# Synthesis of Volatile Inorganic Hydrides by Electrochemical Method

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**Abstract**—Published data and results of our investigations on the problem of electrochemical synthesis of arsenic, phosphorus, and germanium hydrides are generalized. The results of the developments of the physicochemical bases of arsine synthesis by electrochemical reduction of arsenic acid, phosphine by reduction of white phosphorus in organic solvents, and monogermane by reduction of germanate in basic conditions are reported. The current yield of hydrides is 95, 90, and 40%, respectively. The promising guidelines of the practical use of electrochemical methods of the synthesis of the hydrides in the manufacture of semiconductor materials for microelectronics, optics, and laser engineering are discussed. The development of an arsine generator attracts considerable interest, which can serve as a basis for an aggregative continuous apparatus used in complex flow charts of manufacture of semiconductor materials.

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# **INTRODUCTION**

High purity arsine and phosphine are widely used in the synthesis of monocrystals and heteroepitaxial structures of  $A^{III}B^{V}$  semiconductor compounds, promising in micro- and optoelectronics, laser engineering, and solar power engineering. High-purity germane finds use in the manufacture of extremely high frequency integral schemes.

For the synthesis of high-purity arsenic and germanium in an industrial version, chloride technology is the best developed [1, 2]. Its significant drawbacks are relatively low yield of ready production (<70%) and high losses with hydrochloric acid wastes. Chlorides are toxic and corrosive, which makes process extremely dangerous. Up to 70% of capital and maintenance outlays are expenses for the refinement of flows and gas effluents.

Hydride technology does not have many of the mentioned drawbacks; it is especially convenient in the synthesis of the most pure products. However, the step of chlorides synthesis is the weakest link of the given technology with respect to ecology and safety of fabrication.

The approach to the synthesis of hydrides developed in industry is the reaction of magnesium or zinc phosphides, arsenides, or germanides with acid solutions [3]. Improvement of this method is the hydrolysis reaction in the gas phase [4]. Fundamental scientific principles of the synthesis of hydrides by conventional methods, their deep purification, and analysis were developed [5].

Currently arsenic and germanium hydrides are synthesized by reduction of compounds of these ele-

ments by boron or aluminum hydrides of sodium or lithium [3]. Chemical methods of synthesis are nonselective; hydrides of elements present in the reaction medium (N, C, S, Si, Se, Te, Sb, and others) and also taking part as admixtures of arsenic, phosphorus, and germanium, which requires complex multistep purification, are generated concurrently [6]. A large amount of side forming hydrogen is contained in the gas phase. A large amount of liquid wastes, sometimes toxic, with which valuable raw material can be lost (for instance, germanium), remains as a result of synthesis. Synthesis is hardly taken under control. Therefore, a search for alternative ways of synthesis of hydrides is of great practical interest.

A minimal amount of reagents and steps of synthesis should be used in the development of new methods of synthesis, which reduces the contamination of the product. From this point of view, the direct hydrogenation of elements is the most reasonable. Thermodynamic calculation shows that phosphine can be synthesized from elements, but only under high pressure, and this method should not be considered promising. The reaction of arsenic with hydrogen is not observed. Reduction of only arsenic compounds with hydrogen under pressure leads to formation of traces of arsine [3]. The plasmochemical approach to synthesis of arsine or phosphine from elements is well known [7]. The reaction is conducted in the flux of a mixture of argon and hydrogen under reduced pressure and does not feature appreciable yields of the target product.

Starting from the middle of the 20th century, the electrochemical synthesis of hydrides attracted considerable interest. Electrolysis realized at normal temperature and pressure substantially simplifies the development of ecologically safe processes. As the literature review has shown, a significant number of investigations are dedicated to the electrosynthesis of hydrides, but in the last decade, the number of publications is not large and they are not realized enough in practice. At the present time, judging by the published data, analytical works are of great interest. The electrochemical method is used for the reduction of compounds of a number of elements, including arsenic and germanium, to hydrides with further elucidation by spectral methods [8, 9]. The detection of a small concentration of elements is achieved  $(10^{-8}-10^{-9} \text{ M})$ ; however, from the point of view of the synthesis of hydrides, these investigations are not of great interest.

The present review generalizes the results of systematic investigations on the development of physicochemical bases of electrochemical synthesis of arsenic, phosphorus, and germanium hydrides through the reduction of the elements themselves and their compounds at various oxidation states. The problem of practical use of the results in the technology of semiconductor materials attracts considerable attention.

The goal presumes the solution of following problems:

—electrochemical synthesis of arsine by the reduction of elemental arsenic and compounds of As(+3)and As(+5);

—electrochemical synthesis of phosphine by the reduction of white, red, and black phosphorus, and also acids of phosphorous;

—electrochemical synthesis of germane by the reduction of metallic germanium and compounds of Ge(+2) and Ge(+4);

—fabrication of generator of hydrides, by the example of generator of arsine, on the basis of which the reduction of arsenic acid is taken.

#### 1. ELECTROCHEMICAL METHODS OF ARSINE SYNTHESIS

Data on electrochemistry of arsenic are systemized in [10, 11]. In the review [12], particular attention was given to works promising for the solution of practical problems, including the synthesis of arsenic.

Electrochemical reduction of arsenic and its compounds proceeds according to the following scheme:

$$As(+5) \xrightarrow{2\bar{e}} As(+3) \xrightarrow{3\bar{e}} As^{0}$$

$$\xrightarrow{3\bar{e}, 3H^{+}} AsH_{3}.$$
(1)

As is evident, **the reduction of elemental arsenic** is energetically the most preferable. At cathode polarization of the arsenic electrode, two electrochemical processes proceed concurrently: liberation of hydrogen and reduction of arsenic to arsine [13]. Two versions of arsine formation are considered [12]. On the surface of the arsenic cathode, arsenide ions are generated, reacting with protons (in acidic solutions) with the formation of hydrogen or arsine:

As 
$$\xrightarrow{3\bar{e}}$$
 As<sup>3-</sup>  $\xrightarrow{3H^+}$  AsH<sub>3</sub>  
H<sup>+</sup> As<sup>2-</sup> + 0.5H<sub>2</sub>. (2)

Another mechanism is possible, according to which water molecules are preliminarily reduced on the surface of arsenic. The formation of arsine, in the authors' opinion [14], proceeds through the disproportionation of AsH and AsH<sub>2</sub> surface hydrides, which is the limiting step. The direct reduction of AsH<sub>2</sub> is not excluded [15]:

 $AsH_2 + H_2O + \bar{e} \longrightarrow AsH_3 + OH^-$ . (3)

Such a scheme is likely to be realized in basic conditions, in which the current yield of arsine does not depend on the current density in the range of 0.01-0.1 A/cm<sup>2</sup>, and, consequently, the step limiting the rate of the process on the whole is not electrochemical [12]. It is stated that the excess of OH<sup>-</sup> ions facilitates the disproportionation of the surface hydrides [15].

Published data on the electrosynthesis of arsine on the arsenic cathode are quite contradictory (Table 1); however, some laws can be noted. For example, the current yield of arsine primarily depends on the nature and purity of the arsenic electrode. On a cathode fabricated by contact precipitation of arsenic on zinc, the yield of AsH<sub>3</sub> is not substantial. Evidently, upon coating the electrode, arsenic forms layers of modification other than  $\alpha$  [14, 16]. With the increase in the purity of arsenic up to 99.999% and more, the current yield of arsine grows.

According to [15, 17], arsine with the yield of 95– 98% can be synthesized using a cathode from high purity arsenic in neutral and basic media. It is established that the yield of arsine in the solution of 1 M Na<sub>2</sub>SO<sub>4</sub> increases with the growth of current density from 0.01 A/cm<sup>2</sup> to 0.9 A/cm<sup>2</sup> [17, 18], while in 1 M NaOH this dependence is not detected [15]. The synthesis of high-purity arsine is performed on an apparatus having a productivity of 20–25 g/h with a cathode of high-purity  $\alpha$ -As at 20–30°C and 0.1 A/cm<sup>2</sup> in 1 M Na<sub>2</sub>SO<sub>4</sub> [17].

The significant drawback of arsenic synthesis through the reduction of arsenic is the formation of a microfine precipitate (0.46 g/(A h) at electrolysis in 1 M K<sub>2</sub>HPO<sub>4</sub> [18]), which contains both solid hydrides (AsH<sub>2</sub>)<sub>n</sub> and arsenic particles being liberated owing to the dispergation of cathode. It was discovered [17, 18] that process proceeds more intensely the higher the pH. Despite that, it was proposed to construct an arsine generator on the basis of the reduction of  $\alpha$ -arsenic in an alkali medium [15].

