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Application of quartz crystal microbalance and dynamic impedance spectroscopy to the study of copper corrosion inhibitors

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Abstract

The study investigates the application of Dynamic Electrochemical Impedance Spectroscopy (DEIS) and Electrochemical Quartz Crystal Microbalance (EQCM) techniques to examine the corrosion inhibition of copper by Benzotriazole and Sodium Folate in a 0.1 M NaCl solution. DEIS, an advanced version of Electrochemical Impedance Spectroscopy (EIS), allows for real-time monitoring of non-stationary electrochemical systems, while EQCM enables the detection of minute mass changes during electrochemical reactions. Through 24-hour chronopotentiometric measurements, the study observed the effects of 5 mM Benzotriazole and 10 mM Sodium Folate on copper corrosion. Results indicated that Benzotriazole significantly enhances corrosion resistance by forming a protective layer on the copper surface, as evidenced by increased impedance and stable mass changes. Conversely, Sodium Folate exhibited a less effective, dynamic interaction with the copper surface. This research highlights the synergistic use of DEIS and EQCM in understanding corrosion mechanisms and inhibitor efficiency, providing insights into optimizing corrosion protection strategies. The findings suggest that while both inhibitors improve corrosion resistance, Benzotriazole demonstrates superior performance, underscoring its potential for more effective corrosion control in various industrial applications.

Keywords: DEIS, EQCM, Corrosion inhibition, Copper, Benzotriazole, Sodium Folate

1. Introduction

Materials degradation by corrosion can be limited by, among others, using corrosion inhibitors, which are the substances that added to the aggressive medium in a small amount significantly to reduce the corrosion rate. Inhibitors can be divided into several groups according to the inhibiting action mechanism:

- barrier inhibitors- adsorbs on the metal surface and limit the diffusion of species to and from the metal surface, which causes a decrease in reaction rate;
- passivators- support passive layer formation on the metal surface;
- precipitation inhibitors- react with ions unchained from the metal surface during the corrosion process and form the insoluble product, which acts as a protective layer;
- cathodic poisons- inhibit the cathodic reaction;
- oxygen scavengers;
- H+ neutralizers.

This kind of anti-corrosion protection is appropriate and commonly used in the oil and mining industry, for processes with acids, steel reinforcement in concrete, protection from atmospheric corrosion, in heat exchangers and cooling systems [1,2]. Among many valuable properties of copper, high thermal conductivity should be

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distinguished, which makes it an appropriate construction material for heat exchangers [3]. In a chloride-containing environment (for instance seawater, when the device is used in marine industry), corrosion of copper elements occurs: the first product of the corrosion reaction is insoluble cuprous chloride (CuCl). As a result of subsequent reactions, cuprous oxide (Cu_2O), cupric oxide (CuO) and hydroxide ($Cu(OH)_2$), malachite ($CuCO_3$*$Cu(OH)_2$) and atacamite ($Cu_2(OH)_3Cl$) are present on the metal surface and the complexes with the general formula $CuCl_{n(n-1)}$- are transferred to the solution [4]. As it was mentioned before, the application of corrosion inhibitors can limit the corrosion rate and reduce the associated losses.

One of the most important methods used in corrosion inhibitors studies is electrochemical impedance spectroscopy (EIS). It derives numerous significant information, but it can be applied only to stationary processes [5-8]. Dynamic EIS (DEIS) is a technique that allows to pass over the mentioned limitation by measuring impedance spectra in narrow time periods and to observe dynamic changes in the electrochemical system. It has been successfully used for corrosion [9-12] and corrosion inhibitors [13–15] investigations. Another method used to monitor the electrochemical system in time (also in the field of corrosion inhibitors) [16–18] is electrochemical quartz crystal microbalance (EQCM) measurement, in which the electrode mass changes of the order of nanograms are indirectly observed as a function of quartz crystal oscillations frequency. Those resonance frequencies changes can be shown as mass changes according to the relationship:

$$\Delta f = -\left(\frac{2}{\rho_q \upsilon_q}\right) f_0^2 \Delta \mathrm{m}[20] \qquad (1)$$

where Δf is the frequency change, ρ_q is quartz crystal density, ν_q is the acoustic wave velocity in quartz, f_0 is the basic resonance frequency and Δm is the mass change [19]. The resonator can be used as a working electrode in an electrochemical system. This modification of QCM, called electrochemical quartz crystal microbalance (EQCM), allows to perform electrochemical experiments and measure electrode mass changes at one time [2,20,21].

