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Time-dependency of impedance spectroscopic studies of oscillatory systems

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Abstract

Non-steady state nature of impedance spectroscopy for the investigation of electrochemical systems displaying oscillatory behavior was shown. To this aim, an electrochemical oscillator involving metal dissolution was chosen as a typical example. It was demonstrated that the impedance spectra recorded for the Fe/H_3PO_4 system are strongly time-dependent, which is attributed to the growth of passive layer on the electrode surface. Indeed, resistance of the passive film formed on the electrode surface increases gradually, which has a significant effect on the system dynamic. Interestingly, impedance measurements recorded suggest instability of the system (and consequently appearance of oscillatory behavior) for certain values of film resistance and indeed at a certain time range of the experiments. Generally, as a typical example, it was demonstrated that how time-dependency of complex systems with complicated dynamics such as oscillators could be a source of errors in their analyzing.
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1. Introduction

Electrochemical impedance spectroscopy is a powerful technique in electrochemistry. This technique has been well proposed based on both theoretical (mathematical) and experimental developments, and has been widely used for various applications [1–5]. However, the most investigations have been made for stationary electrochemical systems by assuming that the results are independent of time. Only few reports have been devoted to time-dependent nature of impedance spectroscopic measurements of electrochemical systems [6–8]. In other words, impedance spectroscopy is usually considered as a steady state or quasi-steady state technique by electrochemists.

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Whereas, fast reactions (changes and becoming) of most electrochemical systems deserve particular attention to time-dependency of the experimental measurements.

The occurrence of oscillatory behavior in electrochemical systems has been known for more than a century [9,10]. Due to valuable advantages of electrochemical oscillators, they have been widely used as model systems for fundamental studies from both physical chemistry and chemical physics points of view. In this context, different techniques including both electrochemical and non-electrochemical ones were proposed for the investigation of such (electro)chemical oscillators. Impedance spectroscopy has also been used as a powerful technique for this purpose. The concepts of impedance spectroscopic studies of electrochemical oscillators have been well proposed by Koper [11–13]. According to the complicated dynamic of oscillators, time-dependency of impedance spectroscopy of electrochemical oscillators is of great interest, although, it is not usually taken into account in the literature.

The aim of the present Letter is to investigate the influence of such time-dependency on the dynamical behavior of an electrochemical system judged by impedance spectroscopic measurements. The Fe/H_3PO_4 system was typically chosen for the present research, and there is no emphasis on this system. Hence impedance spectroscopy of electrochemical oscillators is a very difficult concept, it is essentially needed to examine its applicability, e.g., by Kramers–Kronig relationships. However, this action is not necessary for the present study, because the system under investigation is well known and the aim of the present Letter is simple comparative studies of time-dependent nature of impedance spectroscopy by simple experimental investigation at different experiment times.

2. Experimental

The experimental measurements were performed at Department of Chemistry, K.N. Toosi University of Technology. The experiments were carried out at room temperature in a conventional three-electrode electrochemical cell. The working electrode was prepared from an iron wire as long as 10 cm with 0.008 inch diameter, which was spiraled, with 0.5 cm in diame-

ter. The Fe was obtained from Hopkins & Williams with purity better than 99.8%. A platinum rod and an Ag/AgCl | sat. KCl, were used as counter and reference electrode, respectively. A volume of 50 ml electrolyte solution was used each time. Due to shape of the Fe electrode and short distance of the electrodes in the electrochemical cell, Luggin capillary was not used. The electrolyte solutions were prepared from doubly distilled water and phosphoric acid (Merck, 85%). No action was taken to remove oxygen from solutions. Voltammetric measurements were carried out using an EG&G (Princeton Applied Research, Princeton, NJ) Model 273A potentiostat/galvanostat. Impedance measurements were performed with a HF frequency response analyser (Solartron 1265) connected to the potentiostat/galvanostat (EG&G M273). Impedance measurements were made in different frequency ranges, as noted in the text, and only reproducible data are presented. Different runs of the experiments were performed to examine reproducibility of the results, and similar spectra were reported for modeling purpose of the present study.

