

Electrochemical Reduction of As(III) in Acid Media

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Abstract—Measurements of the cathode potentials of different electrode materials in the galvanostatic electrolysis of As_2O_3 solutions in sulfuric acid indicate that the Pb cathode ensures the most stable negative potential, favorable for AsH_3 formation. Preparative electrolyses confirm stability of the arsine yield in a series of experiments. The current efficiency for arsine on the Pb cathode is 60–70%. The byproduct of this process is As^0 , with a current efficiency of about 2%. We have designed and tested an electrolyzer with improved hydrodynamics, which makes it possible to avoid the formation of dead zones and to prevent the cathode chamber from being clogged.

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INTRODUCTION

The synthesis of hydrogen arsenide (arsine) through the electrochemical reduction of As(III) has been the subject of much attention [1–5]. This approach was proposed for the preparation of AsH_3 in the laboratory. At the same time, no attempts to scale-up this process have been described in the literature. Given that electrochemical synthesis enables the preparation of purer products in comparison with chemical processes, we have focused our efforts on the application of this process on a production scale:

1. We studied the variation in the potential of various cathode materials during galvanostatic electrolysis.
2. We compared the stability of various cathode materials in a series of consecutive electrolyses without cleaning the electrolyzer.
3. We examined the possibility of reducing the yield of elemental arsenic, a reaction byproduct.
4. We tested an electrolyzer with improved hydrodynamics and measured its main discharge coefficients.

EXPERIMENTAL

Polarization measurements were performed with an IPC-2000 programmed electronic potentiostat. The potential was measured relative to a silver/silver chloride reference electrode in a three-electrode cell. As working electrodes, we used sheet metal plates 0.5 cm^2 in working area. The auxiliary electrode was of platinum. The measurements were made during galvanostatic electrolysis at a polarizing current of 100 mA (current density of 0.2 A/cm^2), while bubbling the solution with argon.

The cathode potential was measured as follows: The electrode was pretreated with sulfuric or hydrochloric acid and then thoroughly rinsed with distilled water.

The electrodes thus prepared were immersed in a background electrolyte solution and cathode-polarized with a current of 100 mA for 30 min (over this time, the cathode potential stabilized somewhat). Electrolysis was stopped, a cyclic voltammogram was recorded, an appropriate amount of As(III) in the form of a concentrated NaAsO_2 solution was added, and a cyclic voltammogram was again recorded. Next, we conducted electrolysis at a current of 100 mA for 30 min, while monitoring the cathode potential, and then recorded yet another voltammogram.

Preparative electrolyses were carried out in a filter-press electrolyzer with a working chamber $2.2 \times 2.2 \text{ cm}$ in dimensions (cathode area of 4.84 cm^2). In the electrolyzer with improved hydrodynamics, the cathode was 30 cm in length and $\approx 1.7 \text{ cm}$ in width. The membrane–cathode separation was 12 mm, and the working surface area of the cathode was 50 cm^2 .

The was circulated by a centrifugal pump. The set temperature was maintained by a remote heat exchanger. The cathode gases were pyrolyzed at temperatures from 650 to 700°C . The arsine yield was determined from the weight gain of the silica tube in the pyrolysis furnace.

The stability of various electrode materials was assessed as follows: After 80 ml of 10% sulfuric acid saturated with As_2O_3 (the As_2O_3 solubility in 10% H_2SO_4 is $\approx 15 \text{ g/l}$) was introduced into the electrolyzer, arsine electrosynthesis was conducted at a temperature of $25\text{--}30^\circ\text{C}$ and cathode current density of 0.2 A/cm^2 . The duration of each run was 1 h. Then, the current was turned off, and the electrolyzer was left filled with the electrolyte for a day. Next, the spent catholyte was replaced with a fresh one, and the next experiment was conducted under the same conditions. The cathode was not treated within a given series of experiments.