In [19–21], construction of such a generator with a bulk cathode and "victim" anode is presented (Fig. 1). It is proposed to use generator [22] for exchange of balloons with liquefied gas in MOCVD technology (Metal Organic Chemical Vapor Deposition). For this

Cathode	Electrolyte	Current density, A/cm <sup>2</sup>	Temperature, °C	Current yield, AsH <sub>3</sub> , %	Reference
As (precipitated on	NaOH	_	_	0.68	[16]
Zn from AsCl <sub>3</sub> )	$H_2SO_4$	0.05	—	1-2	[14]
	1 M Na <sub>2</sub> SO <sub>4</sub>	0.05	—	10.0	[14]
$\alpha$ -As ultrapure	$H_2SO_4$	—	—	2-4	
(99.999%)	NaOH	—	—	2-4	[17]
	$1 \text{ M N}_{2} \text{ SO}$	0.01	20	72	[17]
	$1 \text{ Im} \text{Im} a_2 \text{SO}_4$	0.09	20	95	
	0.125 M H <sub>2</sub> SO <sub>4</sub>	0.01	20	15.8	
	1 M KOH	0.01	20	30.6	[10]
	1 M Na <sub>2</sub> SO <sub>4</sub>	0.02	20	40.9	[18]
	1 M K <sub>2</sub> HPO <sub>4</sub>	0.02	35	42.7	
α-As (99.9999%)	1 M NaOH	0.01–0.1 A	15	95-97	[15]
	8 M KOH	15 A*	—	45	[19]
	1 M NaOH	0.02	—	97	[20]
	1 M KOH	50 A*	—	90 <b>→→</b> 60	[21]
α-As (99.999%)	45% KOH	0.13	21	94.5	
α-As (99%)	45% KOH	0.13	21	89.5	[22]
	2507 NaOU	0.05 - 0.07	21	>80	[23]
_	55% NaOH	0.26-0.32	21	>86	

 Table 1. Results of electrochemical synthesis of arsine on arsenic cathode

\* The current density is not indicated; the cathode is bulk.

purpose, the device is made as a container with a single gas outlet. The electrolyte is a concentrated base solution. The cathode, representing arsenic grains in a polymer net, is supplied with lead current. To prevent the liberation of oxygen, a soluble or easily oxidizable anode is used, for the role of which As, Mo, W, Cd, Pb, and others or redox pairs  $MnO_2/MnO_3$ ,  $Fe(OH)_2/Fe_3O_4$ , and others are suggested.

The current yield of arsine is 45% [19], 90% [21], and up to 97% at the current density of 0.02 A/cm<sup>2</sup> [20]. It is noted that [21], at the end of the service life of the generator with the expense of the As cathode, the yield of AsH<sub>3</sub> drops to 60%. For drying the gas, synthetic zeolites are used (molecular sieves). In [20], it is recommended to use a cation exchange membrane of Naflon type to prevent precipitation on the cathode of the small electrically conductive products of the reduction of  $MOO_4^{2-}$  or  $WO_4^{2-}$  generated at the anode.

This concept of a generator was further developed in [23], where the effect of the base concentration was studied in detail with the goal to increase the specific capacity of the generator and to prevent the crystallization of products of anode oxidation ( $K_2MoO_4$ ). It is recommended to use the bag-free cell, 35–39% KOH, and monolith arsenic cathode with a purity of not less than 99% (optimal is 99.999%), which provides an increase in the yield of arsine. Examples of arsine preparation are presented at the current density from 0.05 to 0.43 A/cm<sup>2</sup> with the production from 2.5 to 16.0 mg/min. The current yield of arsine calculated by the data of [23] is nearly 90%. The profitable use of the cathode approaches 77.8%.

Thus, the main drawbacks of arsine synthesis from arsenic is the dispergation of the cathode material and the impossibility of its complete use; which leads to an unproductive expense of expensive initial raw materials (high-purity arsenic), decreasing the competitiveness of the method. It would be more appropriate to reduce the arsenic compounds in the dissolved state.

Analysis of existing information dedicated to **the** electrochemical behavior of trivalent arsenic confirms the complexity of electrode processes proceeding at cathode polarization. This fact is related to the fact that, in aqueous solutions, As(+3) exists in different forms, depending on pH of medium, having different electrochemical activity. The products of reduction are arsenic, metal arsenides, arsine, and higher arsenic hydrides [12].

To achieve high yields of arsine, it is recommended to carry out the reduction in an acidic medium on cathodes of Pb, Zn, Cd, Ni, Fe, or graphite [24, 25]. On the basis of experimental data [26], it can be concluded that the most suitable material of the cathode is cadmium (Table 2); however, our investigations [27]



Fig. 1. Generator of arsine based on the reduction of arsenic cathode [20]: (1) bulk As cathode, (2) soluble anode (Mo), (3) current inlet of cathode, (4) press block, (5) perforated container, (6) cation exchange membrane, (7) cross-flow of electrolyte (KOH solution).

showed that the most stable negative potential, promoting the formation of  $AsH_3$ , is observed on the lead cathode. The current yield of arsine increases with the increase in current density (Table 2) and hardly changes with the increase in temperature.

Dynamics of the change in the current yield of  $AsH_3$  during electrolysis of acidic solutions of  $As_2O_3$  on lead is presented in [28]. At the beginning of electrolysis, the amount of liberating arsine is not large and most of the current is spent on the increase in thickness of the layer of elemental arsenic on the cathode. With the increase in the arsenic layer, the potential of the cathode shifts to negative values (in galvanostatic mode) until the reduction of arsenic to arsine becomes possible. After the complete "modification" of the cathode surface (coating by a thick layer of arsenic), the main part of the current is spent on arsine synthesis.

Therefore, considerations were made [26, 28] that, for synthesis of arsine, the choice of cathode does not play an important role. Our volt-ampere investigations [29] showed that arsenic does not completely shield the surface of the cathode. The behavior of the arsenic layer depends substantially on the nature of the material of the electrode, and the right choice of electrode plays an important role in devising the method of arsine preparation.

The electrolysis of acidified solutions of  $As_2O_3$  can be set on the basis of the construction of the arsine generator. So, in [30], the construction of an electrolyzer for the preparation of volatile hydrides, including arsine, is suggested. The feature of the electrolyzer is the use of lead cathodes with capillary holes, through which fresh catholyte is forced, and the presence of a cooling chamber on the upper part, which removes the volatile admixtures from the gas phase.

Cathode n	naterial	Pb	Cd	Sn	Fe	Stainless steel	Cu	Zn	Ti	Ni	As	Reference
Current density, A/cm <sup>2</sup>	0.05 0.3	28 75	26* 65* (52**)		21 45	26 54	20 52		22 50			[27]
		56	78	81	45	—	_	66	—	43	16	[26]

Table 2. Current yield of  $AsH_3$  (in %) on various cathode materials in sulfuric acid solution of  $As_2O_3$ 

\* Cadmium is bulk.

\*\* Cadmium is rolled.



**Fig. 2.** Generator of arsine based on the reduction of arsenous acid at  $H^+/As = 1$  [31]: (1, 2) anode and cathode chambers of electrolyzer; (3) insoluble anode; (4) buffer capacity of anolyte; (5) line for anolyte injection; (6) pump for anolyte circulation; (7) cathode (lead); (8) chamber for dissolution of As<sub>2</sub>O<sub>3</sub>; (9) pump for catholyte circulation; (10) buffer capacity of catholyte; (11) Nafion cation exchange membrane; (12) catholyte.

As is stated in [31], the main condition of operation of a generator (Fig. 2) with a high yield of arsine on the lead cathode is the maintenance of constant molar ratio  $H^+/As = 1$ . With allowance for low solubility of arsenous acid and its very weak dissociation ( $K_1 = 7.9 \times 10^{-9}$ ), this ratio can be obtained in 1% H<sub>2</sub>SO<sub>4</sub> (although in [31], 1 M is recommended, i.e., ~10% H<sub>2</sub>SO<sub>4</sub>). It is proposed to continuously saturate the solution of As(+3) during electrolysis, forcing it through the layer of arsenic oxide. The current yield of arsine is not mentioned, only its content in the cathode gas (up to 95%) [31]. This value is not sufficient for the characteristics of the process, since part of the current can be spent on the formation of arsenic.

The test carried out by us [29] showed that the maintenance of the recommended  $H^+/As$  ratio does not make it possible to achieve a high yield. The data obtained with the use of 1 and 10% solutions of  $H_2SO_4$  are quite comparable. Obviously, the choice of the concentration of sulfuric acid should be made from technological considerations.