3. Results and discussion

3.1. Oscillatory behavior of the Fe/H_3PO_4 system

The appearance of oscillatory behavior during electrodissolution of iron in phosphoric acid was first reported by Sazou [14]. The dynamical behavior of the Fe/H_3PO_4 system is similar to other metal dissolution-involved electrochemical oscillators. Different dynamical behaviors of the system under investigation have been reported [15–18]. Fig. 1 shows a typical cyclic voltammogram of the Fe/(10 M H_3PO_4) system. By scanning the potential between −0.5 and 1.5 V (vs. Ag/AgCl), five main regions can be observed: (i) the active region, (ii) the pre-limiting current peak, (iii) the limiting current plateau, (iv) the transition region or the oscillatory region, (v) the passive region. As seen, the current oscillation was occurred at a region between the limiting current plateau and the passive region where the current decreases by increasing the potential (a branch with negative slope).

A typical impedance spectrum of the system under investigation, obtained at a potential corresponding to the negative slope of the voltammogram where the cur-
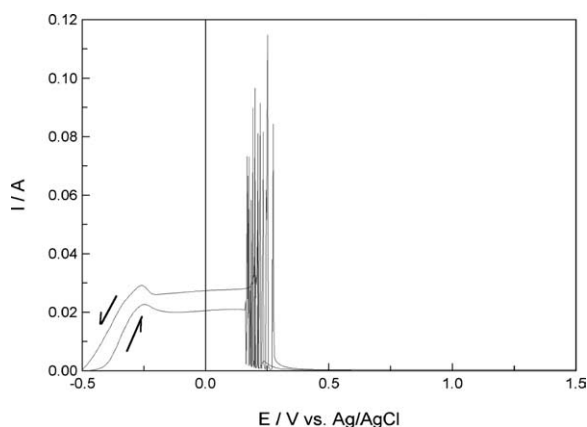
Fig. 1. Cyclic voltammogram of the Fe/(10 M H_3PO_4) system. Scan rate of 1 mV s^{-1}.

rent oscillations are observed, is illustrated in Fig. 2(a). The spectrum shows a semi-circle at high frequencies in the first quadrant where the impedance is always positive. At lower frequencies, it enters to the second quadrant, and subsequently enters to the third quadrant. Finally, it backs to the second quadrant but not enter in it. The spectrum suggests Hopf bifurcation when the system resistance has a value between the Faradaic impedance (Z_F) and polarization resistance (R_p). The other impedance spectrum recorded at a potential out of the oscillatory region but still from the negative branch (Fig. 2(b)) shows that although the sign of the Faradaic impedance is negative and the system is dynamically unstable, it cannot oscillates as it has only unstable saddle-node bifurcation, and Hopf bifurcation (leading to oscillatory behavior) cannot be achieved as Z_F and R_p are coincided (for classification see [11–13]). These two impedance spectra and the general equivalent circuit illustrated in Fig. 2(c) will be used for comparative studies of time-dependency.