The usage of EIS and EQCM techniques together is rarely applied [22-24]. However, when it comes to DEIS coupled with microbalance, those methods are extremely hard to find being used simultaneously by anyone. The reason for its unpopularity might be the technical complexity. In the following work we present the first application of coupled DEIS and EQCM for the study of corrosion inhibitors on the examples of benzotriazole and sodium folate (Figure 1) inhibiting action towards copper corrosion in 0.1 M NaCl solution.

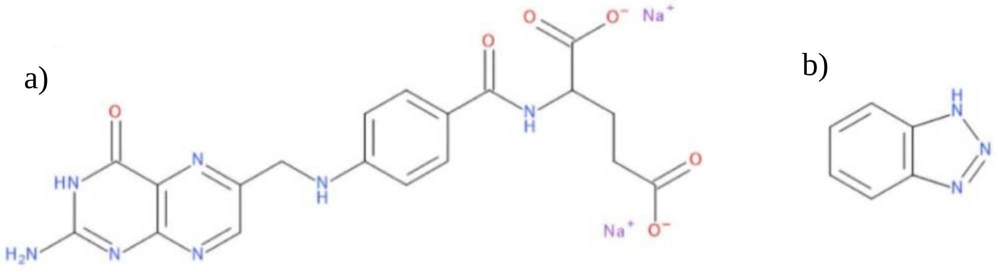

Fig. 1. a) sodium folate, b) benzotriazole structure.

2. Experimental

2.1 Reagents and solutions

Analytical grade reagents and distilled water were used to prepare the following solutions:

- 250 g/l $NiSO_4 \cdot 7 H_2O$; 35 g/l $NiCl_2 \cdot 6H_2O$; 35 g/l H_3BO_3,
- 220 g/l $CuSO_4 \cdot 5 H_2O$; 60 g/l H_2SO_4 96%,
- 1 M HNO_3,
- 10% H_2SO_4,
- 0.1 M NaCl.

Inhibitor solutions were prepared according to the instructions:

Benzotriazole was dissolved in a few drops of methanol before adding to aqueous 0.1 M NaCl solution. Sodium folate solutions were made by adding solid folic acid and sodium hydroxide in molar ratio 1:2 to 0.1 M NaCl solution. All reagents were of analytical grade.

2.2 *Experimental procedure*

During the measurements, a three-electrode system was used, consisting of a platinum mesh acting as an auxiliary electrode, a 3 M KCl reference electrode, and a working electrode which was a simultaneously operating quartz crystal connected to the microbalance. An AT-cut quartz crystal was used, an active surface of 0.196 cm^2 and the nominal oscillation frequency was 10 MHz. It was initially covered on both sides with a 300 nm Au layer, with a Ti film underneath. Before starting the tests, the gold quartz surface was properly prepared by rinsing in demineralized water, then put into ultrasonic bath in a solution of 1M HNO_3 or 10% H_2SO_4 for about 1 hour. After sonication, the quartz crystals were rinsed several times in distilled water and then in ethyl alcohol. The dried electrodes were then subjected to Ni electrodeposition to improve the adhesion of the Cu layer in a solution consisting of 250 g/l $NiSO_4$* 7 H_2O; 35 g/l $NiCl_2$*6H_2O; 35 g/l H_3BO_3 under chronopotentiometric conditions (I= -2 mA, t= 3 min). Then, cleaned by rinsing with demineralized water, electrodes were subjected to proper electrodeposition of Cu in a solution of 220 g/l $CuSO_4$*5H_2O; 60g/l H_2SO_4 96%, under the same conditions as in the case of Ni deposition, however, for 20 minutes.