The test of the arsine generator from As(+3) was carried out [28] with the optimization of technological parameters of electrosynthesis on the scale of a pilot plant with a filter-press type electrolyzer. The initial raw material was As<sub>2</sub>O<sub>3</sub>, the catholyte was 1 M H<sub>2</sub>SO<sub>4</sub>, the current density was 0.03-0.05 A/cm<sup>2</sup>,  $t = 30^{\circ}$ C, and the cathode was lead. The current yield of arsine was 60%, and the content of arsine (in the mixture with H<sub>2</sub>) was 60 vol %. The expense coefficients by raw material, initial and side product, and wastes were found. The technological regulations of the process

were developed. It is noted that the liberating arsine reacts with As(+3) dissolved in the catholyte, forming a suspension of arsenic particles that catalyze the further reaction.

We studied the operation of an arsine generator based on the reduction of a sulfuric acid solution of  $As_2O_3$  [29]. The use of forced circulation of the catholyte makes it possible to obtain a stable current yield of arsine on the order of 65% on the lead cathode (Fig. 3). The current yield of arsenic is nearly 2%. It should be believed that the process can be limited by the transfer of As(+3) to the surface of the cathode, since the use of an As<sub>2</sub>O<sub>3</sub> suspension initially makes it possible to increase the current yield. However, further, the tendency toward its decrease is observed (Fig. 3, curve 5), which can be determined by the precipitation of the mixture of arsenic and its oxide on the cathode.

The use of arsenic oxide as a raw material in the arsine generator (dusty and highly toxic product) is extremely undesirable. It was proposed [32] to add sodium arsenite to the solution of phosphoric or sulfuric acid. However, in this version, the aggregation of salts in the catholyte is inevitable, leading to the necessity of replacing of the solution.

As our investigations showed [33], the electrolysis of sodium arsenite solutions makes it possible to synthesize arsine along with the main product (arsenic). Varying the conditions of the electrolysis, one can obtain one product or another predominantly. In the process, the source of arsenite for the fabrication of arsine can be the products of lewisite detoxication [34].



Fig. 3. Change in the arsine yield in a series of consecutive experiments on various cathode materials [29], 10%  $H_2SO_4$ , 1.4%  $As_2O_3$ , current density of 0.2 A/cm<sup>2</sup>: (1) stainless steel, (2) copper, (3) cadmium (cast), (4) lead, (5) lead (suspension of  $As_2O_3$  in 1%  $H_2SO_4$ , 0.1 A/cm<sup>2</sup>).

The formation of microfine arsenic is one of the most serious drawbacks of this method of arsine synthesis. With the reduction of As(3+) compounds, arsenic accumulates in the solution as a suspension; which determines the necessity of periodic cleaning of the construction. In addition, in the construction of generator, the dosing of the solid raw material (As<sub>2</sub>O<sub>3</sub>) cannot be considered optimal. The liquid reagent feed (sodium arsenite solution) is more technological; however, in this case, the formation of arsenic in comparable amounts is inevitable.

For this reason the possibility of **electrochemical reduction of compounds of pentavalent arsenic** should be considered. Arsenic has the oxidation state +5 in arsenic acid and its salts, which in solutions are present in the forms presented in Table 3.

Polarographic behavior of arsenates was studied quite widely; however, a large number of trials gave a negative result; waves of reduction of As(+5) are recorded only in two cases: on the polarogram in 11.5 M HCl [36] and in the reduction of dihydroarsenates [37]. It was shown that As(+5) does not show activity in a phosphate solution in a wide range of pH (0.9–14) [38], in the background of a whole series of salts, in the presence of polyvalent cations, or in solutions of acids [39, 40]. By the method of polarization curves, it was shown [41–43] that, in sulfuric acid solutions, the rate of reduction of As(+5) depends on the nature of the material of the cathode, the current density, and the composition of the solution. The best results were obtained on cathodes of copper and lead. The products of the reduction, as was suggested, are AsH<sub>3</sub> and As.

The published data mentioned above confirm the low electrochemical activity of arsenate ions, which is determined [12] by kinetic difficulties appearing at the discharge of anions of  $XO_4^{n-}$  type of tetrahedric and octahedric structure on the negatively charged surface of the cathode. On the other hand, in strong acidic media, when there are molecules of arsenic acid in the solution, reduction is possible. There are suggestions on the influence of complexation. So, on the polarogram of  $Na_2HAsO_4$  in 1–3 M HClO<sub>4</sub> in the presence of 0.5 M pyrogallol, three waves are observed [44], corresponding to the reduction by Scheme (1). In [45], the precipitation of elemental arsenic on the cathode at electrolysis of acidic aqueous and nonaqueous glycerol solutions containing As(+5) and citric acid was reported. In our opinion, in both cases, the reduction of the molecular form of  $H_3AsO_4$  takes place.

Although the isolation of arsine in electrolysis of sulfuric acid solutions containing trace amounts of arsenic acid was already mentioned in [46], before the start of our investigations on this topic, only one report [47] was known in which the reduction of As(+5) for preparative use was described. The maximum current yield of arsine (22%) was recorded on a lead cathode in a sulfuric acid solution of magnesium-ammonium arsenate with the addition of catalyst transporter of Ti(+3) salt. Owing to the low yield of arsine in the given conditions and the use of low current densities  $(<0.01 \text{ A/cm}^2)$  in such a version, the method could not be of practical use. However, the fact of high selectivity of the cathode process should be noted, since the formation of As(+3) was not recorded by investigators [47], and As(0) was present only in trace amounts.

In addition to the difficulties with the reduction of arsenate ions, as was mentioned above, the synthesis of arsine by the reduction of As(+5) remained practically uninvestigated, because at first glance it was consid-

**Table 3.** Forms of the presence of As(+5) in 1 M aqueous solutions [35]

pH value	pH≥12	8 < pH <11	рН 7	3 < pH < 6	pH < 2.0
Form As(+5)	AsO <sub>4</sub> <sup>3-</sup>	HAsO <sub>4</sub> <sup>2–</sup>	$HAsO_4^{2-}: H_2AsO_4^{-} = 1:1$	$H_2AsO_4^-$	H <sub>3</sub> AsO <sub>4</sub>

ered to be the most energy intensive, since it requires 8 F/mol of electricity:

$$H_3AsO_4 + 8H^+ + 8\bar{e} \longrightarrow AsH_3 + 4H_2O.$$
 (4)

The net energy expenses in electrolysis are mainly determined by the applied voltage to the cell, which is lower the higher the conductivity of the solution. Owing to the good conductivity of solutions of arsenic acid, there is no need to use background electrolytes. This fact attracted our attention, and the  $H_3AsO_4-H_2O$  system was studied in detail.

Electrochemical activity of As(+5) primarily depends on the state in which it exists in solution (see Table 3). We showed [48] that, in basic and neutral media, As(+5) does not reduce, and in strong acidic solutions (pH < 2), the effective reduction to arsine is observed on a whole series of metals. It can be concluded that nondissociated molecules of  $H_3AsO_4$  take part in the cathode process.

The feature of the process is that the main product of the reduction is arsine. Side products containing arsenic in various oxidation states hardly form in definite conditions. This can be explained by the fact that, for the reduction of arsenic acid, a more negative potential is required than for the reduction of elemental and especially trivalent arsenic.

We studied [33] the influence of basic parameters of the electrolysis on the yield of arsine. It is unexpected that the yield of arsine is low on lead. Consequently, the value of hydrogen overvoltage on the cathode material does not play the decisive role in the formation of arsine from arsenic acid. The formation of the elemental arsenic was also studied, since it is capable of accumulating in the catholyte, preventing its circulation. It was determined that the liberation of arsenic takes place only at the very beginning of electrolysis; at long operation, its yield does not exceed 0.5%.

The aforementioned method of synthesis of arsine is patented [49]. With the use of this method, we also devised the physicochemical bases of technology of complex processing of arsenic-containing wastes of the industry of nonferrous metals [50]. The feature of the process is that the solution after sulfuric acid leaching of waste is injected into the anode chamber of electrolyzer, where As(+3) is oxidized, and then to the cathode chamber, where obtained As(+5) reduces to arsine. The process was checked at a pilot plant at a load of 120 A.

In order to study the possibility of using this method of arsine synthesis in an industry version, we devised a prototype of an electrochemical generator (Fig. 4) and a series of experiments were performed on the determination of the stability of its operation. The construction of the generator specifying the dosing of liquid reagent seems to be the most convenient.

The basis of the generator is a filter-press electrolyzer. The circulation of the catholyte and anolyte is performed by the gas lift principle by the liberating gases. To compensate the expense of  $H_3AsO_4$ , the concentrated acid is continuously injected into the catholyte. The catholyte level is regulated automatically with an equalizing line. Precipitating on the lower part of the buffer volume, arsenic is added periodically (once every 3-4 days) to the anolyte, where it is oxidized to  $H_3AsO_4$ . Gas coming out  $(AsH_3 + H_2)$  is liberated from the main amount of water in a reverse condenser. The ultimate drying is performed in a cryofilter at  $-60^{\circ}C$ .