At this section, oscillatory behavior of the Fe/(x M H_3PO_4) system with $x = 10$ M was described as an ideal oscillatory behavior of the system under investigation, as the most strong current oscillations can be observed at this concentration [14]. However, we continue our investigation using $x = 14.8$, as the Fe/(14.8 M H_3PO_4) system displays oscillatory behavior only at certain values of controllable parameters. The latter is a sensitive electrochemical oscillator, which the appearance of its oscillatory behavior is highly dependent on the experimental conditions.
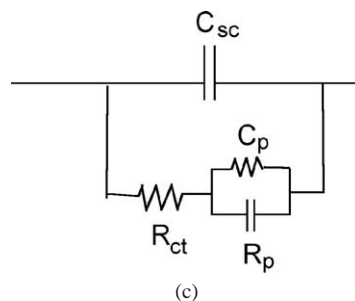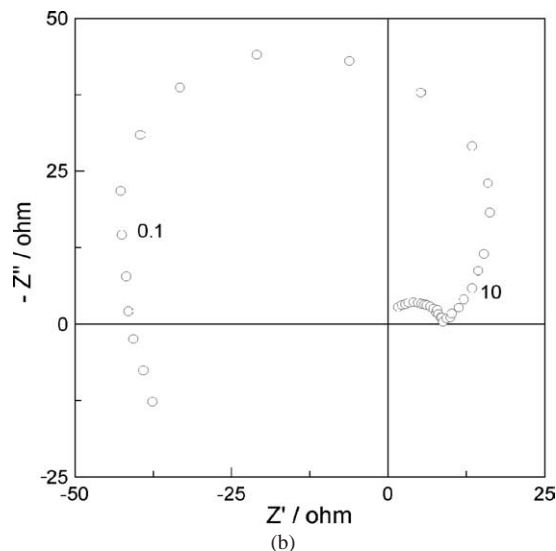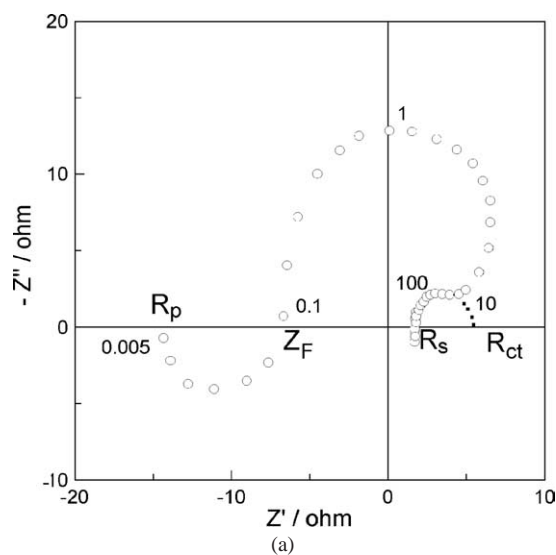

Fig. 2. Typical impedance spectra of the Fe/(10 M H_3PO_4) system recorded at (a) $E = 200$ mV and (b) $E = 300$ mV vs. Ag/AgCl. (c) A general equivalent circuit for metal dissolution involving the formation of a single passive layer.

3.2. Effect of time during pre-passivation of the electrode

At this stage, we are obliged to perform impedance measurements at a narrower frequency range (which is accompanied by a shorter experiment time) to compare time-dependency of the results. Fig. 3 compares the impedance spectra of the Fe/H_3PO_4 system with fresh and aged Fe electrodes. The impedance spectrum of the system using a fresh Fe electrode does not suggest the appearance of oscillatory behavior. It is what expected, as the $Fe/(14.8 M\ H_3PO_4)$ can display oscillatory behavior at certain values of controllable parameters such as external resistance (which was not employed in the present study) [15]. However, the impedance spectrum of the system using a Fe electrode aged at the electrolyte solution for 1 h before the measurements indicates negativity of the Faradaic impedance. This behavior disappears for longer aging of the Fe electrode, and the impedance spectrum of the system using a 3 h-aged electrode does not show negative Faradaic impedance, like the fresh Fe electrode.

According to the generalization made in [11–13] for impedance spectroscopy of electrochemical oscillators, two main necessity conditions for the occurrence of oscillatory behavior is $Z_F < 0$ and $R_s > |Z_F|$. It is aimed here to investigate the entrance of the impedance spectrum into the second quadrant at due frequencies (e.g., in the frequency range recorded here), though, the spectrum will finally enter into the second quadrant, as the applied potential belongs to the negative branch of the polarization behavior. In the latter case (when the spectrum is entered to the second quadrant at very low frequencies, i.e., out of the range of the present measurements), the spectrum cannot enter into the third quadrant to form a spectrum like that illustrated in Fig. 2(a). Thus, the spectrum will be similar to that illustrated in Fig. 2(b) suggesting a saddle-node bifurcation (which does not predict oscillatory behavior).