Freshly prepared copper electrodes were placed into the electrochemical cell (V=120 ml) immediately. Measurements were performed right after immersing the working electrode in a 0.1M NaCl solution maintaining a constant temperature of 25 ºC. The inhibitors were injected into the electrochemical cell approximately 5,000 seconds after the start of the measurement. The electrodes were connected to an AutoLab VSP 300 potentiostat connected to an acquisition system (National Instruments NI PXIe-1071) and a microbalance (Seiko EG&G QCM 922A), which enabled both tests to be performed simultaneously. Changes in the system were observed during a chronopotentiometry scan under direct current Idc= 0 μA. Frequency changes, which were then converted into changes in the mass of the working electrode, were recorded in time, relative to the open circuit potential (OCP). Typical diagram of the experiment is shown in Figure 2.

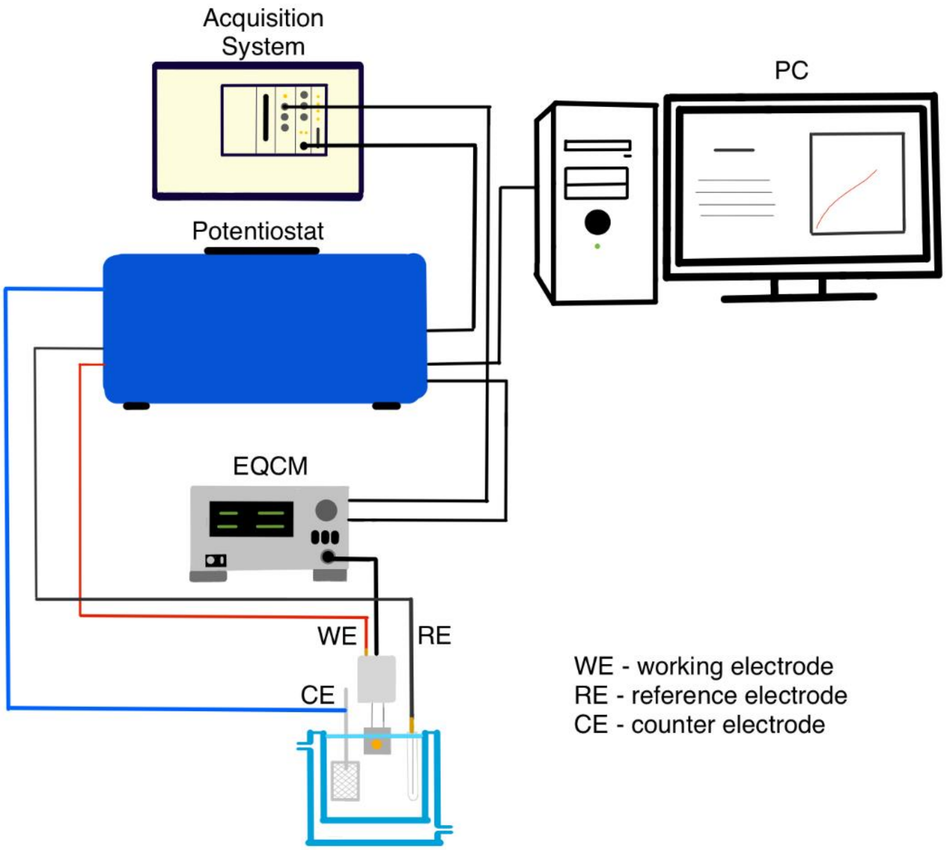

Fig. 2. Scheme of the experiment.

In case of such a changing reaction environment as it is with the corrosion studies, the DEIS technique is the perfect solution. In this method all the voltage signals of different frequencies are generated simultaneously, not in a sequence like it was with classical EIS approach.[2] Thanks to these changes, the non-stationarity of the system is no longer a limitation for research. The impedance measurements were conducted using a self-made program using a frequency pack of 0.3 Hz up to 4.5 kHz and voltage response amplitude not bigger than 30 mV peak to peak. Then, the collected data were subjected to the Short Time Fourier Transformation and impedance spectra were obtained. The results were analyzed using the programs designed at our department and the ZSimpWin program.