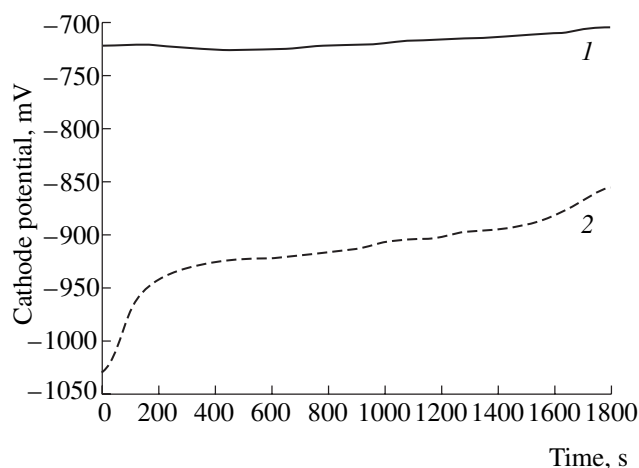


Fig. 1. Variation in the potential of an iron cathode (steel-3) during galvanostatic electrolysis (0.1-A current, 1.0 N H_2SO_4 solution with As(III) additions): (1) background electrolyte, (2) background + 0.01 M As(III).

In experiments with continuous saturation of the catholyte with arsenous acid (arsenic(III) oxide), the solution was pumped through a tank in which the arsenic oxide suspension was agitated by a mechanical stirrer. To the bottom part of the tank, we introduced the spent catholyte from the electrolyzer; from the top part, we withdrew a saturated As_2O_3 solution free of solid oxide particles.

RESULTS AND DISCUSSION

It is well known [1] that, during electrolysis of acid As_2O_3 solutions, the cathode becomes covered with a layer of elemental arsenic, and, during further electrolysis, the cathodic process takes place at the arsenic electrode. In light of this, Nilov [2] and Vorotyntsev et al. [3] believe that the cathode material is of no significance in the preparation of arsine. To check this

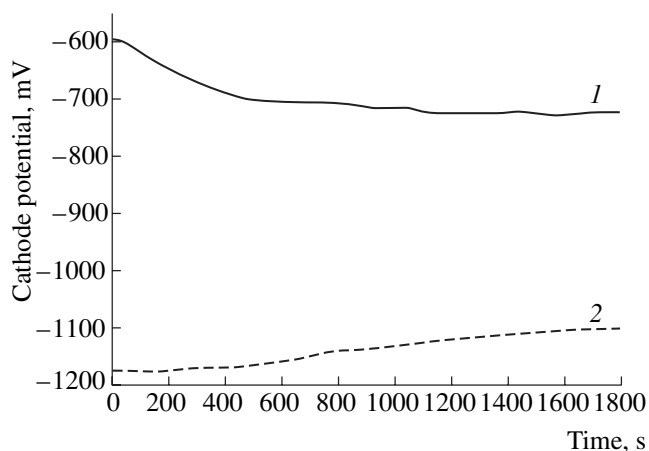


Fig. 2. Variation in the potential of a platinum cathode (the same conditions and designations as in Fig. 1).

assumption, it is reasonable to measure the cathode potential under galvanostatic electrolysis conditions. We tested glassy carbon, titanium, zinc, lead, copper, iron, and platinum cathodes.

The most stable potential in a sulfuric acid solution over a period of 30 min in the absence of arsenic was offered by the iron cathode (Fig. 1). After recording the voltammogram in the presence of As(III), the cathode potential shifts sharply to more negative values, which can be accounted for by the deposition of an elemental arsenic film onto the cathode surface. At the same time, if arsenic fully shielded the cathode surface, the shift in potential would be substantially greater (at a current density of 0.2 A/cm^2 , the potential of arsenic cathodes is -1.02 V [1]). Thus, we are led to conclude that arsenic forms a porous coating. During further electrolysis, the shift in potential decreases, indicating that no dense arsenic coating is formed during electrolysis. As(III) additions had a similar effect on the potential of the platinum cathode (Fig. 2).

For cathode materials with a high hydrogen overpotential, an opposite picture was observed after voltammetric measurements: the potential shifted to less negative values, approaching that of the arsenic electrode. As an example, Fig. 3 shows the data for the lead cathode. At the same time, during electrolysis the observed depolarization value decreases. Our data on the variation in cathode potential over a period of 30 min are presented in Table 1.

