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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

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Electrochemical Synthesis of Arsenic Acid

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Abstract—The possibility of oxidizing arsenic(III) oxide to arsenic acid in quantitative yield in the presence of hydrochloric or hydrobromic acid as a catalyst was studied.

Arsenic acid and arsenic(V) oxide are used to synthesize dyes and pharmaceuticals, to manufacture optical glass, etc. Commonly, arsenic acid is prepared by oxidation of As_2O_3 with nitric acid [1]. A shortcoming of the method is that toxic wastes are formed. Of interest in this connection is the possibility of performing this process electrochemically. As is known, As_2O_3 oxidizes on a rotating platinum electrode in acid medium at a potential of about 1.3 V [2, 3]. The oxidation rate is the highest in a sulfate solution at $\text{pH} < 1$ [4].

A procedure for preparing arsenic acid by oxidation of As_2O_3 suspension on a tin dioxide anode in a 1% sulfuric acid solution containing 1% Na_2SO_4 was described in [5]. However, this technique fails to yield pure, impurity-free arsenic acid.

Much more attention has been given to oxidation of As_2O_3 in an alkaline solution to obtain reagent-grade arsenates, e.g., those of sodium [6] and lithium [7].

The aim of this study was to develop a method for synthesis of pure arsenic acid.

EXPERIMENTAL

We used in the study reagent-grade arsenic(III) oxide containing 99% main substance. Other reagents were of chemically pure grade.

The experiments were performed in a filter-press electrolyzer with platinum or ruthenium oxide anode and a tungsten or titanium plate as a cathode. The anode and cathode spaces were separated by a MF-4SK or Nafion cation-exchange membrane. The anolyte was circulated at a rate sufficient for maintaining As_2O_3 in the form of a suspension with a centrifugal pump. The working area of the anode was 30 cm^2 .

In a typical run, 0.5M HCL solution (60 ml) was fed into the cathode chamber of the filter-press electrolyzer equipped with tungsten cathode and ruthenium oxide anode, and 0.5 M HCL solution (70 ml) and 15 g As_2O_3 (0.15 mole As), into the anode chamber. The electrolysis was performed with a current of 6.0 A (current density $i = 0.2 \text{ A cm}^{-2}$) for 1.5 h (110% of the theoretically necessary quantity of electricity, Q). In the course of the experiment, the anolyte temperature increased from 20 to 45°C . The catholyte volume increased by 18 ml owing to electrophoresis. H_3AsO_4 was found in the catholyte in amount of 0.0012 mol, i.e., 0.8% of the initial As_2O_3 .

The anolyte was evaporated until dry, together with the wash water from the anode chamber, and calcined at 250°C . The resulting dry residue (18.2 g) contained 92.7% As_2O_5 . Arsenic acid was obtained by dissolving the residue in water. The yield of the arsenic acid by substance was 97%, and the current efficiency by the acid, 88%.

First, we checked the possibility of oxidizing an aqueous suspension of As_2O_3 on platinum or graphite without addition of any supporting electrolytes. As is known, arsenic(III) oxide is poorly soluble in water and is present in aqueous solutions in the form of a weak arsenous acid, responsible for low electrical conductivity of the solution. The results of these experiments are presented in Table 1.

It can be seen that the voltage across the electrolyzer is high at the beginning of the process and then gradually decreases owing to accumulation of the stronger arsenic acid, which raises the electrical conductivity of the solution. The oxidation is slow, and a nearly sixfold current excess is necessary for oxidizing only half the feed at the Pt anode.

Table 1. Oxidation of aqueous suspension of As_2O_3 in the absence of supporting electrolyte (tungsten cathode; MF-4SK membrane; anolyte 5 g As_2O_3 and 100 ml H_2O ; catholyte 0.5 M H_2SO_4 solution)

| Anode | Electrolysis conditions | | | Q , % of theoretical value | As(V) yield, % | Current efficiency by As(V), % |
|----------|--------------------------|------------------------|--------------------------|------------------------------------|----------------|--------------------------------------|
| | i , A cm^{-2} | U , V | T , $^{\circ}\text{C}$ | | | |
| Pt | 0.33 | 12.0 \rightarrow 4.5 | 22–50 | 550 | 40 | 7 |
| Graphite | 0.17 | 20.0 \rightarrow 8.0 | 22–25 | 140 | 53 | 38 |

* Q is quantity of electricity.

Table 2. Oxidation of aqueous suspension of As_2O_3 in the presence of electrically conducting additives (tungsten cathode; MF-4SK membrane; anolyte 5 g As_2O_3 and 100 ml supporting electrolyte; catholyte 0.5 M H_2SO_4 solution)

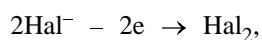
| Supporting electrolyte, M | Electrolysis conditions | | | Q , % of theoretical value | As(V) yield, % | Current efficiency by As(V), % |
|---------------------------------|--------------------------|---------|--------------------------|------------------------------------|----------------|--------------------------------------|
| | i , A cm^{-2} | U , V | T , $^{\circ}\text{C}$ | | | |
| H_2SO_4 , 1.0 | 0.07–0.03 | 3.9–3.2 | 17–19 | 450 | 83 | 18 |
| H_3AsO_4 , 1.0 | 0.03 | 4.0–3.7 | 20–23 | 300 | 81 | 27 |
| HCl, 1.0 | 0.067 | 3.7–3.8 | 23–28 | 110 | ~100 | 90 |
| HBr, 0.5 | 0.033 | 3.2 | 25–28 | 110 | 98 | 88 |