3. Findings and Discussion

The DEIS technique was used to investigate the effect of the presence of both folate and benzotriazole on the changes occurring in the copper surface immersed in 0.1M NaCl. In order to record the changes, measurements were made for a pure solution of 0.1 M sodium chloride and for solutions to which 5 mM benzotriazole and 10 mM sodium folate were added, respectively. Each test lasted 10 hours, was carried out at a constant temperature of 25 ºC and repeated 5 times. The repeatability of the obtained data was noted, and the representative experimental results are presented in Figure 3. The results for measurements in NaCl solution (Fig. 3a) show a typical picture of corrosion developing on the metal surface, where over time the shape of the spectra does not change, the visible semicircle only enlarges a bit. In the case of spectra taken for a solution with the addition of benzotriazole (Fig. 3b), the difference is easily noticeable. Immediately after adding the inhibitor to the solution, the impedance began to increase, and this trend continued over time. The explanation for this phenomenon is most likely the adsorption of benzotriazole on the copper surface, which created a protective layer thanks to which the corrosion process was disturbed. In the case of the solution containing folate (Fig. 3c), the results are not as stable as in other solutions, where permanent corrosive or inhibitory effects were observed. There is no evidence of lasting interactions between the metal surface and the inhibitor. The entire process is significantly more dynamic. Although the inhibitor present in the solution exhibits protective properties, the lack of a permanent bond with the metal surface leads to alternating inhibitory and corrosive interactions. This results in a less effective reduction in the rate of corrosion.It should be noted, however, that the impedance results obtained when using both types of inhibitors are significantly higher than in the case of corrosion in NaCl alone (the scale on the graphs is different), proving that both solutions increase the corrosion resistance.

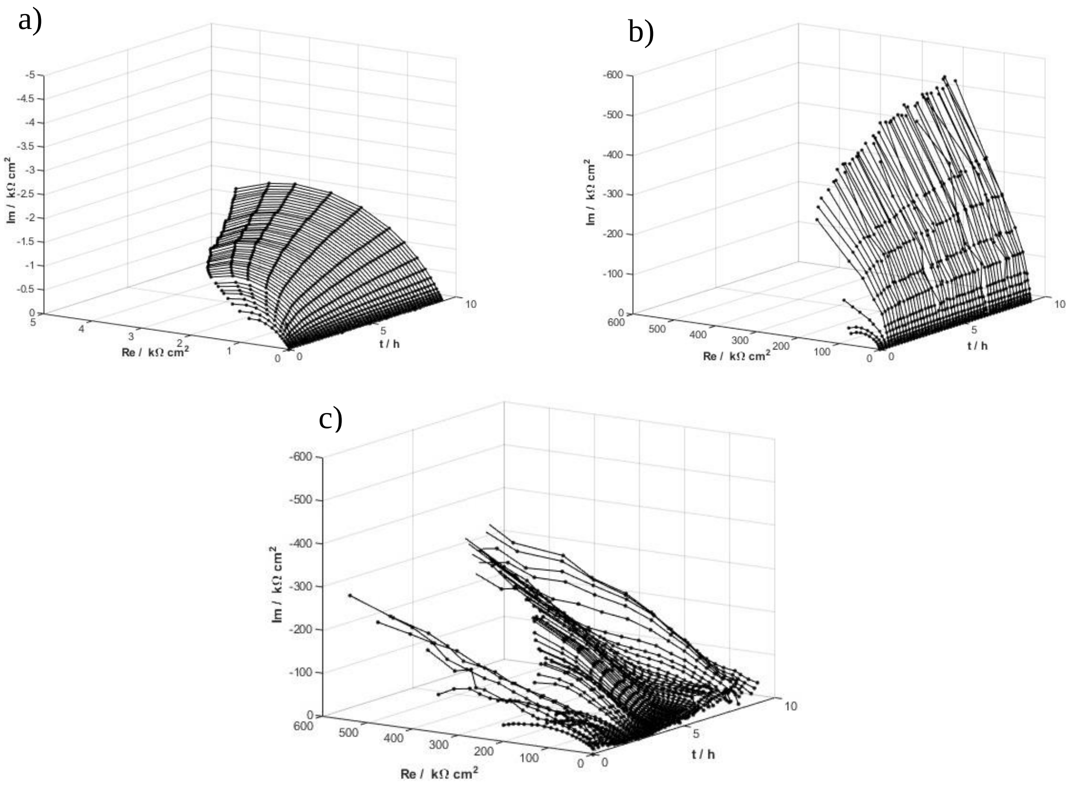

Fig. 3. DEIS results of 0,1M NaCl solution a) without inhibitor, b) with Benzotriazole, c) with Sodium Folate.