In the first two series, experiments lasting for 3-4 h were performed every day and synthesized arsine was decomposed in a quartz tube, heated to  $750^{\circ}$ C, to arsenic; in the third set, the last experiment was carried out in the continuous mode for 38 h, and arsine was collected into a trap, cooled by liquid nitrogen. These investigations showed the high stability of operation of the generator (Fig. 5).

We performed a study of the behavior of admixtures during the synthesis using technical grade 81% arsenic acid [51]. From the comparison of the data (Table 4), it is concluded that Ge and Sb admixtures reduce to hydrides and transfer to arsine during electrolysis, and other admixtures concentrate in the catholyte. The high content of Al, Ca, Si, Fe, and Ni admixtures in arsenic, synthesized by arsine pyrolysis, probably is determined by the sample preparation of samples for atomic emission analysis. The admixtures of B, N, Si, P, and S in the conditions of the synthesis do not form volatile hydrides.

The obtained arsine was subjected to the refinement by low-temperature rectification, and the content of germane in arsine was reduced to a value lower than the detection limit ( $10^{-3}$  vol %) of known methods (gas chromatography and IR Fourier spectroscopy). The most sensitive method for the detection of electrically active admixtures is the method of functional control. With this aim, from the synthesized arsine, layers of gallium arsenide were grown by the MOCVD method. According to their electrophysical parameters, it was determined that the obtained GaAs had quite a low level of legation (concentration of carriers is  $7 \times 10^{14}$  cm<sup>-3</sup>), which confirms the satisfactory quality of the arsine purification.

Analysis of the presented material on arsine electrosynthesis and its practical application makes it possible to make the following generalization:

Electrochemical reduction of the  $\alpha$ -modification of arsenic with the goal to synthesize arsine has practical application at the present time. However, the casting of the cathode from high-purity metallic arsenic is a difficult technical problem and the use of electrodes that are consumed leads to the necessity of replacement of the entire electrochemical node.

The conditions of electrolysis of aqueous solutions of As(+3) were described that make it possible to obtain arsine with high current yields, but in testing of the pilot plant, the stable yield on the order of 60% was achieved. The main drawback of this method is the



**Fig. 4.** Scheme of arsine generator based on the reduction of arsenic acid: (1) electrolyzer; (2) Nafion cation exchange membrane; (3, 6) gas removers; (4, 7) condenser; (5) buffer capacity for catholyte; (8) container with initial  $H_3AsO_4$ ; (9) dosing pump; (10) leveling line; (11) reverse condenser; (12) cryofilter.

accumulation of ultrafine arsenic, which determines the necessity of periodic refinement.

Results of the study of the electrode behavior of As(+5) compounds make it possible to conclude the impossibility of cathode reduction of arsenate ions in basic and neutral media. In a strong acidic medium, the reduction of arsenic acid proceeds with high effectiveness.

We developed and tested an arsine generator based on the reduction of arsenic acid. The stability of operation at high yields of arsine was shown, nearly 90% by current and 99% by the compound. An evaluation of the behavior of admixtures during synthesis was performed. Ge and Sb admixtures transfer to arsine during electrolysis, and others concentrate on the catholyte. The purification of synthesized arsine by low temperature rectification provides the synthesis of a product of high purity, suitable for the preparation of  $A^{III}B^{V}$  films by MOCVD. The obtained results can serve as a basis for the construction of an industrial generator.

#### 2. ELECTROCHEMICAL METHODS OF PHOSPHINE SYNTHESIS

Data on the electrochemistry of the phosphorus are systemized in [52]. Phosphorus exists in three modifications: white, red, and black. There are data on the formation of the phosphine under electrochemical reduction of all three modifications. The data on the reduction of phosphorus and hypophosphorous acid are of great interest.

In most works on **electrochemical synthesis of phosphine from white phosphorus**, molten phosphorus was used. Different electrode materials were used in the electrolysis of the emulsion of the phosphorus (Table 5). The nature of the acid used as an electrolyte hardly affects the yield of phosphine. The increase in the current



**Fig. 5.** Tests of arsine generator in series of experiments. Cathode is Cu (50 cm<sup>2</sup>), anode is Pt (32 cm<sup>2</sup>), membrane is Nafion-450, and cathode current density is  $0.1 \text{ A/cm}^2$  (series 1),  $0.3-0.4 \text{ A/cm}^2$  (series 2),  $0.5 \text{ A/cm}^2$  (series 3).

density and temperature acts well [53]. To carry out a prolonged electrolysis, it is recommended [54] to add soluble salts of zinc to the electrolyte.

The data [55] on the kinetics of the isolation of phosphine are of great interest during exhausting electrolysis (Fig. 6). Initially, the reduction of  $P_4$  proceeds



**Fig. 6.** Formation of gaseous products in electrolysis of emulsion of white phosphorus [55]. Current yield of (1) phosphine and (2) hydrogen. Composition of catholyte: 1% P<sub>4</sub> in solution of 12% CH<sub>3</sub>COOH, 0.6% CH<sub>3</sub>COONa. Anolyte is 50% CH<sub>3</sub>COONa. Temperature is 45°C, and current density is 0.03 A/cm<sup>2</sup>.

without the formation of phosphine, then the content of the latter in the liberating gases increases, and the net current yield of products of the electrolysis substantially exceeds 100%. Then, the rapid growth of the yield of  $PH_3$  is observed. After the maximum, the formation of phosphine rapidly decreases, and the yield

Table 4. Behavior of admixtures in electrosynthesis from technical  $H_3AsO_4$ . Cathode is Cu, anode is Pt, and the quantity of electricity is 712 A h

	Weight fraction of element, %									
Determined elements	Initial 81%	And	lyte	Cath	As, synthesized					
	H <sub>3</sub> AsO <sub>4</sub>	initial	final	initial	final	by pyrolysis of AsH <sub>3</sub>				
Ge	$9.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	$7.0 \times 10^{-3}$	$3.0 \times 10^{-3}$	$8.0 \times 10^{-4}$	$2.0 \times 10^{-1}$				
Sb	$1.8  imes 10^{-2}$	$8.5 \times 10^{-3}$	$1.5  imes 10^{-2}$	$6.0 \times 10^{-2}$	$3.0 \times 10^{-3}$	$3.9  imes 10^{-2}$				
Ga	$5.0 \times 10^{-2}$	$5.7 \times 10^{-2}$	$5.7 \times 10^{-2}$	$1.7  imes 10^{-2}$	$9.0 \times 10^{-2}$	absent				
In	$1.5 \times 10^{-3}$	$1.6 \times 10^{-3}$	$1.2 \times 10^{-3}$	$5.0 \times 10^{-4}$	$1.2 \times 10^{-3}$	absent				
В	$1.5 \times 10^{-3}$	$2.0 \times 10^{-3}$	$1.5 \times 10^{-3}$	$5.0 \times 10^{-4}$	$1.7 \times 10^{-3}$	absent				
Pb	$5.0 \times 10^{-4}$	$6.0 \times 10^{-4}$	absent	$2.0 \times 10^{-4}$	$1.0 \times 10^{-3}$	absent				
Cr	$4.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	$1.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	absent				
Sn	$3.0 \times 10^{-4}$	$9.0 \times 10^{-4}$	$9.0 \times 10^{-4}$	$1.0 \times 10^{-4}$	$3.0 \times 10^{-4}$	absent				
Zn	$6.5 \times 10^{-3}$	$6.0 \times 10^{-3}$	$5.0 \times 10^{-3}$	$2.2 \times 10^{-3}$	$1.4 \times 10^{-3}$	absent				
Al	$2.0 \times 10^{-3}$	$2.7 \times 10^{-3}$	$1.6 \times 10^{-3}$	$7.0  imes 10^{-4}$	$2.0 \times 10^{-3}$	$4.0 \times 10^{-2}$				
Ca	$2.0 \times 10^{-3}$	$6.0 \times 10^{-3}$	$2.0 \times 10^{-3}$	$7.0 \times 10^{-4}$	$7.0 \times 10^{-3}$	$7.8  imes 10^{-2}$				
Mg	$3.0 \times 10^{-4}$	$5.6 \times 10^{-3}$	$1.5 \times 10^{-3}$	$1.0 \times 10^{-4}$	$6.0 \times 10^{-3}$	$3.0 \times 10^{-3}$				
Ni	$8.0 \times 10^{-4}$	$7.0  imes 10^{-4}$	$6.0 \times 10^{-4}$	$3.0 \times 10^{-4}$	$6.0 \times 10^{-4}$	$1.4 \times 10^{-2}$				
Fe	$9.0 \times 10^{-3}$	$6.8 \times 10^{-3}$	$1.6 \times 10^{-2}$	$3.0 \times 10^{-3}$	$7.0 \times 10^{-3}$	$3.3 \times 10^{-2}$				
Mn	$3.0 \times 10^{-4}$	$5.0 \times 10^{-4}$	$3.0 \times 10^{-4}$	$1.0 \times 10^{-4}$	$7.0 \times 10^{-4}$	$9.0  imes 10^{-4}$				
Cu	$2.0 \times 10^{-4}$	$2.1  imes 10^{-1}$	$2.0 \times 10^{-3}$	$7.0 \times 10^{-5}$	$7.0 \times 10^{-5}$	$1.0 \times 10^{-3}$				
Si	absent	$3.7 \times 10^{-3}$	$9.0  imes 10^{-4}$	absent	$9.0 \times 10^{-4}$	$1.4 \times 10^{-1}$				

