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INFLUENCE OF ELECTRODE MATERIAL ON THE ELECTROCHEMICAL BEHAVIOR OF THE ABSORBING SOLUTION OF THE QUINHYDRONE METHOD OF GASES PURIFICATION FROM HYDROGEN SULFIDE

<https://doi.org/10.23939/ctas2021.01.053>

The electrochemical behavior of carbonate solutions of the quinhydrone at different concentrations 1, 5, 10, 20, and 30 g/dm³ at the exposure time 0...12 days on different electrode materials – Ni and Au were studied by the cyclic voltammetry (CV) method. The catalytic properties of gold different from nickel in the anodic oxidation reactions of the quinhydrone catalyst are noted.

Key words: quinhydrone oxidant; electrochemical behavior; exposure time; electrode material; cyclic voltammetry.

Introduction

In cyclic liquid-phase (oxidative) methods of gas purification from hydrogen sulfide, the necessary stage is the regeneration of the catalyst – oxidant of chemisorbed hydrogen sulfide to sulfur [1–3]. Most often, the regeneration of its activity, i.e. the transition from the reduced form to oxidative, occurs during the interaction with air oxygen.

In addition to the chemical regeneration of absorbing solutions with oxygen, it is also proposed to carry out their electrochemical regeneration [4]. This method allows the removal of oxygen from the oxidation reactions of chemisorbed hydrogen sulfide and dramatically reduces the yield of a by-product – sodium thiosulfate. However, the vast majority of the components of the quinhydrone absorption solution are compounds active in the redox interaction. Thus, the quinhydrone absorption solution may contain, g/dm³: 10...40 sodium carbonate, 5...20 quinhydrone, 200...350 sodium thiosulfate, and after chemisorption – up to 1...4 H₂S [2, 5]. That is why in the process of electrolysis of quinhydrone absorbing solution of the above composition is the formation and oxidation of sulfur compounds, which creates competition with the anodic oxidation of the quinhydrone catalyst, formation and blocking the surface of the electrode by sulfur [4]. Therefore, it is expedient to carry out

semi-electrochemical regeneration, i.e. to oxidize chemisorbed hydrogen sulfide with a quinhydrone catalyst chemically, and to oxidize a quinhydrone catalyst in a solution without dissolved hydrogen sulfide – electrochemically. The use of semi-electrochemical regeneration also makes it possible to use an absorption solution without sodium thiosulfate to purify gases from H₂S.

Quinhydrone oxidant-catalyst is obtained by oligomerization of quinhydrone in carbonate solution with the access of air [5]. During the interaction of Quinhydrone with alkalis, the formation of the anionic radical – semiquinone occurs [6]. During the exposure of the alkaline solution of quinhydrone with access to air, the growth of the polymer chain and the transition of monomeric semiquinone radicals into stable polysemiquinones are observed [7]. For the preparation of quinhydrone absorption solution using a solution of quinhydrone oxidant with a molar ratio of sodium carbonate: quinhydrone, equal to 2:1, and which was exposed with air for at least 5 days [8].

Analysis of literature sources [9–12] shows that almost only platinum has the chemical and electrochemical stability in the quinhydrone absorption solution which containing sodium thiosulfate and chemisorbed hydrogen sulfide.

Therefore, the study of the electrochemical properties of the quinhydrone absorption solution was carried out using a platinum electrode [7, 13]. It is shown that these properties depend on the aging time (exposure) of carbonate solutions of quinhydrone, the composition, and structure of quinhydrone oligomerization products, the ratio of components, the presence of sodium thiosulfate in the initial stages of oligomerization, etc.

The absence of sulfur-containing ions in the solution that will enter the electrolysis during semi-electrochemical regeneration allows an expansion of the list of electrode materials for anodic oxidation of the quinhydrone catalyst. These materials, in addition to chemical resistance in the carbonate solution, must have high activity and selectivity for the main electrochemical process and have a low cost.

Many electrode materials [14], including platinum [15–16], gold [17–18], composite electrodes Ti-Pt, Ti-Ir [11], graphite [15], and glassy carbon – $\text{Co}(\text{OH})_2$ [19], etc are most often used for studies of oxidation and reduction processes in the system of quinone-hydroquinone and other quinone compounds. Platinum titanium anodes and PbO_2 were used in the industrial processes of obtaining quinones by electrolysis of hydroquinone solutions in acidic sulfate media [10].