The obtained impedance spectra were analyzed using the equivalent circuit $R_1(QR_2)$, where R_1 - electrolyte resistance, Q - element representing the electric double layer, R_2 - charge transfer resistance. To better understand the processes occurring during measurements, graphs were generated to show changes in potential (Fig. 4a), frequency (Fig. 4b), and resistance (Fig. 4c) over time. The results obtained for each solution are markedly different. Both inhibitors influence the reaction in the solution to varying degrees. The presence of benzotriazole in the solution causes a significant and rapid increase in potential, which then remains constant. This indicates the immediate formation of a protective layer on the metal surface. In contrast, the addition of folate to the solution causes a temporary increase in potential, followed by a decrease, indicating a lack of sustained interaction between the substance and the copper surface. The frequency change results obtained from

EQCM confirm the DEIS results. The presence of benzotriazole allowed for the maintenance of constant frequency values, indicating effective protection of the copper surface without damage. The curve representing mass changes for the folate solution is similar to that for the solution without the inhibitor, although the mass changes occur on a smaller scale. This suggests that folic acid has a minor impact on the corrosion rate. The resistance graphs confirm that both substances positively affect the reduction of copper surface degradation, but benzotriazole has a much stronger effect. However, the results for the folate solution are not as stable as those for the other solutions, highlighting the dynamic nature of the solution, in which both corrosion and inhibition reactions are continuously occurring. Consequently, it is challenging to determine which of these reactions has a greater impact on the overall process.