**Table 5.** Influence of the material of the cathode on the yield of phosphine from white phosphorus. Catholyte is 40% H<sub>2</sub>SO<sub>4</sub>, the current density is 0.025 A/cm<sup>2</sup>, and the temperature is  $65^{\circ}$ C [53]

Cathode material	Zn*	Hg	graphite	Cd	Pb	Fe	Sn	Cu	Ti
Current yield of PH <sub>3</sub>	57.0	37.4	19.4	13.0	9.8	8.9	1.8	1.8	Traces

\* Catholyte is 40% H<sub>3</sub>PO<sub>4</sub>.

of hydrogen approaches 100%, which confirms the depletion of phosphorus and the end of electrode reactions related to its reduction. It is suggested [55] that the initial step is the addition of four electrons and protons to the  $P_4$  molecule with the formation of hypothetical  $P_4H_4$  hydride, which reduces to  $PH_3$  step by step:



The method of reduction of molten white phosphorus is described in patent literature in detail. For the first time, the possibility of phosphine synthesis by an electrochemical method is mentioned in [56]; however, no example is given. Systematic work on the reduction of white phosphorus started only in the 1960s at Hooker Chemical Corp. A series of patents were given in the United States [57–70], England [71–74], and Federal Republic of Germany [75–77]. Differ-

ent versions of constructions of electrolyzers for the synthesis of phosphine are proposed. Mainly, the process of reduction of phosphorus in aqueous solutions of acids is considered. The methods of phosphine synthesis can be classified by the type of apparatus used.

—*Reduction by electrochemically generated amalgam [61, 64, 71].* The electrolyzer (Fig. 7) consists of a glass with an immersed glass cylinder with the bottom made from porous glass, on which mercury and liquid phosphorus layers are stirred slowly. During electrolysis, zinc [61, 71] or sodium [64] ions, passing through the porous glass, form amalgam, which decomposes in the internal cylinder in the acid solution, reducing phosphorus at that time, for example, by reaction (6). The use of both a soluble anode (Zn) and an insoluble anode is possible:

$$P_4 + 6Zn + 12H_3PO_4 \longrightarrow 4PH_3 + 6Zn(H_2PO_4)_2$$
. (6)

—*Reduction on a liquid cathode [58, 59, 69, 71, 75, 77].* The electrolyzer (Fig. 8) is similar to the one above in construction, but the mercury is poured on the bottom of the glass. On the surface of the mercury, there is a layer of



Fig. 7. Electrolyzer with zinc amalgam: (1) material of electrolyzer, (2) container for the reduction of  $P_4$  by amalgam, (3) porous glass, (4) mercury cathode, (5) zinc anode, (6) white phosphorus, (7) electrolyte (ZnSO<sub>4</sub> solution), (8) acid solution, (9) stirrer, (10) current inlet of cathode.



**Fig. 8.** Bag electrolyzer with liquid cathode: (1) material of electrolyzer, (2) container for anolyte, (3) porous glass, (4) liquid cathode, (5) anode, (6) phosphorus, (7) anolyte, (8) catholyte, (9) stirrer, (10) current inlet of cathode.

SYNTHESIS OF VOLATILE INORGANIC HYDRIDES

phosphorus. It is recommended to carry out the electrolysis in 1-2 M H<sub>3</sub>PO<sub>4</sub> at 0.0087 A/cm<sup>2</sup> and 65–70°C. The content of PH<sub>3</sub> in the cathode gas is 81.4% at the production of 0.239 g/h; the expense of electrical energy is 88 kWh/kg PH<sub>3</sub> [71]. As the liquid cathode, Wood alloy can be used [65].

-Reduction on a solid cathode in the bag electro*lyzer* [57, 60, 64, 68-77]. Since the application of a liquid cathode is connected with a set of technological difficulties, it is within reason to carry out electrolysis with the use of a solid cathode (Fig. 9). As the cathode material, usually lead is used. The catholyte and anolyte are usually a solution of phosphoric acid. It is noted that, during the electrolysis, the phosphorus starts to wet the surface of the cathode and come up under the effect of surface tension [57, 64, 69, 71, 73, 77]. After one day of electrolysis, the entire cathode is coated with a phosphorus layer and the current yield of phosphine reaches 90%. In the process, hydrides of  $P_4H_4$  type and phosphate polymers, coating the cathode and bag and preventing the passage of current, are formed. It is proposed to cover the bag from the side of the cathode by a material not wetted by the phosphorus: fiberglass, polyethylene, or polyurethane [69, 72, 75]. In order to reduce the viscosity and the coating of the phosphorus, it is recommended to blow hydrogen, hydrogen sulfide [76], or part of the cathode gas through its layer [68, 74]. The other difficulty is the collection on the cathode of a layer of porous precipitate by the disintegration of the material of the cathode or the precipitation of metals used for enhancing the characteristics of the process [58, 60]. The precipitate forming on the cathode leads to the decrease in the yield of phosphine. To decrease the shielding of the cathode by the phosphorus and to increase the longevity of its use, it is recommended to use a cathode with ribbing, forming acute sides [67, 70, 77].

-Reduction in a bag-free electrolyzer. The electrolvsis is conducted with the use of an easily oxidizable anode (Fig. 10), for which graphite is suggested [65]. According to the claim of the authors, oxygen does not form on it; the main product is  $CO_2$  with the admixture of CO.

In Table 6, the data on the phosphine electrosynthesis modes are systemized. The most frequently, concentrated  $H_3PO_4$  serves as the electrolyte, and Hg, Pb, and Zn, i.e., materials with high hydrogen overvoltage, serve as the cathode. Recommended materials for the bag are alundum, porous glass, and porcelain. In most cases, the electrolysis is conducted at 80-85°C and low current density (<0.03 A/cm<sup>2</sup>). Under these conditions, the current yield of phosphine is 80-95%. With the decrease in the temperature, the effectiveness of the phosphorus reduction decreases, although the phosphorus remains liquid. The drawback of the method is the danger of working with white phosphorus, which is capable of spontaneous combustion in air at a temperature of  $>34^{\circ}$ C.



Fig. 9. Bag electrolyzer with solid cathode: (1) material of electrolyzer, (2) ceramic bag, (3) cathode, (4) layer of liquid phosphorus, (5) anode, (6) catholyte, (7) anolyte.

White phosphorus for the synthesis of phosphine can be used not only as a melt but also in the form of a solution in a polar organic solvent, particularly, in ethanol [78]. On the cathode area of the electrolyzer supplied with a lead cathode, one part of alcohol preliminarily saturated with phosphorus and two parts of



Fig. 10. Bag-free electrolyzer with liquid cathode: (1) material of electrolyzer, (2) degradable anode, (3) liquid cathode, (4) layer of white phosphorus, (5) electrolyte, (6) stirrer, (7) current inlet of the cathode.