Two general trends warrant attention. During voltammetric measurements, depolarization was only observed for the lead cathode. Arsenic deposition on the other electrode materials shifted the cathode potential to more negative values. The shift was particularly large for titanium and glassy carbon. This may be due to the deposition of a low-conductivity form of arsenic. Another general trend is that, during the first 30 min of electrolysis, the cathode potential gradually shifts to less negative values. The shift depends significantly on

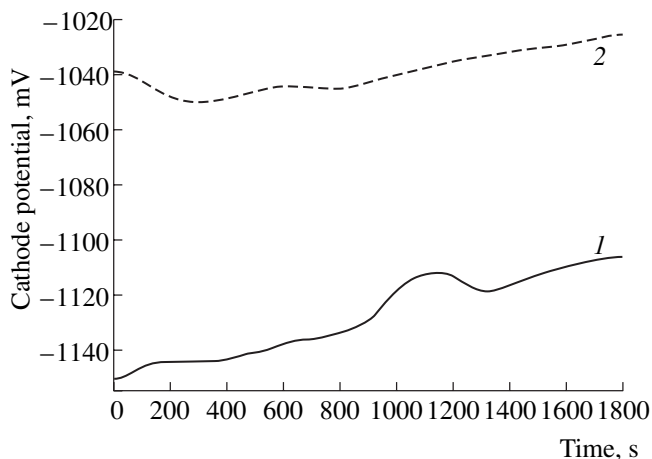


Fig. 3. Variation in the potential of a lead cathode (the same conditions and designations as in Fig. 1).

Table 1. Variation in the cathode potential during electrolysis of 1.0 N H₂SO₄ in the presence of 0.01 M As(III) (current density, 0.2 A/cm²)

Cathode material	Cathode potential in 1.0 N H ₂ SO ₄ , mV	Cathode potential in the presence of As(III), mV		Potential change in 30 min, mV
		at the beginning of electrolysis	after 30 min	
Lead	1100	1040	1020	20
Zinc	1140	1140	1120	20
Copper	815	860	790	70
Platinum	740	1180	1200	80
Stainless steel	850	1140	1010	130
Iron	725	1020	880	140
Titanium	1200	1370	1180	190
Glassy carbon	1500	1350	1160	210

Table 2. Effect of current density on the current efficiency for arsine on various electrode materials (10% H₂SO₄, ≈2 g/l As₂O₃)

Current density, A/cm ²	AsH ₃ yield, %						
	lead	cast cadmium	cold-rolled cadmium	stainless steel	copper	titanium	iron
0.05	28	26	–	26	20	22	21
0.3	75	65	52	54	52	50	45

the cathode material and seems to be due to structural changes in the arsenic coating.

Thus, voltammetry data indicate that arsenic is deposited on all of the electrode materials studied, but the deposit does not suppress the influence of the cathode material. The behavior of arsenic coatings depends significantly on the nature of the cathode material, and an appropriate choice of the cathode material is of key importance in developing the process for the preparation of arsine. It can be seen from Table 1 that, during the first minutes of electrolysis, a high negative potential is observed on metals with a low hydrogen overpotential, which drops rapidly over time. Lead and zinc, metals with a high hydrogen overpotential, have a sufficiently stable potential. These materials would be expected to ensure a stable arsine yield over a long time.

Taking into account voltammetry results, we continued experimental studies of electrochemical arsine synthesis using different electrode materials with the aim of optimizing the conditions for long-term electrolysis without disassembling the electrolyzer.

As shown previously [5], the AsH₃ yield on a lead cathode increases significantly with increasing current density. The maximum current efficiency for arsine, about 75%, was achieved at a current density of 0.2–0.25 A/cm², whereas at 0.05 A/cm² the current efficiency was 28%. Our experiments show that increasing

the current density increases the arsine yield on all of the cathode materials studied (Table 2). The highest yield was reached on lead, and the lowest yield was obtained on iron.

Testing various electrode materials, we found that the activity of cadmium cathodes depended on the fabrication process (Fig. 4). The yield on an electrode prepared by casting into a glass mold was equal to that on the lead cathode. The arsine yield on cold-rolled cadmium was substantially lower.

An interesting trend was revealed in testing the lead cathode. In a number of electrolyses, the cathode was activated. Reducing the current density in each subsequent experiment with the same electrode reduced the arsine yield more slowly than was observed during the initial increase in current; that is, a significant hysteresis was observed (Fig. 5). It seems likely that the activation of the cathode is due to the modification of its surface through arsenic incorporation into the lead lattice.