The study of electrochemical regeneration of quinhydrone absorption solution was carried out using platinum, as well as graphite – a material that is also chemically and electrochemically stable in quinhydrone absorption solution under conditions of anodic polarization without oxygen release [4]. However, during operation, graphite anodes are subject to destruction (both chemical and mechanical). Besides, the fabrication of graphite electrode structures is complex.

Based on the analysis of the chemical properties of the quinhydrone solution (in the absence of sulfides and thiosulfates), gold and nickel were also proposed as anode materials for its electrochemical regeneration. It is known that during anodic polarization in an alkaline medium, Nickel is covered with a defensive film, and the dissolution potential of the metal is shifted to a range of more positive values than the potentials at which the oxidation reaction occurs. And gold in its chemical stability and mechanical strength is only slightly inferior to most platinoids but has a higher ductility,

which allows you to form the desired working surface of the electrode.

The research aimed to establish the electrochemical behavior of solutions of quinhydrone oxidant - catalyst during its exposure on nickel and gold electrodes.

Materials and methods of research

A solution of a quinhydrone catalyst was prepared for research with an initial content of quinhydrone (1, 5, 10, 20, and 30 g/dm^3) and sodium carbonate, which corresponded to a mass ratio to quinhydrone of 1:1. We used reagents classification “pure grade” and distilled water. The prepared solutions were left to exposure (aging) under access to air and stirred periodically. The pH value of the solutions of the quinhydrone catalyst was determined using a pH meter-millivoltmeter pH-673M. Potentiometric studies were performed in freshly prepared solutions of the quinhydrone catalyst and for 1, 5, 7, and 12 days of its exposure. The research was carried out by the method of cyclic voltammetry (CV) [20] on the potentiostat PI-50-1.1 with a programmer controlled by a computer program PI-50. The working electrodes were smooth Au and Ni, auxiliary – platinum, and the comparison – Ag/AgCl electrode. Area of anodes, cm^2 : gold – 0.36, nickel – 0.50. The potentials were transferred to a reversible hydrogen electrode (RHE). Research conditions: temperature 20 °C, potential scan rate 20 mV/s, scan direction - to the anode side.

Results and discussion

Table 1 presents the results of studies of the solutions pH at different concentrations of quinhydrone and the exposure time.

Table 1

Influence of quinhydrone concentration and exposure time on pH of solutions

No.	Quinhydrone concentration, g/dm^3	pH of solutions				
		Exposure time, days				
		1	5	7	9	12
1	1	8.9	8.0	8.1	8.3	8.6
2	5	9.1	8.2	8.3	8.4	8.9
3	10	9.3	8.4	8.4	8.5	8.9
4	20	9.6	8.6	8.5	8.6	8.9
5	30	9.8	8.7	8.7	8.6	8.9

As the results show, the pH of solutions no. 1–5 first decreases with the increase of the exposure time, reaching the minimum values for 5–7 days, and then increases slightly. The pH of the solutions with increasing quinhydrone concentration for each time of exposure increases slightly.

This change in the pH of the solutions also affects the steady-state redox potential (ROP) of Au and Ni electrodes in quinhydrone solutions. The change of the ROP for the two electrode materials in the solutions of quinhydrone catalyst depending on the time of its exposure has a similar character (Figs. 1 and 2), although its initial values are higher for the Ni electrode.

From the 1st to the 5th day of exposure of the solutions there is an increase in ROP (steady-state potential becomes less negative), and then changes slightly. This change in ROP is due to [7, 13] change in the composition of oligomeric products during oligomerization and is interrelated with the change in pH of the solution during exposure (Table 1).

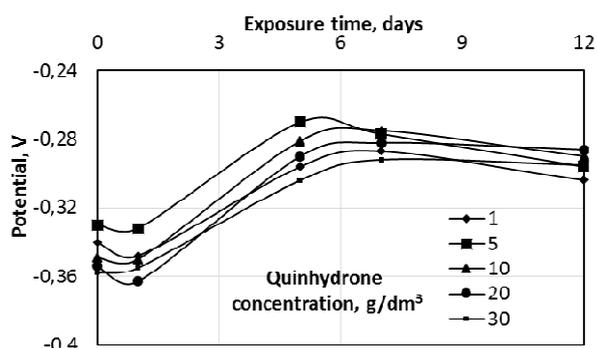


Fig. 1. Change in the steady-state potential of the Au electrode during the exposure time of solutions at different concentrations of quinhydrone