Electrolyzer			Catholyte	Condi	tions of electro	Content	Deference	
cathode	anode	bag	Catholyte	$I, A/cm^2$	<i>U</i> , B	t, °C	of $PH_3$ , vol %	Reference
Hg	graphite	porous glass	20% HCl	3.0	4.5	85	66.5	[66]
		absent		3.0	10.2		40.6	[65]
	Pb	alundum	80% H <sub>3</sub> PO <sub>4</sub>	5.0	5.3	77	85.5	[64]
	Pt	porous glass	$1-2 \text{ M H}_3\text{PO}_4$	(0.005-0.03)	26.5	80	81.4	[59]
Hg-Bi			$2 \text{ M H}_2 \text{SO}_4$		_		18	
Hg–Cr					_		60	
Hg–Zn			$4 \mathrm{M} \mathrm{H}_{3} \mathrm{PO}_{4}$		_		79	
			$1-2 \text{ M H}_3\text{PO}_4$	(0.0064)	2.9		13.6	
Pb		ceramic	40% H <sub>3</sub> PO <sub>4</sub>	(0.026)	_	85	90—95	[67]
	graphite	alundum	10% HCl	4.6	_	95	96	[75]
Zn	Fe	porous glass	4 M H <sub>3</sub> PO <sub>4</sub>	(0.03)	_	_	83.1	[59, 71]
Wood alloy	graphite	porous glass	40% H <sub>3</sub> PO <sub>4</sub>	1.5	8.0	85	95	[64]
		alundum	saturated NaCl	1.0	18	80	50	[57]

 Table 6. Electrosynthesis of phosphine from liquid white phosphorus

**Table 7.** Electrosynthesis of phosphine in nonaqueous solutions of  $P_4$  at  $20-25^{\circ}C$  in an electrolyzer with cation exchange membrane. Cathode is Pb and anode is graphite

Initial composition of catholyte and anolyte		Current density $\Delta/cm^2$	Voltage V	Current vield of PH. %	
alcohol	electrolyte	Current density, 74 cm	voltage, v	Current yield of 1 113, 70	
C <sub>2</sub> H <sub>5</sub> OH	$1 \text{ M} (\text{C}_2\text{H}_5)_4\text{NCl}$	0.1	17-18	31.9 (12.1*)	
	1.7–2 M HCl	0.01	3.3-3.4	40.4	
		0.05	6.5-6.7	60.5	
		0.1	12-13	57.1	
	$1.7-2 \text{ M} n-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01	4.5-6.0	80.7	
		0.05	1226	74.4	
	$1.8 \text{ M} \alpha$ - $C_{10}H_7SO_3H$	0.05	17-20	57	
CH <sub>3</sub> OC <sub>2</sub> H <sub>4</sub> OH	2.0 M HC1	0.01	4.3-4.5	54.6	
		0.05	9-12	45.0	
	2.0 M <i>n</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> H	0.01	5-8	89.3	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OH	3.5 M HCl	0.05	30→60	72.4	
CH <sub>3</sub> OH	$1.8-2 \text{ M} n-\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$	0.01	2.7-3.2	64.9	
		0.05	8.5→25	45.8	

\* Cathode is copper.

 $H_3PO_4$  are loaded. The electrolysis is conducted by a current of 0.2 A at a voltage of 46.5 V and a temperature of 65°C. The concentration of phosphine in the cathode gas is 42.5% (the calculated current yield is 52.6%).

In order to decrease the fire hazard of the process, it should be conducted at a lower temperature. We showed [79] that, with the use of a phosphorus suspension in water-free alcohol, a substantially better result can be achieved even at room temperature. The experiments were conducted in an electrolyzer with a cation exchange membrane and lead cathode. The current yield increases in the following series of alcohols: methanol > methylcellosolve  $\approx$  ethanol > benzyl alcohol and electrolytes: H<sub>2</sub>SO<sub>4</sub> > HCl > *n*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H. The increase in the yield compared to [78] probably is due to the constant saturation of the solution by the phosphorus during electrolysis and also its higher solubility in water-free alcohols. The increase in the yield with the transfer from methyl to benzyl alcohol and in the aforementioned order of electrolytes can be explained by the increase in the solubility. During these investigations, we obtained new data (Table 7).

 Table 8. Influence of pH on the yield of phosphine on cathode from black phosphorus [83]

pH of catolyte	1.0	4.7	6.8	7.5	9.0	14.0
Current yield PH <sub>3</sub> , %	1.2	3.5	6.1	12.5	7.0	5.4

The possibility of phosphine synthesis in an electrolyzer without a bag was shown. So, in the solution of HCl in  $C_6H_5CH_2OH$ , the current yield of PH<sub>3</sub> is 62%, but half of the phosphorus transfers to phosphoric acid esters [79].

It should be noted that, with the use of solutions of white phosphorus, the above-mentioned problem of cutting-off of the cathode is absent.

The other possibility of reducing the fire hazard of the process via its conduction at room temperature is the suggestion in [80] to use a pseudocompressed cathode, the grains of which are molded from a mass containing 150 g of carbon soot and a solution of 30 g of  $P_4$  in 20 g of  $CS_2$ . After the evaporation of carbon sulfide, the grains are dispergated in the cathode chamber of the bag electrolyzer in a solution of 3 M  $H_3PO_4$ . Probably, it is assumed that, with the larger surface of the cathode, an enhanced effectiveness of the process should be anticipated; however, the yield of phosphine is not indicated.

Thus, the use of a solution of white phosphorus in an organic solvent makes it possible to achieve a high yield of phosphine (up to 90%) with maintenance of fire safety, and this process can be laid on the basis of development of an electrochemical generator of phosphine. It should be noted that white phosphorus in the form of a melt can be easily dosed.

The most obvious way to increase safety is the use of **red phosphorus** as an initial raw material for the electrochemical synthesis of phosphine. The attempts at electrochemical reduction of red phosphorus in aqueous solutions of acids did not end successfully. It is reported [81] that, in electrolysis of a suspension of red phosphorus in 15-20% NaOH at  $70-100^{\circ}$ C on a lead cathode, the yield of phosphine by the substance is 83%. The variation of current density from 0.01 to 0.15 A/cm<sup>2</sup> has little effect on the yield. Our calculations by the data of [81] show that the volume of the cathode gas corresponds to the formed hydrogen, and the phosphine, probably, forms by the following reaction:

$$4P + 3NaOH + 3H_2O \longrightarrow PH_3 + 3NaH_2PO_2.$$
 (7)

The possible use of a suspension of red phosphorus in contact with the current from a metal with high hydrogen overvoltage for the synthesis of phosphine is mentioned in [19]. In the authors' opinion, it is possible to produce a cathode from a sintered mixture of fine powders of a weakly conducting element (probably phosphorus) and a well-conducting material, alloy, or solid solution of a hydrogenated element (also phosphorus) and such metals as Cd, Pb, Hg, and Zn. In the case of phosphorus, the formation of a wellconducting material is doubtful.

We have carried out a systematic investigation [82] of the possibility of the electrochemical synthesis of phosphine from red phosphorus. It was shown that, during electrolysis of its suspension in alkali conditions, phosphine is formed with the formal current yield at 3-8%. And in the solution, hypophosphite and phosphate ions are detected. The current yield of hydrogen approaches 100%. Irradiation by ultrasound increases the rate of the reaction of the suspension of the phosphorus with the base, but does not enhance the effectiveness of the electrolysis. In order to provide maximum contact of the phosphorus particles with the surface of the cathode, a series of experiments were performed with cathodes pressed from a mixture of red phosphorus and graphitized soot. As a result, in the solution, the amount of hypophosphite corresponding to formed phosphine was detected. The obtained results confirm that red phosphorus does not have any electrochemical activity and phosphine forms by reaction (7), which is accelerated owing to the local increase in the base concentration in the near-electrode layer of the solution.

As a cathode material, **black phosphorus** can be used, having electrical conductivity. The investigation of polarization of an electrode made from the black phosphorus showed that it is related to materials having low hydrogen overvoltage [83]. In electrolysis at the current density of  $0.03-0.07 \text{ A/cm}^2$ , phosphine is liberated, the yield of which depends substantially on the pH of the medium (Table 8).

In [19, 20, 23], the construction of an electrolyzer for the synthesis of volatile hydrides is described (see Fig. 1). For the synthesis of phosphine, it is recommended that the cathode be constructed from grains of black phosphorus [20]. There is a report of the possibility of using a suspension from powder of black phosphorus [19]. Quantitative data are given only in [23]. In a solution of 35% KOH at a current of 1-1.2 A and 0.15-0.2 A on a whole cathode made from black phosphorus (>99%) with an area of 2.8 cm<sup>2</sup>, phosphine was liberated at the rate of 2.0 and 0.3 mg/min, respectively. The current yield calculated by this data is 21-28%.

In order to study the effectiveness of electrochemical synthesis of phosphine from black phosphorus, we carried out a series of experiments in an electrolyzer with a Naflon cation exchange membrane. The electrodes were prepared by pressing at 200 atm of a powder of black phosphorus without and with the addition of 5% polyvinyldifluoride as a binder. The catholyte was 10% KH<sub>2</sub>PO<sub>4</sub>. Phosphine was obtained with an 8– 10% current yield; however, the cathode was destroyed in operation of more than 2 h with the current density of 0.1 A/cm<sup>2</sup>.

The use of an electrode from black phosphorus in an phosphine generator has the same drawbacks as the use of an arsenic electrode in an arsine generator: the high cost of the preparation with the impossibility of full use; partial dispergation of the cathode material, owing to which the accumulation of waste in the apparatus takes place; and the necessity of periodic replacement of the electrodes.

**Oxygen-containing acids of phosphorus** are a potential raw material of phosphine synthesis. The calculations by the standard potentials of the reduction of  $H_3PO_2$  (-0.174 V) and  $H_3PO_3$  (-0.282 V) [52] show the fundamental possibility of phosphine preparation by electrochemical reduction of those acids. From the point of view of minimal expenses of electrical energy on the synthesis of phosphine, the most rational is the use of hypophosphorous acid. For its reduction to phosphine, 4 F/mol is sufficient.