Next, we assessed the stability of electrode materials (lead, copper, and cadmium) in successive electrolyses. The results are displayed in Fig. 6. These experimental data lend support to the conclusion drawn from voltammetry data that a stable arsine yield can be achieved on a lead cathode: the yield was about 70% in the first run, then decreased to a level of 60%, and remained unchanged in the next ten runs. The arsine yield on the iron and copper cathodes was low even in

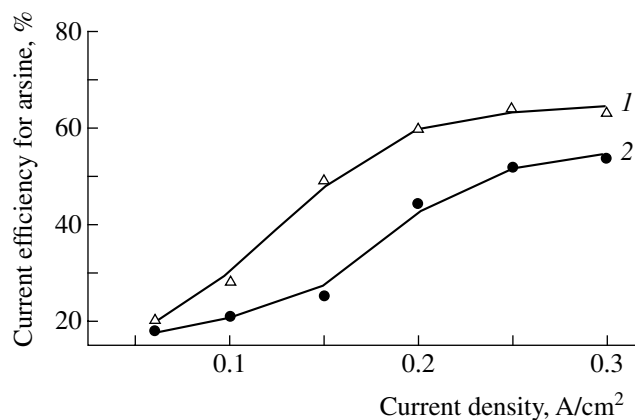


Fig. 4. Effect of current density on the arsine yield on cadmium cathodes (10% H_2SO_4 , 1.4% As_2O_3): (1) cast cadmium, (2) cold-rolled sheet cadmium.

the first run and had a pronounced tendency to decrease in subsequent runs.

For all of the cathode materials tested, arsine synthesis with a low yield was always accompanied by the formation of elemental arsenic. Its amount decreases with increasing current density, and at 0.2 A/cm^2 the current efficiency for arsenic is about 2.5% [6]. Although the yield of arsenic is rather low, its deposition notably impedes maintenance of the electrolyzer and makes periodic cleaning of the cathode chamber necessary.

Since we failed to reduce the yield of elemental arsenic to below 2.5% by varying the current density in 10% sulfuric acid, it was of interest to check the results obtained by Bouard et al. [7], who reported that the highest arsine yield was achieved at an $\text{As}^{3+} : \text{H}^+$ ratio

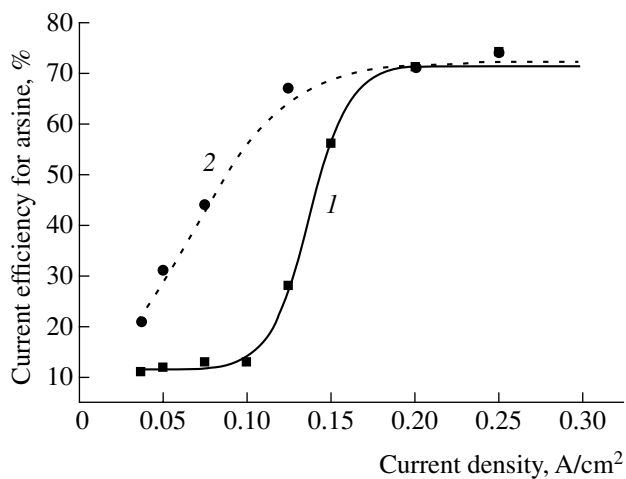


Fig. 5. Activity of a lead cathode as a function of (1) increasing and (2) decreasing current density (10% H_2SO_4 , 1.4% As_2O_3).

near unity. Given the low solubility and very weak dissociation of arsenous acid, HAsO_2 , this ratio can be obtained in 1% sulfuric acid solutions (Bouard et al. [7], however, recommend a 1 M ($\approx 10\%$) H_2SO_4 solution). The current efficiency for arsine is then essentially independent of current density: 25 $\text{l}/(\text{h m}^2)$ at 0.02 A/cm^2 and 225 $\text{l}/(\text{h m}^2)$ at 0.15 A/cm^2 , which corresponds, according to our calculations, to current efficiencies of 89.7 and 92.9%, respectively. Bouard et al. [7] propose constantly saturating the solution with arsenic(III) ions during electrolysis by pumping the solution through a layer of arsenic oxide.

The drawback to the filter-press electrolyzer with a working chamber 2.2×2.2 cm in dimensions is the presence of dead zones in which elemental arsenic is deposited. In connection with this, the data from [7] were checked using an electrolyzer with improved hydrodynamics, in which the height of the working chamber was almost 20 times its width. This made it possible to raise the linear velocity of the catholyte by about one order of magnitude, without changing its volumetric circulation rate. Preliminary testing of the electrolyzer with 10% H_2SO_4 showed that the increased circulation velocity had no effect on the arsine yield but eliminated the dead zones in which elemental arsenic accumulated.