Although, this approach (investigation of the spectra at such given frequency range) is not very appropriate for the investigation of the occurrence of oscillatory behavior, but it is of interest for comparative study, which is the aim of the present study. On the other hand, as performing impedance measurements at low frequencies is time-consuming, it is not
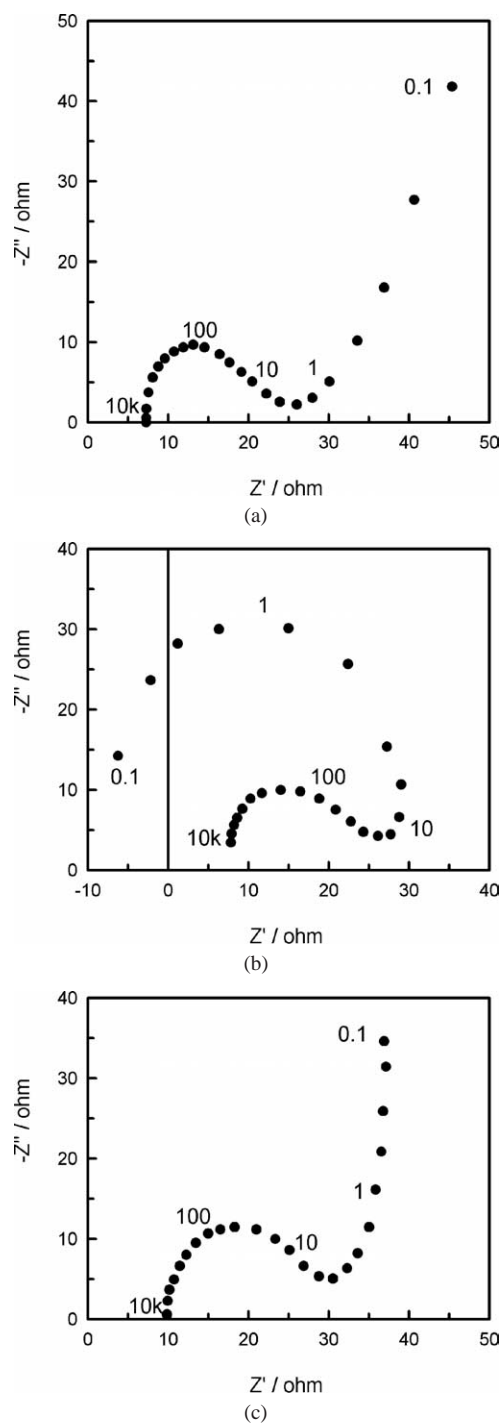

Fig. 3. Impedance spectra of the $Fe/(14.8 M\ H_3PO_4)$ system at $E = 200$ mV for (a) a fresh Fe electrode, (b) a Fe electrode aged for 1 h in the electrolyte solution before the measurements, and (c) a Fe electrode aged for 3 h before the measurements.

possible to compare aging effects on such long-time recorded impedance spectra. This failure is described in the following section. In the results reported above, the appearance of negative Faradaic impedance, which suggests possibility for the occurrence of oscillatory behavior, is understandable in light of our previous report decreasing the need for the formation of passive surface on the metallic electrode for the occurrence of oscillatory behavior [19].

3.3. Effect of time during experimental measurements

Now, it is appropriate to investigate whether time-dependency of the impedance spectra is related to initial state of the electrode surface or it is also true for measurement duration. Fig. 4 shows impedance spectra of the Fe/(14.8 M H_3PO_4) system recorded by measuring different numbers of points. It is known that impedance spectroscopy technique measures the impedance data at different frequencies and measurement at each point (at each given frequency) takes a certain time. Thus, the experiment time is longer when more points are measured. As seen, the above-mentioned behavior (Section 3.2) is also observable for the measurement duration. Thus, the results suggest time-dependency of the impedance studies of an electrochemical oscillatory during measurements as well as the time spent before starting the measurements. The influence of aging on electrochemical systems is known and can be monitored by various tools, e.g., we have recently used irreversible thermodynamics [20,21] and fractal geometry [22] to this aim somehow in a different context. However, the results reported here for the influence of numbers of points used for impedance measurements is not addressed in the literature.

