Research Paper

Electrochemical oxidation of sulfite and sulfur dioxide at a renewable graphite electrode

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ABSTRACT

Electrochemical oxidation of S(IV) species which are present in the aqueous solutions of sodium sulfite or are formed during the dissolution of gaseous sulfur dioxide was studied on a renewable graphite electrode as the dependence on the concentration of these particles, electrode potential and pH of solution. The voltammograms in acid and alkaline sulfite solutions have different shapes. In acid solutions, this is a voltammograms with a sole maximum of current near 1.0 V. In alkaline solutions, this is a curve with two maxima; the first of them appears around 0.6 V, while the second one is near 1.0 V, similarly to the case of acid solutions. Analysis of the behavior of j-E curves and calculations of the equilibrium composition of the solution indicate that the maximum of current near 0.6 V is connected with the oxidation of SO_3^{2-} ions. The maximum of current near 1.0 V is mainly due to the oxidation of HSO_3^- ions which are present in acid solutions in bulk, while in alkaline solutions they might be formed in the near-electrode layer of solution as a product of the chemical reaction that follows the reaction of oxidation of sulfite ions. The results give use reason to assume that acid or basic surface oxides that are formed on graphite surface participate not only in the processes of oxygen evolution on this electrode but also in the processes of oxidation of S(IV) species. Their participation causes substantial difference in the potentials of oxidation of the indicated particles in alkaline and acid solutions.

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1. Introduction

Electrochemical oxidation of sulfite ions (SO_3^{2-}) and sulfur dioxide dissolved in water ($SO_2(aq)$) was studied on the anodes made of different materials because these processes are industrially essential [1]. Much attention was paid to the oxidation of sulfite and sulfur dioxide on the electrodes made of noble metals (Pt, Au, Pd) [2–6] because these electrodes exhibit catalytic activity towards the indicated reactions. Anodes made of metal oxides were also studied [7], as well as electrodes with modified surface [8]. The rate of the oxidation of indicated compounds of tetravalent sulfur S(IV) was observed to be strongly dependent on the nature of the electrode material, on the pre-history of electrode surface, on the state of metal surface, and on the potential range within which the oxidation current is measured. For noble metals these effects are related mainly to the influence of adsorbed sulfur species [9,10] on the kinetics of the electrode process. However, the oxidation rate of sulfur dioxide and sulfite ions might also be influenced by

oxidation processes on the surface of gold and other noble metals [11].

The processes of sulfite and sulfur dioxide oxidation were also studied on the anodes made of carbon materials. The anodes made of graphite; pyrographite, glassy carbon, activated carbon, carbon black etc. were studied [12–16]. For these anodes, the catalyst activity was observed less than anodes made from noble metals. The results of measurements on these electrodes depend both on the type of carbon material used and on pre-treatment of electrode surface. Most frequently, pre-treatment of carbon electrodes in the system under study involves mechanical polishing and electrode activation by cycling its potential from 0.0 V to approximately 2.0 V in the solution of base electrolyte. It is difficult to ensure identical reproducible electrode properties because the surface structures of different carbon materials are different, and a range of oxygen-containing surface compounds is formed during activation of carbon electrodes [13].
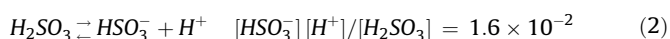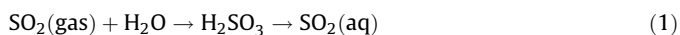
In the present work, voltammetric measurements of the rate of sulfite and sulfur dioxide oxidation are carried out on a renewable graphite electrode. Its surface is renewed before each measurement by cutting off a thin graphite layer directly in the solution under investigation at the given electrode potential value. This

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method provides better reproducibility of measurement results because they are independent of electrode pre-history. This method for preparing the electrode surface was applied successfully in studies of peculiarities of sulfite oxidation at a gold electrode [10]. We found it useful to assess the possibilities of its application for measurements at a graphite electrode.

In this work, attention will be paid to the electrochemical behavior of the system under study in the solutions with different acidity because the composition and concentrations of components in aqueous sulfite solutions depend on solution pH. Indeed, the composition and amount of S(IV) species formed in the electrolyte solution as a result of the dissociation of a salt of alkaline metal and SO_3^{2-} anion in water or as a result of the dissolution of gaseous sulfur dioxide SO_2 in water depend on pH of the solution. For the dissolution of sulfur dioxide in water, the concentrations of components in solutions are determined by the following reactions [15]:

$$SO_2(gas) + H_2O \rightarrow H_2SO_3 \rightarrow SO_2(aq) \qquad (1)$$

$$H_2SO_3 \rightleftarrows HSO_3^- + H^+ \quad [HSO_3^-][H^+]/[H_2SO_3] = 1.6 \times 10^{-2} \qquad (2)$$

$$HSO_3^- \rightleftarrows SO_3^{2-} + H^+ \quad [SO_3^{2-}][H^+]/[HSO_3^-] = 10^{-7} \qquad (3)$$

Sulfurous acid (H_2SO_3) is unstable and is present in solution almost completely in the form of SO_2(aq) – hydrated sulfur dioxide molecules. The equilibrium concentrations of particles that participate in homogeneous reactions (1), (2) and (3) depend on solution acidity and can be calculated using the above-listed equilibrium constants. The results of calculations that were carried out in [2] show that in solutions with pH > 7.2 SO_3^{2-} particles dominate. In solutions with $1.85 < pH < 7.2$ HSO_3^- particles dominate. In the region of pH < 1.85, the aqueous solution of H_2SO_3. rapidly decomposing to form sulfur dioxide dominates. Changes of the solution pH cause changes in the composition of electroactive particles, so the rate of the anode process can change, too. One of the goals of the present work was to reveal the features of the anode behavior of indicated S(IV) compounds on the graphite electrode in solutions with different acidity.