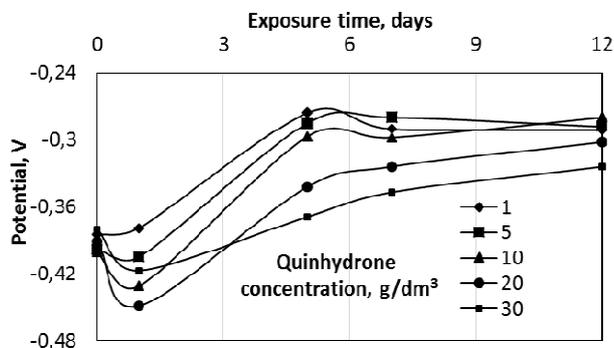


Fig. 2. Change in the steady-state potential of the Ni electrode during the exposure time of solutions at different concentrations of quinhydrone

The results of studies of the electrochemical behavior of the quinhydrone solutions no. 1–5 at the exposure time 0–12 days on Ni and Au electrodes are presented in Fig. 3–6.

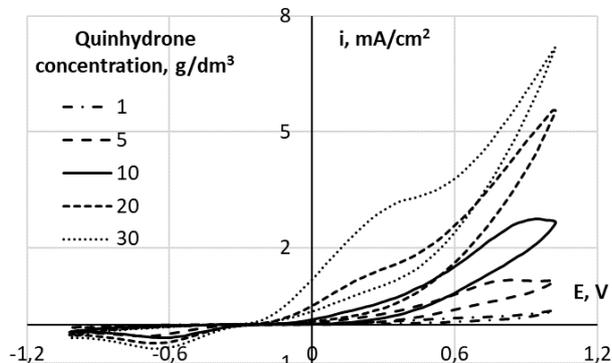


Fig. 3. CV curves of quinhydrone solutions at different concentrations on the 5th day of exposure on the Ni electrode

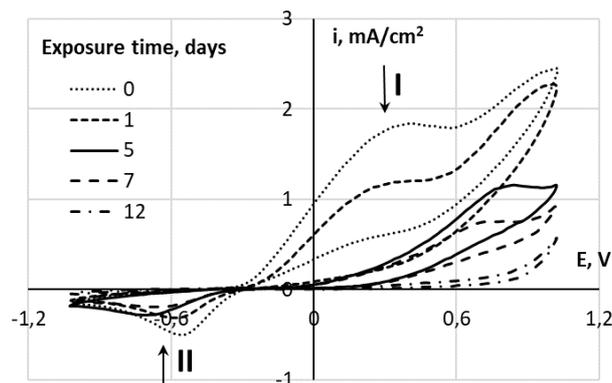


Fig. 4. CV curves of the quinhydrone solution no. 2 (Table 1) on the Ni electrode at different exposure times

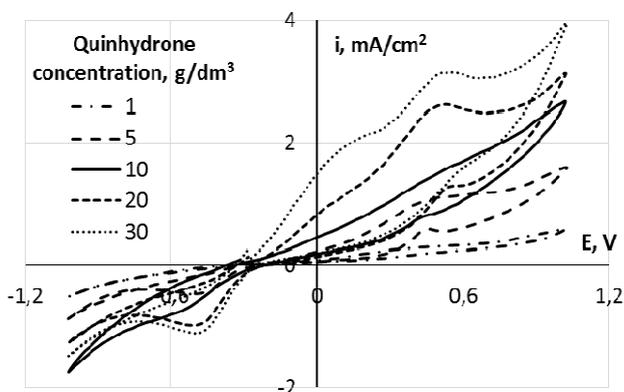


Fig. 5. CV curves of quinhydrone solutions at different concentrations on the 5th day of exposure on the Au electrode

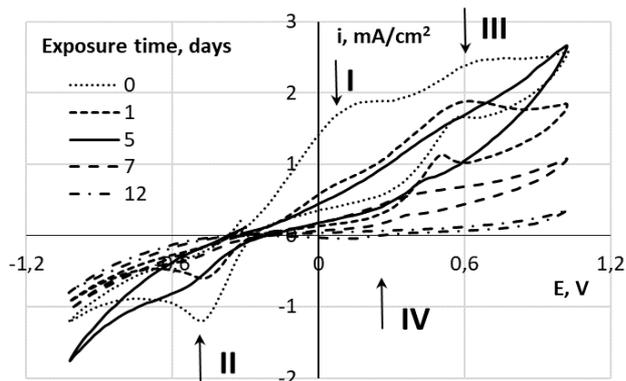


Fig. 6. CV curves of the quinhydrone solution no. 2 (Table 1) on the Au electrode at different exposure times