3.4. Theoretical consideration

The results reported in Sections 3.2 and 3.3 obviously suggest time-dependency of impedance spectroscopy both before and during the experimental measurements. It is not aimed to formulate such behavior here, however, a brief theoretical consideration will be made to understand the phenomena. Passivation/dissolution of Fe in acidic medium is associated with intermediate species $(FeOH)_{ads}$ and the passivating species $[Fe(OH)_2]_{ads}$, which cover a fraction
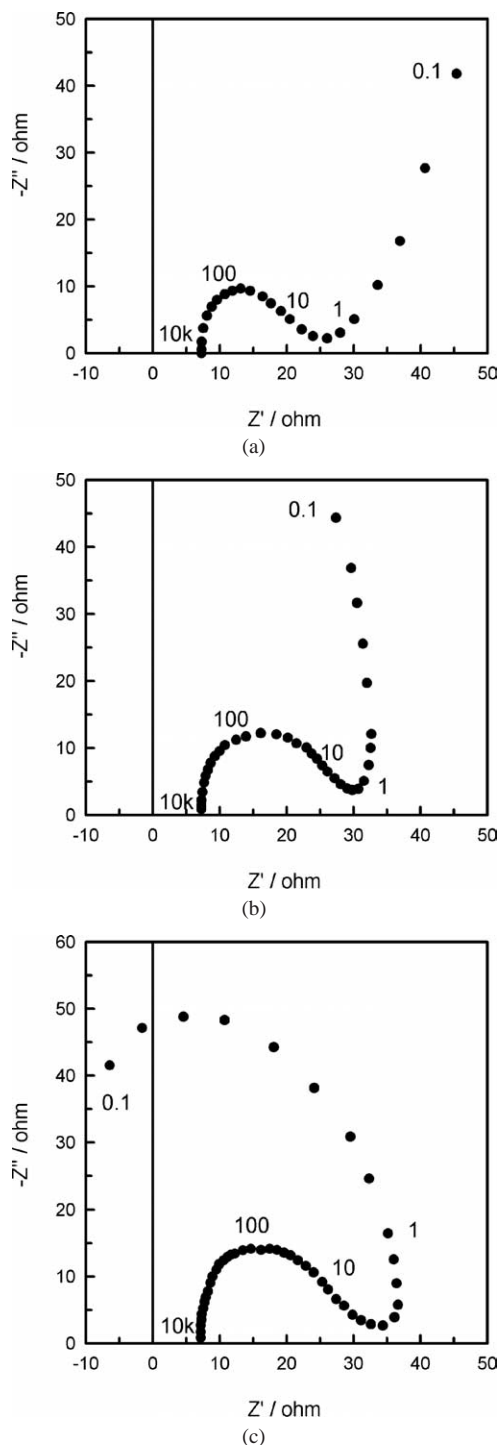

Fig. 4. Impedance spectra of the Fe/(14.8 M H_3PO_4) system at $E = 200$ mV with different numbers of data samples. The working electrode was a fresh Fe electrode.

θ_1 and a fraction of θ_2, respectively [23]. According to this mechanism proposed in [23] and the general analysis of the Faradaic impedance of a reaction involving adsorbed intermediate, an expression for the system under investigation which follows the rate equation can be derived:

$$\frac{d\theta_1}{dt} = k_1(1 - \theta_1 - \theta_2) - k_2\theta_1 - k_3\theta_1 n. \tag{1}$$

The general equivalent circuit is illustrated in Fig. 2(c). For the impedance spectra shown in Fig. 2(a): $R_{ct} > 0$, $R_p > 0$, and $C_p > 0$, whereas the spectra shown in Fig. 2(b): $R_{ct} > 0$, $R_p < 0$, and $C_p > 0$. Indeed, the behavior observed can be understood in the light of change of the sign of the polarization resistance. According to the typical model described in Section 3.1, negativity of the polarization resistance is needed for the appearance of oscillatory behavior.

The capacity of the double layer C_{dl} and the charge transfer resistance R_{ct} are independent of the experiment time, but the polarization resistance R_p can be significantly changed in the course of electrode aging. This is the main reason for the dependence of the impedance spectrum shape on the electrode aging, as the sign of R_p is changed upon aging. It can be understood by expressing the main parameters:

$$R_{ct} = \left[\frac{e|j|}{kT} \frac{d\phi_{sc}}{d\phi} \right]^{-1}, \tag{2a}$$

$$R_{dl} = -\left[2e\Gamma_m k_1 \frac{d\theta_{dl}}{d\phi} \right]^{-1}, \tag{2b}$$

$$C_p = \frac{1}{k_3 n R_{ct}} \frac{R_{dl}}{R_{dl} + R_{ct}}, \tag{2c}$$

$$R_p = \frac{R_{ct}(1 + R_{ct}/R_{dl})}{\frac{k_1 + k_2}{k_3 n} - R_{ct}/R_{dl}}. \tag{2d}$$

It is known that double layer resistance increases during passivation. Upon aging, the R_{ct}/R_{dl} was sufficiently increased to be higher than $k_1 + k_2/k_3n$, thus, the sign of R_p changes. The negativity of R_p achieved as a result of electrode aging satisfies the entrance of the impedance spectrum into the second quadrant.