We conducted two types of experiments, saturating the catholyte with arsenous acid (arsenic(III) oxide) in a separate apparatus or utilizing an As_2O_3 suspension in the catholyte. The results revealed no significant advantage of the process described by Bouard et al. [7]. The $\text{As}^{3+} : \text{H}^+$ ratio recommended by them did not ensure a high yield. Continuous saturation of the catholyte with arsenous acid (see above) had low efficiency: we failed to achieve a stable arsine yield. The current efficiency

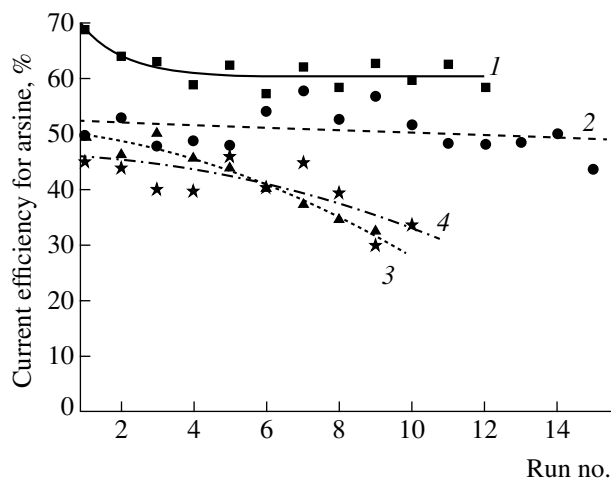


Fig. 6. Variation in arsine yield in a series of successive experiments (10% H_2SO_4 , 1.4% As_2O_3 , current density of 0.2 A/cm^2) without cleaning the cathode or disassembling the electrolyzer: (1) lead, (2) cast cadmium, (3) copper, and (4) stainless steel cathodes.

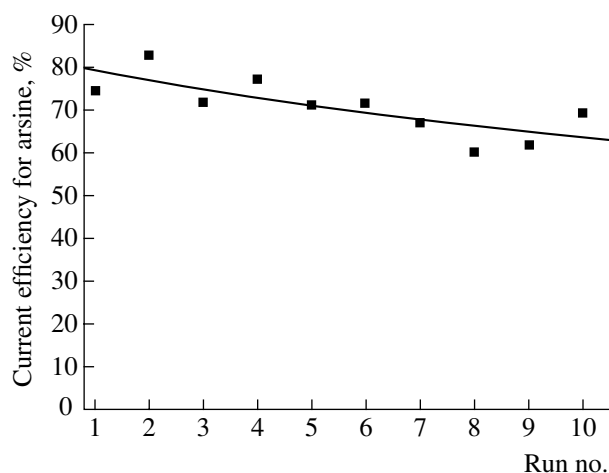


Fig. 7. Current efficiency for arsine in a series of successive experiments (lead cathode, 1% H_2SO_4 , As_2O_3 suspension, current density of 0.1 A/cm^2) in an electrolyzer with improved hydrodynamics.

in those experiments varied from 35 to 75%. An As_2O_3 suspension in the catholyte ensured a more stable yield (Fig. 7), which, however, had a tendency to decrease with an increase in the voltage applied to the electrolyzer. The likely reason for this is the deposition of As and As_2O_3 on the cathode. The current efficiency for elemental arsenic was 1.8–2.1%.

With 1 and 10% H_2SO_4 , we obtained comparable data. Clearly, the sulfuric acid concentration must be chosen in the implementation context.

The material and energy balances for experiments with 1% H_2SO_4 and a current density of 0.1 A/cm^2 indicate that the preparation of 1 kg of arsine requires an energy of about 20 kW h. Under these conditions, the current efficiency for arsine is 64.6% and the substance yield is 95.5%.

CONCLUSIONS

The present experimental data demonstrate that arsine can, in principle, be synthesized through the electrochemical reduction of arsenous acid in sulfate solu-

tions, but the process parameters achieved are inferior to those in the reduction of As(V) compounds, e.g., arsenic acid, H_3AsO_4 [8].

The use of a filter-press electrolyzer with forced catholyte circulation makes it possible to achieve a stable current efficiency for arsine on the cathode of order 65%, with a selectivity of 97–98%. About 2% of the power goes to arsenic release (the rest, to hydrogen release). Varying the sulfuric acid concentration from 1 to 10% has an insignificant effect on the process parameters. The electrolyzer we tested can be regarded as a prototype of an industrial apparatus.

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