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Electrochemical Preparation of Germane

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Abstract—Germane has been prepared through the electrochemical reduction of the germanate anion in alkaline solutions with a current efficiency of 40–45%. Active solution circulation in the cathodic zone and the use of an Sn or Cd cathode are shown to raise the germane yield. The current density and initial solution concentration have a weak effect on the reduction process.

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INTRODUCTION

High-purity germane, GeH_4, is widely used in the fabrication of semiconductor materials for micro- and optoelectronics and IR applications. It is well documented [1–3] that the thermal decomposition of high-purity germane yields single-crystal germanium containing extremely low levels of harmful microimpurities (at a level of $n \times 10^{10}$ cm^{-3}), which is suitable for the fabrication of high-energy-resolution nuclear radiation detectors. The preparation of high-purity germane by the hydride process offers significant advantages over the conventional chloride route [4]. In this context, there is considerable interest in devising unconventional approaches for the preparation of germane, including electrochemical processes, which are also attractive for the synthesis of other inorganic hydrides (arsine and phosphine) and can be run at low temperatures and atmospheric pressure, i.e., are environmentally friendly [5, 6].

One way of producing crude germane to be used as a raw material for the preparation of a high-purity germane product is electrolysis of aqueous germanate solutions [7, 8]. The reduction of the germanate anion can be represented by the overall scheme

$$GeO_3^{2-} + 7H_2O + 8e^- \longrightarrow GeH_4 + 10\,OH^-$$

Since the transfer of eight electrons in one step is unlikely, Devyatykh et al. [7] assumed that the first step is the attachment of four electrons, resulting in the deposition of elemental germanium on the cathode. The germanium is then reduced to germane by the released atomic hydrogen. That assumption, however, has not been confirmed. Nilov [9] proposed the following scheme for the reduction of the germanate anion:

$$GeO_3^{2-} + 3H_2O \xrightarrow[-4OH]{+2e^-} -GeO \cdot H_2O_{ads} \xrightarrow[-2OH^-]{+2e^-} Ge_{ads}$$

$$\longrightarrow Ge_{ads}^{4-} \xrightarrow[-2OH^-]{+4H_2O} GeH_4,$$

which has been confirmed by current–voltage measurements and appears the most plausible.

Thus, the reduction of GeO_2 in alkaline solutions may yield two products: germane and elemental germanium.

Devyatykh et al. [7] examined the possibility of preparing high-purity germane via the electrochemical reduction of aqueous alkaline solutions of germanium dioxide. They propose running the process in an H-shaped apparatus with a large electrode separation, with no diaphragm. The anode and cathode gases are only separated by a glass membrane situated in the upper part of the working space. The recommended current density is up to 6.0 A/cm^2, which is a factor 20 higher than that in large-scale processes. Judging from the composition of the cathode gas, the current efficiency for germane under such conditions is within 10%. Clearly, this process cannot be used to produce germane even on a laboratory scale and is of no commercial interest. The current density recommended in [9, 10] is 1.0–1.5 A/cm^2. From indirect data, the current efficiency for germane can be estimated at 15–18%. However, since the voltage applied to the electrolyzer was not indicated, the actual power consumption in this process cannot be evaluated.

The purpose of this work was to develop physicochemical principles of the electrochemical synthesis of germane through the reduction of germanium dioxide in alkaline aqueous solutions.

EXPERIMENTAL

We used high-purity (99.9999%, 6N) germanium and germanium dioxide prepared from it via oxidation

Table 1. Effect of GeO_2 concentration and current density j on the germane yield η

j, A/cm^2	η_{GeH_4}, %	
	50 g/l GeO_2	150 g/l GeO_2
0.1	7.5	–
0.15	–	13.0
0.2	9.1	31.0
0.3	11.4	31.8
0.4	9.1	–
0.5	9.8	30.8
0.6	9.8	–

Note: Nickel cathode, 3 M KOH, quantity of electricity $Q = 3.6$ A h, catholyte volume of 75 ml.