The research results show that regardless of the exposure time of the solution and the change of the electrode material, during cyclic polarization the processes of oxidation and reduction of quinhydrone and its oligomerization products take place, as evidenced by the anode and cathode peaks. Since the electrodes began to cyclically polarize anodically, the anodic peaks indicate the presence of a reduced

(hydroquinone) form of the quinhydrone catalyst. With a linear change in the potential of the Ni electrode on the CV curves, there is mainly an anodic peak (I) of oxidation current densities, and with reverse polarization, there is a cathode peak (II) of reduction current densities (Fig. 4). For the Au electrode, in addition to the anode (I) and cathode (II) peaks, an anode peak (III) and a cathode peak (IV) are observed (Fig. 6). The value of current density peaks (I) and (II) depend on the quinhydrone concentration and characterize its redox interaction. These peaks were observed in studies using a Pt electrode [13].

Increasing the quinhydrone concentration shifts the oxidation peaks to the right, and recovery - almost does not change during all days of solution exposure. Analysis of CV curves by peak potentials and current densities are presented in Table 2.

Oxidation of the reduced form of the quinhydrone catalyst occurs for the Ni electrode at potentials $E = +0.22... +0.84$ V, and for the Au - $E = +0.10...+0.53$ V. For the Pt electrode, these processes occurred at lower potentials $E = -0.14...+0.45$ V [13].

Table 2

Characteristics of oxidation (I) and reduction (II) peaks of Au and Ni electrodes on CV curves during the exposure time of solutions

Expos. time, days	Quinhydrone concentration, g/dm ³	Peaks of potentials, V				Peaks of currents density, mA/cm ²			
		Oxidation		Reduction		Oxidation		Reduction	
		Au	Ni	Au	Ni	Au	Ni	Au	Ni
1	2	3	4	5	6	7	8	9	10
0	1	0.289	0.391	-0.511	-0.591	0.483	0.342	0.355	0.192
	5	0.267	0.411	-0.489	-0.551	1.889	1.838	1.494	0.580
	10	0.220	0.472	-0.501	-0.564	3.904	3.814	2.580	0.994
	20	0.362	0.653	-0.533	-0.556	7.358	7.586	3.296	1.526
	30	0.517	0.804	-0.557	-0.568	10.631	10.996	3.467	1.805
1	1	-	0.263/0.903*	-0.543	-0.638	-	0.188/0.434*	0.239	0.126
	5	0.103	0.433	-0.475	-0.584	0.769	1.206	0.603	0.313
	10	0.230	0.396	-0.593	-0.567	3.442	2.752	1.389	0.452
	20	0.321	0.576	-0.503	-0.549	5.500	5.912	1.635	0.884
	30	0.411	0.776	-0.493	-0.629	8.058	9.278	2.103	0.950
5	1	0.443	-/0.621*	-	-0.618	0.289	-/0.176*	-	0.032
	5	0.580	-/0.838*	-0.543	-0.707	1.656	-/1.156*	0.720	0.284
	10	0.512	-/0.946*	-0.503	-0.614	1.108	-/2.754*	0.467	0.336
	20	0.533	0.293	-0.506	-0.666	2.611	1.436	0.980	0.476
	30	0.513	0.393	-0.495	-0.656	3.125	3.246	1.110	0.614
7	1	0.321	-	-	-0.680	0.075	-	-	0.003
	5	0.521	-/0.796*	-0.523	-0.659	0.647	-/0.752*	0.328	0.196
	10	0.517	-/0.829*	-0.519	-0.653	0.894	-/1.976*	0.525	0.366
	20	0.490	0.228	-0.492	-0.650	2.108	0.972	0.951	0.556
	30	0.529	0.275	-0.511	-0.657	3.411	1.976	1.260	0.718

1	2	3	4	5	6	7	8	9	10
12	1	0.297	–	–/0.122**	–	0.078	–	–/0.036**	–
	5	–	–	–/0.117**	–	–	–	–/0.039**	–
	10	–	0.505	–/0.069**	–	–	0.166	–/0.019**	–
	20	0.308	0.657	–0.471	–0.754	0.344	0.870	0.225	0.181
	30	0.342	0.833	–0.483	–0.676	1.100	2.340	0.600	0.423

Note: * – anode peak (III); ** – cathode peak (IV)

Calculations show that the oxidation overvoltage at the Pt electrode [13] is the smallest and at the Ni electrode – the largest. With an increase of exposure time of solution, the oxidation overvoltage for the Ni electrode only decreases, and for the Au, it has a complex character, which can confirm the difference in the mechanism of anodic oxidation and indicate the different nature of surface adsorption.