The experiments on the reduction of phosphorous acid on a mercury cathode showed that the main product is the  $H_3PO_2$  [84]. Hypophosphite ion in glycerol on the background of  $(C_2H_3)_4NClO_4$  reduces at the potential of minus 0.64 V [85]. Phosphine probably does not form in the given conditions since less than 1 F/mol is expensed on its reduction.

The possibility of phosphine synthesis by electrochemical reduction of hypophosphite ions is noted [19]. The formation of phosphine is noted in the reduction of phosphorous acid on cathodes from Pb, Zn, and Hg [86]. It is mentioned that lead and zinc rapidly lose their activity and the yield of the phosphine decreases. On mercury, according to the claim of the authors, phosphine forms with a high yield, but its value is not indicated. Sodium hypophosphite does not reduce in the same conditions. The absence of quantitative data makes it possible to conclude that the yield of phosphine is not satisfactory.

Hypophosphorous acid  $H_3PO_2$  exists in two tautomeric forms (8), having pentavalent or trivalent phosphorus, the first of which is inactive [87]. In usual conditions, the equilibrium is almost completely shifted to the left, owing to which  $H_3PO_2$  is titrated as monobasic:

$$HO - P = O \iff HO - P - OH.$$
(8)

We studied the reduction of hypophosphorous and phosphorous acids on mercury and lead cathodes, and also on potassium and lithium amalgams [88]. It was shown that these acids are classified as hardly reduced substances. The current yield of phosphine on a mercury cathode does not exceed 2.5%. The method of indirect reduction on the amalgams did not show a better result. On lead, the yield of phosphine increases in the presence of sulfuric acid and in a solution of polyethyleneglycol (up to 5.5%), i.e., in conditions promoting the decrease in dissociation of the acid. Probably,  $H_3PO_2$  molecules undergo reduction in the active form.

Evaluating the modern state of the given data on electrochemical synthesis of phosphine, four main ways of investigations should be selected.

The most studied and technologically developed is the process of reduction of white phosphorus. The drawback of the process is the danger of working with white phosphorus, which is capable of spontaneous combustion in air. High current yields of phosphine (up to 90%) are achieved in a solution of phosphoric acid at  $80-90^{\circ}$ C. With the decrease in the temperature, the effectiveness of the reduction of liquid phosphorus decreases. The fire safety of the process with the conservation of a high yield is achieved at room temperature by carrying out the electrolysis of a white phosphorus solution in an organic solvent.

Red phosphorus, owing to its safety and low toxicity, is considered to be the most convenient initial raw material for the electrosynthesis of phosphine. However, upon a detailed observation, it was determined that red phosphorus is electrochemically inactive. The formation of phosphine is determined by the chemical reaction of the phosphorus with the base. The role of the electrolysis results in its concentration at the cathode surface.

The results obtained in the reduction of black phosphorus can be considered preliminary. Its advantage is electron conductivity, i.e., electrodes can be fabricated from it. But owing to the strict conditions of synthesis of black phosphorus and its commercial unavailability at the present time, the application of this raw material for the electrosynthesis of phosphine has great difficulties. With allowance for the necessity of periodic replacement of an electrode made from black phosphorus, the economic profit of its use in a phosphine generator should be evaluated.

Hypophosphorous and phosphorous acids are classified as hardly reducible substances. Their electrochemical reduction proceeds with low current yields. The yield increases in conditions promoting the suppression of dissociation of the acids. The most likely is that nondissociated molecules in the active form are subjected to reduction, where the phosphorus is trivalent. In order to increase the yield of phosphine, the conditions for increasing the concentration of an active form should be studied.

### 3. ELECTROCHEMICAL METHODS OF GERMANE SYNTHESIS

Germanium forms hydrides of  $Ge_nH_{(2n+2)}$  composition and also  $GeH_2$ ,  $(GeH_2)_x$ , GeH, and  $(GeH)_x$ . Monogermane (or germane)  $GeH_4$  at the present time

is obtained by the reduction of Ge(+4) compounds by borhydrides of alkali metals [3].

**Metallic germanium** is related to materials with high hydrogen overvoltage, close to that of zinc and cadmium [89]. The data on electrochemical reduction of germanium are not numerous. The application of cathode etching of germanium at 155 A/cm<sup>2</sup> in the flux of the electrolyte [90] is well known. The formation of germane is qualitatively determined. At a current density of <15 A/cm<sup>2</sup>, the etching of germane is not observed.

In [19–23], the construction of a generator of volatile hydrides is described (see Fig. 1), including germane with the use of a cathode made from the metallic germanium in an alkali electrolyte. It is recommended [19, 21] to maintain the potential of the cathode at the level of minus 2V compared to a calomel comparison electrode (c.c.e.). In [23], the data on the effectiveness of the generator with respect to germane are given (up to 0.5 mg/min) at various currents. The current yield hardly depends on the current density (Table 9).

We determined [91] that the reduction of germanium proceeds ineffectively, regardless of the composition of the medium and the current density. The attempt to reproduce the data [23] did not end successfully (see Table 9).

A generator of germane based on the reduction of germanium has the drawbacks, mentioned earlier, related to the replacement of the consumed cathode.

There are no reports in the literature about the possibility of germane formation from Ge(+2) compounds. The polarographic behavior of germanium compounds was studied [92–95]. In a hydrochloric acid solution, Ge(+2) irreversibly reduces on a mercury drop electrode to the metal [92].

In acidic solutions at pH < 3.1, Ge(+4) is not detected on the polarogram of reduction; at pH 3.7-10.6, two waves of the reduction are obtained; at pH > 10.6, one is obtained [92, 93]. These phenomena are explained by the presence of various types of germanium acids dependent on the pH of the solution: pentagermanic at pH < 4; equivalent mixture of pentagermanic acid and monomer at pH 4-5, reducing at different potentials. At a further increase in pH, all of the pentamer dissociates, and in the solution bigermanate ions appear, reducing at more negative potentials than molecules of germanic acid. On the polarogram in these limits of pH, also two waves are observed. At pH > 10.6, all Ge(+4) is present as anions and gives one wave of the reduction, corresponding to the discharge of bigermanate ions.  $GeO_3^{2-}$  ion, in the authors' opinion [93], does not discharge on the mercury at potentials more negative than the potential of the hydrogen liberation in those solutions.

However, in acidic solutions on cathodes with high hydrogen overvoltage, germane is recorded in the presence of Ge(+4) in the solution [89, 95]. So,  $GeH_4$  is obtained on a lead cathode in electrolysis of 1.5 g

 Table 9. Reduction of metallic germanium in aqueous solutions

Catholyte	Current den- sity, A/cm <sup>2</sup>	Current yield, GeH <sub>4</sub> , %	Reference
1 M NaOH	-2 B*	30	[19, 21]
10% NaOH	0.05 - 0.5	<0.96	[91]
$10\% \text{ H}_2\text{SO}_4$	0.05 - 0.5	< 0.33	
35% KOH	0.054-0.43	3.4-4.4**	[23]
	0.07 - 1.0	<0.8	Our data

\* The potential of the cathode is minus 2V compared to c.c.e.

\*\* Calculated by data of [23].

 $GeO_2$  in 200 ml of 40%  $H_2SO_4$ , but the yield is not mentioned [96].

Germanium dioxide has weak acidic properties and forms germanates with bases. According to [95], in water—basic solutions,  $\text{GeO}_2$  dissolves with transfer to the anionic form of  $\text{GeO}_3^{2-}$ . The electrolysis of aqueous solutions of germanates in order to obtain germane was studied by a series of investigators [97–99]. On the whole, the process is described by the following equation:

$$\operatorname{GeO}_3^{2-} + 7\operatorname{H}_2\operatorname{O} + 8\overline{\operatorname{e}} \longrightarrow \operatorname{GeH}_4 + 10\operatorname{OH}^-.$$
 (9)

Since the proceeding of the eight-electron process in one step is unlikely, in [99-101] the scheme is considered according to which initially as a result of the addition of four electrons on the cathode germanium is liberated, which further reduces by liberation of atomic hydrogen to germane. However, such a process is not confirmed experimentally and, in our opinion, can hardly take place.

The most likely is the step-by-step scheme of the reduction of germanate, which is confirmed by the data of voltamperometric measurements [28]:

$$GeO_{3}^{2-} + 3H_{2}O \xrightarrow{+2\bar{e}} GeO \cdot H_{2}O_{adsorbed}$$
(10)  
$$\xrightarrow{+2\bar{e}} Ge_{adsorbed} \xrightarrow{+4\bar{e}} Ge_{adsorbed} \xrightarrow{+4\bar{e}} GeH_{4}.$$

Thus, in the reduction of basic solutions of germinates, it is possible to obtain two products, germanium and germane.