Indeed, growth of passive film on the electrode surface and consequently increase of the film resistance (or system resistance) results in negativity of the

Faradaic impedance at a sufficiently high frequency to form a Hopf bifurcation, which is needed for the oscillations to occur. However, long-time aging of the electrode increases the system resistance superfluity. It is known that increase of the system resistance or the external resistance from a critical value leads to the disappearance of oscillatory behavior, as the system has achieved a stability condition [24]. It is also understandable from electrode morphology point of view: (i) the surface of the fresh electrode is still stable (as not corroded yet) to avoid participation in the active-passive transition, however, (ii) the film formed on the aged electrode is unstable, whereas, (iii) the thick passive formed on the over-aged electrode became stable during a long-term passivation and does not break down to participate in the active–passive transition.

It can be understood from theoretical consideration and a mathematical model such as that proposed in [8], as time-dependency of impedance spectroscopy leads to a gradual increase of the system impedance (and consequently changes of the corresponding parameters). However, such small changes lead to significant difference in dynamical behavior of a complicated system such as an electrochemical oscillator, as judged by the shape of impedance spectrum at low frequencies.

It should be emphasized that this is not an approach for the observation of oscillatory behavior. It is an experimental error, which involves in our measurements and is not usually taken into account in the literature. For example, we can consider the results presented in Figs. 3 and 4 (curves (a), (b) and (c)) as Fe/(14.8 M H_3PO_4) (fresh), Fe/(14.8 M H_3PO_4) (short-delayed) and Fe/(14.8 M H_3PO_4) (long-delayed). While cyclic voltammetric characterization of the Fe/(10 M H_3PO_4) (fresh) system does not suggest oscillatory behavior (not shown, a CV similar to those illustrated in Fig. 1, but featureless without any current oscillations), impedance spectroscopy may suggest oscillatory behavior if the cell was simply stayed for a while before experiment (Fig. 3(b)) or when the measurements were performed using more data during a longer experiment time (Fig. 4(c)). Surely, it is an experimental problem. The cyclic voltammetric measurements are performed for the Fe/(14.8 M H_3PO_4) (fresh) system, whereas the impedance spectra for the Fe/(14.8 M H_3PO_4) (short-delayed) system or the Fe/(10 M H_3PO_4) (long-delayed) system. In fact, it is aimed here to clarify that

these are three different systems, but their differences are not usually addressed in the literature.

On the other hand, the results can be used for design of new oscillators; as can be seen, the Fe/(14.8 M H_3PO_4) (fresh) is not an electrochemical oscillator, but Fe/(14.8 M H_3PO_4) (short- or long-delayed) systems may display oscillatory behavior. Based on the results reported, it is suggested that when talking about an electrochemical oscillator, it is necessary to address the time of experiments as well as other parameters such as electrolyte concentration. Non-linear scientists well know this problem that time-series will show oscillatory behavior at certain ranges of time. Indeed, as well as chronoamperometric measurements for recording time-series of an electrochemical oscillator, the time parameter is of importance and should be taken into account during impedance spectroscopic measurements.

By definition, impedance spectroscopy is a sensitive technique, which should be applied only to systems having well-defined time-independent steady state. On the other hand, impedance spectroscopy is a powerful tool to investigate complicated systems such as electrochemical oscillators. Therefore, impedance spectroscopy can be applied for study of electrochemical oscillators, only by taking into account the problem of severe time-dependent nature of such complicated systems. This issue is of great importance for comparative studies.

4. Conclusion

It was demonstrated that impedance spectroscopy is strongly time-dependent and this time-dependency is very important for the investigation of complicated systems such as electrochemical oscillators. For a sensitive system (which oscillates only at certain values of controllable parameters), depending on the rest time spent before the experiment or length of measurement duration, the impedance spectra suggested different dynamical behavior for the system under investigation. Indeed, it was demonstrated that how much a system with non-linear dynamics such as electrochem-

ical oscillators are time-dependent, and how much this time-dependency has influence on its dynamical behavior.

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