When using the Ni electrode, the potentials of the recovery peaks during the exposure time are shifted to the negative side (–0.55...–0.75 V), and Au – almost unchanged (–0.49...–0.59 V). For solutions no. 1 and 2 at the time of exposure more than 7 days, the peaks of oxidation (I) and reduction (II) disappear. For the Au electrode, the peaks (IV) remain for all 12 days of exposure. It is obvious that Au, due to its additional catalytic properties in the oxidation and reduction reactions of oligomerization products of quinhydrone, will not be able to find practical application as an electrode material.

The currents densities of the maxima of the oxidation peaks for the two electrode materials are almost the same (Table 2) only for solutions of freshly prepared quinhydrone catalyst. And then, during the exposure time, the oxidative processes at the two electrodes differ. Comparison of the currents densities of the reduction peak (II) for the two electrodes indicates a higher rate of electrochemical reduction for the Au electrode.

Increasing the exposure time of the solutions reduces the rate of electrochemical oxidation and reduction of the quinhydrone catalyst, as evidenced by the decrease in the values of the peak current densities of these processes. And for more concentrated solutions it is slower. Thus, for the Ni electrode, the anode peak (I) on the CV curve decreases and disappears on the 7th day of exposure for the solution no. 1 and the 12th day for the solution no. 2 (quinhydrone concentration 1 and

5 g/dm³, respectively). The reason for this is the oligomerization of quinhydrone in the carbonate solution in the presence of oxygen, so during the exposure time (0–12 days), the reduced forms of quinhydrone are gradually oxidized, after which the solution acquires stable properties [7, 13].

Increasing the concentration of quinhydrone at the same mass ratio of sodium carbonate to quinhydrone 1:1 leads to an increase in the absolute values of peaks (I) and (II). The mechanism of reactions is characterized by inequality of heights of anode and cathode peaks. The cathode peaks on all CV curves are shifted relative to the anodic ones, which indicates the formation of unstable compounds, in our case – semiquinone radicals [6, 7]. The difference between the potentials of the anode and cathode peaks $E_{pa} - E_{pk} = 120 \dots 210$ mV is quite large. Also, areas of limiting currents are observed on cyclic voltammograms. Therefore, such characteristics of the obtained CVs indicate the irreversibility of the electrochemical stage of oxidation of reduced forms of the quinhydrone catalyst, the presence of induced chemical reactions due to oxygen access (continuation of chemical oligomerization processes), and adsorption of formed compounds [20].

Of the two studied electrodes, in our opinion, only the nickel electrode can find a practical application for the electrochemical regeneration of quinhydrone solution. Compared with platinum, it is much cheaper but is characterized by greater overvoltage of electrochemical reactions.

Conclusions

Electrode materials (Ni, Au) have different effects on nature, current density, and potential of anodic oxidation of reduced and cathodic reduction of oxidized forms of the quinhydrone catalyst.

The stationary redox potential of ROP of the studied electrodes in quinhydrone solutions is more

negative for the Ni electrode. During the exposure of the catalyst solution, an increase in the redox potential is observed, but differently for Ni and Au electrodes.

The Au electrode, in comparison with the Ni, exhibits other redox properties, which is manifested in a relatively higher rate of electrochemical reduction and additional electroactivity of secondary products of the reaction of electrochemical oxidation of the reduced form of the quinhydrone catalyst.

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**ВПЛИВ ЕЛЕКТРОДНОГО МАТЕРІАЛУ НА ЕЛЕКТРОХІМІЧНУ ПОВЕДІНКУ
ПОГЛИНАЛЬНОГО РОЗЧИНУ ХІНГІДРОННОГО МЕТОДУ
ОЧИЩЕННЯ ГАЗІВ ВІД СІРКОВОДНЮ**

Методом циклічної вольтамперометрії (ЦВА) досліджено електрохімічну поведінку карбонатних розчинів хінгідрону 1, 5, 10, 20 та 30 г/дм³ під час його вистоювання 0–12 діб на різних електродних матеріалах – Ni та Au. Виявлено відмінні від нікелю каталітичні властивості золота в реакціях анодного окиснення хінгідронного каталізатора.

Ключові слова: хінгідронний окисник; електрохімічна поведінка; час вистоювання; електродний матеріал; циклічна вольтамперометрія.