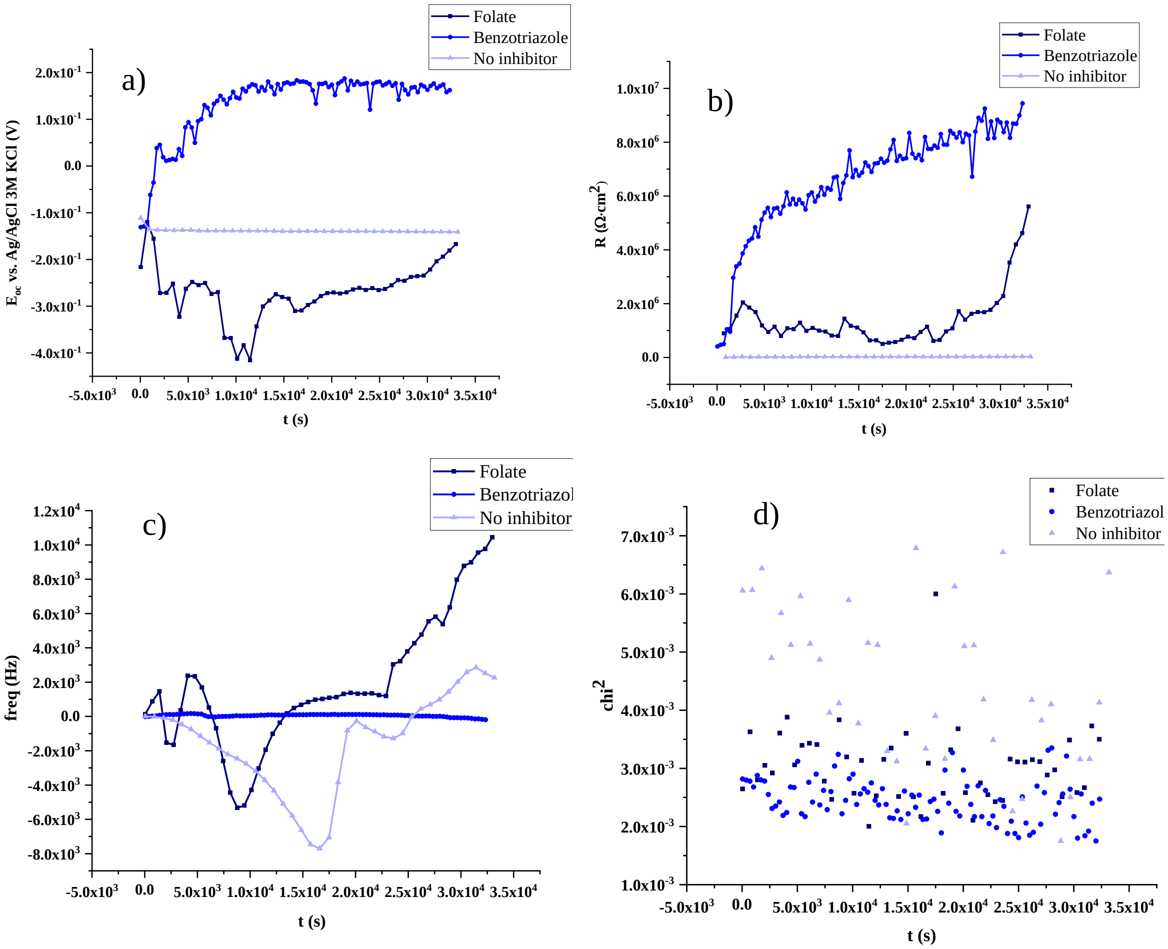

Fig. 4. Graphs of a) potential, b) charge transfer resistance c) quartz crystal frequency d) chi^2 changes against immersion time.

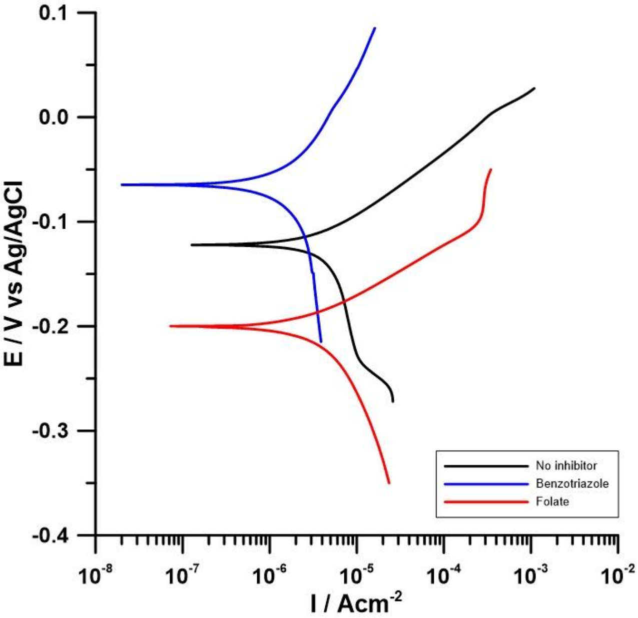

Fig. 5. Polarization behaviour of Cu in 0.1M NaCl solution in the absence and presence of different inhibitors, scan rate 1 mV/s, potential limits +/- 150 mV vs. E_{OC}.

Table 1. Comparison of values obtained for each experiment.

	Ecorr [V] vs Ag/AgCl (3M KCl)	Corrosion current density [µA/cm^2]	Ba [V/dec]	Bk [V/dec]
No inhibitor	-0.122	10.84	0.083	∞
Benzotriazole	-0.065	4.15	0.178	∞
Folate	-0.200	4.65	0.066	0.196

In order to identify the factors influencing the corrosion of copper in a 0.1M NaCl solution and to check the quality of inhibition of both compounds, Tafel curves were also prepared after 24 hours of exposure of the metal in the solutions. As shown in Figure 5, it can be seen that the copper corrosion reaction is controlled by processes occurring on the cathode side. This observation aligns with previous studies indicating that cathodic processes play a crucial role in copper corrosion in chloride-containing environments . [5,11] While benzotriazole shows mixed control, its effect on slowing down and changing the course of the reaction is significant, corroborating findings from other research on its effectiveness as a corrosion inhibitor .[16,2] Although sodium folate also affects the cathodic process, it only affects it slightly, which is consistent with studies highlighting the variable efficiency of folate compounds in corrosion inhibition .[25]

4. Conclusion

The conducted research has shown that although it is demanding to combine DEIS and EQCM methods due to the high sensitivity of both techniques, it is an excellent way to examine corrosion processes. The presented results clearly prove that both sodium folate and benzotriazole have properties typical of corrosion inhibitors. However, despite the lower concentration, benzotriazole has a much better effect in the case of copper.

Nevertheless, it is worth noting that folic acid has additional benefits. It is a substance that naturally occurs in nature and has a beneficial effect on human organisms which allows the use of this substance in many ecological processes or in industries that have a substantial impact on living organisms; however, it is necessary to refine this technology.

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