2. Experimental

The solutions were prepared using twice distilled water, and the reagents: Na_2SO_3, Na_2SO_4, H_2SO_4 and NaOH (analytical grade). The solutions were prepared immediately before measurements to decrease the probability of their decomposition before experiments. Solution pH was measured with the help of a glass electrode.

The method and instrumentation for voltammetry on the electrode with renewable surface were the same as those described in [17]. The use of this method provides the results unaffected by the pre-history of the surface of working electrode. This is achieved by cutting off a thin ($\approx 5\,\mu$) layer of the surface of working electrode directly in solution at a given potential. The graphite working electrode was a butt of a cylinder made of graphite-epoxide composite 2 mm in diameter with insulated side surface. This renewable graphite electrode is used to analyze the composition of solutions [18]. Measurements were carried out at 25 °C in a three-electrode cell with a Pt counter-electrode with the large surface area and a Ag/AgCl (saturated KCl) reference electrode. The potential of the latter is 0.197 V with respect to the standard hydrogen electrode (SHE). Potential values are presented in the SHE scale.

3. Results and discussion

3.1. Voltammograms in the solutions of the base electrolyte

Voltammograms measured on the graphite electrode in 0.1 M solutions of H_2SO_4 and NaOH are shown in Fig. 1. Voltammograms measured in 0.1 M solutions of Na_2SO_4 with pH varied within a broad range by adding sulfuric acid or sodium hydroxide are shown in the same Figure. The electrode surface was renewed before each measurement by cutting off at the open circuit potential (OCP), then the electrode potential (E) changed at a rate of 50 mV/s in the following sequence: from $E_{start} = 0.0$ V to -1.1 V, then in the opposite direction to 2.0 V and back to 0.0 V. Sulfate ions are not electrochemically active in this potential range, so the cathode Faraday current in this system is due to the reduction of dissolved molecular oxygen, while the anode current is connected with the oxidation of the surface of graphite electrode and oxygen evolution.

The results shown in Fig. 1 demonstrate that within potential range from approximately 0.5 V to approximately -1.0 V the density of measured current (j) is small and independent of the solution acidity. The reduction of dissolved molecular oxygen is responsible for the current density in this potential range. For potential more positive than 0.5 V, there is a dependence of the measured current on the acidity of solution. In the solutions of 0.1 M H_2SO_4 and in 0.1 M solutions of Na_2SO_4, with pH < 11.0, the current density remains rather small, too, till the potential of about 1.5 V. For a more positive potential, the current in the mentioned solutions increases sharply; at a potential of about 1.8 V it transforms into a plateau, and then at $E \approx 2.0$ V permanent increase in the current density is observed, which is likely connected with oxygen evolution. In the solutions of 0.1 M NaOH, oxygen evolution and an increase in current density start at less positive potential: at about 1.0 V. No plateau of current is observed in the solutions of alkali till the potential of 2.0 V (insert in Fig. 1.). However, even after insignificant acidification of the solution, for example, to pH ≈ 12.2 (Fig. 1) the current density in the region 1.5–2.0 V decreases. At pH ≈ 11 and smaller, the dependences of j on E almost coincide with the curves that were recorded in the solutions with pH ≈ 2.0. The processes of the oxidation of graphite electrode surface and their dependence on the acidity of solution

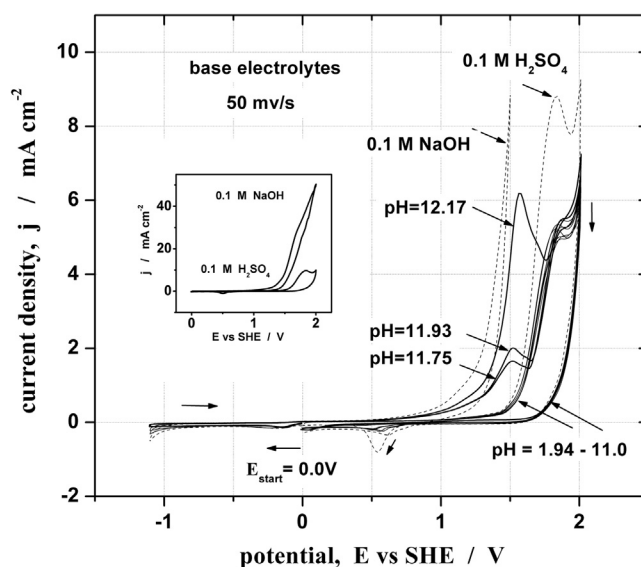**Fig. 1.** j-E curves measured at the graphite electrode in 0.1 M solutions of H_2SO_4 and NaOH (dash) and in 0.1 M Na_2SO_4 solutions with different pH (solid).