,2}$ ratio, the oscillating potential asymptotically approaches the shape close to curve (1), when practically only Ox_1/Red_1 couple decides the mixed potential.

Analogous essential trends of the mixed potential variations are observed if in the model, the total concentrations of $[Ox_1+Red_1]$ and $[Ox_2+Red_2]$ are assumed so high (e.g., 100 times more than above), compared to the oscillating Ox_1 and Ox_2 concentrations, that the Red_1 and Red_2 concentrations are practically constant, so it is not necessary to consider them the dynamical variables. Another possible assumption is that the electrodes are sensitive to Ox_1 and Ox_2 activities only. In both these cases, two dynamical variables coming from the Brusselator model are entirely sufficient to simulate the potentiometric responses explaining the essential phenomenon; only the detailed shapes of $E_{mixed}-t$ courses appear then to be not so close to the experimental ones, as those shown in Fig. 6.

Concluding, irrespective of the detailed model relation between Ox and Red species, the presented approach explains the difference in phase of the oscillations and in the average oscillating potential reported experimentally for various inert indicator electrodes immersed in H_2O_2 -containing media.

Identification of Ox_1/Red_1 and Ox_2/Red_2 couples

Since the kinetic mechanism of $H_2O_2-SCN^-OH^-Cu^{2+}$ oscillator is not yet completely recognized, the redox couples involved in the creation of the mixed potential cannot be unambiguously identified and quantitatively characterized. Nevertheless, one can suggest the redox systems which could most probably constitute the Ox_1/Red_1 and Ox_2/Red_2 couples.

According to Orbán [6], the (oscillating) yellow color of the $H_2O_2-NaOH-KSCN-CuSO_4$ system comes from Cu^1OOH species, the decrease in concentration of which (and simultaneous increase in $[Cu(II)]$) is associated with the decrease in the Pt electrode potential. Since, in view of our analysis, this means the correlation of the increase in $Cu(II)$ species concentration with the increase in Au (or GC) electrode potential, one can suggest that the Au (or GC) electrode potential is determined largely by the $Ox_1/Red_1=Cu(II)/Cu(I)$ redox couple [involving, among others, $CuSCN$, $CuOOH$, $Cu(OH)_2$ and presumably other species] [6, 7, 13].

In search of the identity of the Ox_2/Red_2 couple for which the electron transfer should be remarkably enhanced by the interaction with the Pt or Pd surface, one can easily find that such an effect there reveals redox couples involving oxygen, including peroxides, which were also suggested to be involved in the oscillations for the H_2O_2-

$SCN^-OH^-Cu^{2+}$ system, e.g., OH/OH^- or HO_2/HO_2^- [6, 7]. A survey of literature data (see Table 1) clearly proves the catalytic effect of either Pt or Pd electrode, compared to Au electrode, on the redox processes involving oxygen. For example, for KOH solutions, the exchange current density increases for about 50–300 times if Au electrode is replaced by Pd or Pt electrode, respectively. It is noteworthy that our simulations predicted similar ratios for the standard rate constants (not exactly for the exchange currents which depend also on the oscillating concentrations). In Fig. 6, $k_{s,2}$ for curve (3-“Pd”) is higher for the factor of 10 than for the curve (2-“Au”), and $k_{s,2}$ for the curve (4-“Pt”) is 100 times higher than for the curve (2-“Au”). Of course, according to the model assumption that $k_{s,1}=const$, the corresponding $Cu(II)/Cu(I)$ couple should not exhibit simultaneous catalytic effect upon changing the electrode material. Unfortunately, analogous kinetic data for $Cu(II)/Cu(I)$ couples at different electrodes seem to be missing in the literature. Nevertheless, one should note that the process $Cu^{2+} + HO_2^- \rightarrow Cu^+ + HO_2$ was suggested in [6] as one of numerous elementary reaction steps whose fact is a sound premise that Ox_1/Red_1 and Ox_2/Red_2 systems may be identified as $Cu(II)/Cu(I)$ and, e.g., HO_2^-/HO_2 couples, respectively, engaged in a process (2).

Finally, it is noteworthy that the shape of oscillations, dividing the studied four electrodes into two groups, (GC, Au) and (Pd, Pt), is concordant with the literature classification of Au and GC electrodes to the same group of metal surfaces, and Pt to the other group, based on the difference in the detailed mechanism of O_2 reduction [19].

Summary and conclusions

The concept of the mixed potential allows one to understand the potentiometric oscillatory responses of various chemically inert electrodes in H_2O_2 -containing media. In particular, it appears that the coexisting Ox/Red

Table 1 Representative kinetic data for the O_2 to OH^- reduction (involving H_2O_2 as the intermediate) at different electrodes, showing the strong electrocatalytic effect of both Pt and Pd surfaces, compared to Au surface

Medium	Electrode	i_0 ($A\ cm^{-2}$) ^a	α ^b	Reference
1 M KOH	Au	3×10^{-14}	0.83	[14]
0.1 M KOH	Au	1.9×10^{-14}	0.62	[15]
1 M KOH	Pt	1×10^{-11}	0.54	[16]
0.1 M KOH	Pd	1×10^{-12}	0.65	[17]
1 M NaOH	Pd	3.2×10^{-10}	0.50	[18]

^a Exchange current density

^b Cathodic transfer coefficient

couples in the solution may exhibit so different exchange current densities for various electrode materials that the potentiometric response of some electrodes (like GC or Pt in our case) may appear highly selective with respect to a given Ox/Red couple. Then even the direction of oscillations monitored with one electrode may be reversed compared to another electrode material. Our studies refer to the oscillatory systems containing hydrogen peroxide, one of the most intensively studied compounds, but the importance of a report showing how different the potentiometric responses of various inert electrodes can (and explaining the origin of these differences) go beyond the area of oscillatory processes.

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