Table 3. Influence of current density on As_2O_3 oxidation (tungsten cathode, Pt anode; MF-4SK membrane; anolyte feed: As_2O_3 (10 g) and 0.5M HCl solution (100 ml); catholyte 0.5 M HCl solution)

| i , A cm^{-2} | Electrolysis conditions | | Q , % of theoretical value | As(V) yield, % | Current efficiency by As(V), % |
|--------------------------|-------------------------|--------------------------|------------------------------------|----------------|--------------------------------------|
| | U , V | T , $^{\circ}\text{C}$ | | | |
| 0.033 | 3.3–3.5 | 25–29 | 120 | ~100 | 83 |
| 0.067 | 3.9–4.4 | 25–30 | 120 | ~100 | 80 |
| 0.10 | 5.1–5.3 | 20–26 | 120 | ~100 | 85 |
| 0.15 | 6.7–6.8 | 23–25 | 120 | ~100 | 83 |
| 0.20 | 7.9–8.6 | 20–27 | 110 | ~100 | 90 |

In view of the aforesaid, we performed runs with introduction of electrically conducting additives, such as arsenic, sulfuric, hydrochloric, and hydrobromic acids. The results obtained in this series of experiments are presented in Table 2.

It can be seen that As(III) oxidation is slow in solutions of arsenic and sulfuric acid, and much faster in the presence of hydrohalic acids. Probably, the increase in rate of anodic oxidation is due to the fact that free halogens liberated at the anode in this case act as catalysts and transporting agents, namely: free halogen released at the anode



oxidizes As_2O_3 by the reaction



Since the results obtained for HCl and HBr were about the same, further experiments were done with the cheaper and more readily available hydrochloric acid. Runs were performed with a 0.5 M HCl solution at different current densities. The results obtained demonstrated that the oxidation is fast and can be performed at current densities of up to 0.2 A cm^{-2} (Table 3). It is appropriate, however, for economical reasons, to perform oxidation at current densities not exceeding 0.1 A cm^{-2} , since at higher densities the electrolyzer voltage increases essentially.

The control runs showed that the efficiency of arsenic(III) oxidation is about the same for ruthenium oxide and platinum anodes. Therefore, further experiments on the influence exerted by the hydrochloric acid concentration were performed with a ruthenium oxide anode (Table 4). It was found that raising the hydrochloric acid concentration to 4.0 M has virtually

Table 4. Influence of HCl concentration on As₂O₃ oxidation (Ag cathode, ruthenium oxide anode; Nafion membrane; 10 g As₂O₃; current density 0.1 A cm⁻²)

| $c_{\text{HCl}}, \text{ M}$ | Electrolysis conditions | | Q , % of theoretical value | H_3AsO_4 yield, % | Current efficiency by H_3AsO_4 % | As transfer into catholyte % | Current efficiency by O_2 % |
|-----------------------------|-------------------------|----------|------------------------------|-----------------------------------|--|------------------------------|--------------------------------------|
| | U , V | T , °C | | | | | |
| 0.5 | 5.3–5.6 | 22–23 | 110 | 94 | 85 | 2.2 | 9.6 |
| 1.0 | 5.0–5.2 | 22–27 | 102 | 98 | 96 | 1.7 | 3.4 |
| 2.0 | 4.5 | 23–27 | 102 | 98 | 98 | 1.4 | 1.5 |
| 3.0 | 4.3 | 24–26 | 102 | 93 | 91 | 1.0 | 0.7 |
| 4.0 | 4.0–4.3 | 23–27 | 102 | 99 | 97 | 0.7 | 0.8 |

no effect on the oxidation, but diminishes somewhat the loss of arsenic for its migration into the cathode space. However, it is inappropriate, for technological reasons, to make the concentration of hydrochloric acid in the anolyte higher than 1.0 M.

Finally, we studied the possibility of preparing a concentrated solution of arsenic acid in a single run. For this purpose, we carried out an experiment in which fresh portions of arsenic(III) oxide were fed into the anodic space at regular intervals. The test was performed at a current density of 0.2 A cm⁻² in a 0.5 M HCl solution, to which As₂O₃ (50 g) was gradually added. As a result, a 5.0 M H₃AsO₄ solution was obtained in 96% yield at a current efficiency of 81%. The loss of arsenic for its migration into the cathode space was 3.7%.

CONCLUSIONS

(1) The study yielded a simple and efficient method for oxidation of arsenic(III) oxide to arsenic acid. The advantage of this technique is the feasibility of

preparing sufficiently pure arsenic acid in a single stage.

(2) Hydrogen chloride present in the anolyte is completely removed upon solution evaporation. The HCl-containing distillate is used for preparing a fresh portion of the anolyte. This opens up the possibility of organizing a nearly waste-free production.

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