The influence of various factors on the process of reduction of Ge(+4) to germane in alkali electrolytes on a nickel cathode was studied [102]. Anode and cathode areas of the electrolyzer were divided by a bipolar membrane of brand MB-1 or cation exchange MK-40. It is recommended to carry out the electrosynthesis of germane at a current density of 0.6 A/cm<sup>2</sup> in a catholyte of 20 g/l GeO<sub>2</sub> and 2.5 mol/l NaOH composition. The yield of germane is 50–55%.

It should be noted that, owing to the restricted solubility of  $GeO_2$  in solutions of NaOH (maximum 100 g/l at 7% NaOH) [103], it is within reason to use potassium hydroxide to dissolve germanium dioxide.



**Fig. 11.** Apparatus for germane electrosynthesis [105]: (1) electrolyzer; (2) cathode chamber; (3) anode chamber; (4) bag; (5, 6) gas removers; (7, 8) bubblers; (9) feed container; (10) moisture condenser; (11) cryostat; (12) traps; (13) analytic ampoule; (14) water seal; (15) vacuum meter; (16) taps; (17) container with germanium dioxide; (18) balloon.

A matter of interest is the study of the dependence of the current yield of  $\text{GeH}_4$  in  $\text{GeO}_2$  in a 20% KOH solution on acopper electrode on the conditions of the electrolysis [104]. At 8 A/cm<sup>2</sup>, the current yield increases to 31% with the increase in the concentration of  $\text{GeO}_2$  from 10 to 150 g/l. At the content of 10 g/l of  $\text{GeO}_2$ , the maximum current yield (5%) is recorded at 7 A/cm<sup>2</sup>.

The possibility of the synthesis of extremely pure germane by the electrochemical reduction of alkali solutions of  $\text{GeO}_2$  is considered [101]. It is proposed to carry out the process without a bag in an H-shaped apparatus. The influence of the material of the cathode on the yield of germane is studied (steel, copper, lead, nickel, tin). The highest yield is observed on Ni and Sn at 100–105°C and a current density of 1.3–1.4 A/cm<sup>2</sup>. Judging by the composition of the cathode gas, in these conditions, the current yield does not exceed 20%.

In [105], it is proposed to conduct electrolysis on a nickel cathode at a current density of  $1.0-1.5 \text{ A/cm}^2$ , temperature of 75–85°C, and concentration of GeO<sub>2</sub> of 25–35 g/l with repeated residence of the electrolyte in the cathode and anode area of an electrolyzer. Electrolyte from the cathode area after the liberation of germane and hydrogen is transferred back to the cathode area (Fig. 11). The current yield of germane also does not exceed 20%.

In [106], the authors clarified the modes of electrosynthesis: current density of 2-4 A/cm<sup>2</sup> and temperature of  $30-50^{\circ}$ C. In this case, the current yield of germane was 15% (at the concentration in the gas of 6 vol %). It is emphasized that, upon the reduction of

the current density or the temperature below those limits, the yield of germane decreases by a factor of two, and upon exceeding them, germanium is liberated; for this reason, the yield of germane decreases. It is mentioned [107] that, to achieve the maximum yield, the process should be carried out on a nickel cathode at 1.0-1.5 A/cm<sup>2</sup>, a temperature not higher than 65°C, and a content of GeO<sub>2</sub> of 50 g/l in a 2.5 M solution of KOH according to the scheme presented in Fig. 11. By the given example, the current yield can be calculated, which is 9.3%.

The results of experiments of the pilot plant for the synthesis of germane are presented in [28]. It is proposed to use a bipolar electrolyzer with electrodes made from nickel for the electrosynthesis of germane from basic solutions of  $GeO_2$ . It is noted, that with the increase in the current density from 0.1 to  $0.4 \text{ A/cm}^2$ , the yield of germane by the substance increases from 20.0 to 80.0%. The further increase in the current density leads to a small increase in the yield to 85% and a rapid decrease in the current yield. At current densities less than  $0.2 \,\text{A/cm}^2$ , the cathode is covered with a layer of elemental germanium, which at prolonged electrolysis leads to blockage of the electrode surface and stoppage of electrolysis. The optimal value is  $0.4-0.6 \text{ A/cm}^2$ , and the yield of germane is 85% by the substance and nearly 10% by the current. The side products are determined, digermane and trigermane, forming with the yields by the substance of 0.3 and 0.2%, respectively.

It should be noted that current densities recommended in [101, 104, 105, 107] exceed those usually used in technical electrolysis. As a result, the current

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yield of germane is quite low. Owing to the absence of data on the voltage on the electrolyzer, it is not possible to estimate the energy expenses of the electrolysis. On an industrial scale, this version can be expensive and have no commercial value.

Because of this fact, we carried out a systematic investigation of the influence of parameters of electrolysis on the yield of germane [91]. It was shown that, in the range of current densities of 0.3-0.6 A/cm<sup>2</sup> and content of GeO<sub>2</sub> of 165-250 g/l, the current yield of germane hardly changes, confirming the kinetic restrictions of the process. The increase in the temperature from 25 to 70°C increases the yield only by a small amount. The most important factor is the material of the cathode. The current yields of germane are >30% and are obtained on metals having high hydrogen overvoltage of liberation. But the difference is not as high as was anticipated. The leveling of the influence of the cathode material can be explained by the fact that mainly the formation of germane proceeds on the surface of the germanium precipitated on the cathode. The liberation of hydrogen proceeds both on the surface of a cathode coated with germanium and on one not coated. In the latter case, the process is limited by the value of the hydrogen overvoltage on the specific material of the cathode. The most effective cathode material is tin. In optimal conditions (3 M KOH,  $150 \text{ g/l GeO}_2$ , 0.3 A/cm<sup>2</sup>), germane is obtained with a current yield up to 44%. It should be noted that tin is capable of reduction to stannane and contaminating the product. As a result of long operation of an electrolyzer, the decrease in the current yield of germane takes place, the reason for which is probably the formation of a germanium coating on the cathode, featuring a developed surface, promoting the decrease in the real current density.

Thus, the analysis of the given data showed that the reduction of metallic germanium proceeds with a low yield, regardless of the composition of the medium and the current density, and Ge(+2) compounds are not stable and easily oxidize; therefore, their use as a raw material for the synthesis of germane is unsuitable. From compounds of Ge(+4), germanate ions in a basic medium are the most effectively subjected to reduction. The molecules of germanic acid reduce more difficultly, maybe owing to the formation of polynuclear complexes. Technologically developed is the version of electrolysis of basic solutions of  $GeO_2$ , but the data of different authors are contradictory. The current yield of germane depends little on the electrolvsis conditions, which confirms the kinetic restrictions of the reduction process of germanate ions. The most important factor is the material of the cathode. The current yield of germane reaches 40%, but under long operation of an electrolyzer, its reduction takes place. It is within reason to continue the systematic investigations of the given process.

# CONCLUSIONS

In the review, the modern state of the problem of electrochemical synthesis of arsenic, phosphorus, and germanium hydrides is elucidated. The whole analysis of the electrochemical reduction of elements and their compounds in various oxidation states is performed from the point of view of practical realization. The physicochemical bases of the electrochemical synthesis of hydrides are considered.

The main problems of the chemical synthesis of hydrides are the nonselectivity, the complexity of the control of the process, and the large amount of wastes. These drawbacks can be overcome with the use of electrochemical methods of synthesis.

In the realization of the concept of an electrochemical generator of hydrides, the most developed way is the simplest principle, electrochemical reduction of the material of the cathode, in the capacity of which conducting modifications of elements are applied, in particular, metallic arsenic, germanium, and black phosphorus. This universal construction can also be used for electrosynthesis of antimony, selenium, and tellurium hydrides. A generator with a consumable cathode and victim anode producing only cathode gas is proposed as a replacement for balloons with compressed gas. However, a device based on this principle is only for one-time use, which economically is not justified and is not always convenient for practical use.

In our opinion, the most effective is an individual approach based on the unique properties of each element. For the construction of both industrial and compact electrochemical generators, promising is a construction with a constant input of initial (preferably liquid) raw material. For the practical realization of this approach, we have devised the processes of synthesis:

—arsine from arsenic acid in a two-component system with a current yield up to 95%;

—phosphine by the reduction of white phosphorus in organic solvents at room temperature, which substantially decreases the flammability of the process, the phosphine being obtained with a current yield of 90%;

—germane from a basic solution of germanate, making it possible to synthesize germane with a current yield up to 40%.

Using the example of arsine, a continuous electrochemical generator of hydrides was produced, and technological tests of it were performed. This device, after equipping with a unit for final deep purification, can be applied directly in the complex flow charts of fabrication of semiconductor materials.

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