Table 2. Temperature effect on the germane yield

t, °C	η_{GeH_4}, %	
	$j = 0.5$ A/cm^2, 50 g/l GeO_2	$j = 0.3$ A/cm^2, 150 g/l GeO_2
28–30	9.8	15.2
40–45	9.3	25.8
67–70	13.7	26.9

Note: Nickel cathode, 3 M KOH.

by a mixture of extrapure-grade nitric acid and reagent-grade hydrochloric acid. Catholyte and anolyte solutions were prepared using reagent-grade potassium hydroxide and sulfuric acid, respectively.

Experiments were carried out in a filter-press electrolyzer. The cathodic and anodic compartments were separated by a Nafion-304 cation-exchange membrane. The cathode was 2.0 × 2.0 cm in dimensions. In most experiments, the catholyte solution was circulated by a centrifugal pump, and the anolyte solution, by a gas-lift system. The set temperature was maintained by a heat exchanger in both circulation circuits. The anode was a platinum spiral, and the cathode was fabricated from a sheet of the material to be tested.

The experimental procedure was as follows: Before each experiment, the cathode and anode circulation circuits were filled with the corresponding solutions. The cathode chamber and cathode gas collection system were purged with argon, the catholyte circulation system was turned on, and electrolysis was started. The cathode gas was passed through a drying system and then through a pyrolysis furnace, where the germane was decomposed at 500°C to give germanium metal at the outlet of the hot zone. The hydrogen was collected in a Marriott bottle. The germane yield was evaluated from the weight gain of the quartz tube in which the germane was decomposed.

Electrode materials were tested as follows: the cathode to be tested was pretreated with sulfuric or hydrochloric acid, cleaned with soda, washed with distilled water, and mounted in the electrolyzer, following which three or four experiments were performed without disassembling the electrolyzer. Each process was run for 3 h. After the experiment, the catholyte was poured off, and an appropriate amount of germanium dioxide was added in order to compensate for the germanium consumption during electrolysis.

In assessing the temporal stability of the germane preparation process, we also used a filter-press electrolyzer, but with a larger cathode: 2.5 × 6.0 cm. As the cation-exchange membrane, we used an MF4-SK. The catholyte and anolyte were circulated on a gas lift principle. After each experiment, the catholyte was saturated with a germanium dioxide solution, without pouring it off.

In a series of preliminary experiments, germane was synthesized under conditions very similar to those described by Vorotyntsev [11] but at a lower current density. The cathode used was of nickel. The initial GeO_2 concentration in the catholyte was 50 g/l in 3 M KOH. The catholyte was stirred by a gas-lift system. At a current density of 0.3 A/cm^2, the current efficiency for germane was 11.4%.

Assuming that the efficiency of the process may be limited by mass exchange, we performed a series of experiments under the same conditions in which the catholyte was stirred by a centrifugal pump. The average germane yield in four successive experiments was 9.6%. At the same current density but at a GeO_2 concentration of 150 g/l and with mechanical stirring, the current efficiency for GeH_4 was 31.0%.

RESULTS AND DISCUSSION

Table 1 illustrates the effect of current density on the germane yield in solutions with GeO_2 concentrations of 50 and 150 g/l. At both concentrations, the germane yield is independent of the current density starting at 0.2 A/cm^2, indicating that the process is kinetically limited. Raising the current density from 0.3 to 0.6 A/cm^2 has an insignificant effect on the germane yield. In view of this, all subsequent experiments were performed with the catholyte circulated by a centrifugal pump. Raising the temperature from 25 to 70°C increases the germane yield only slightly (Table 2).

The germanate concentration in the catholyte is of considerable interest. Since the germanium dioxide solubility in an aqueous solution depends on the alkali concentration, the germanate content of the solution was raised by increasing the potassium hydroxide concentration. The results (Table 3) demonstrate that increasing the GeO_2 concentration from 165 to 250 g/l has an insignificant effect on the germane yield. This suggests that the reduction of the germanate anion is also kinetically limited. In all of our experiments, a thin layer of elemental germanium was deposited on the nickel cathode, and some of the fine-particle germanium passed into the catholyte. The germanium deposition takes no more than 1% of the quantity of electricity passed; the rest goes to the hydrogen release.

To check the assumption that germane may be formed via the reduction of the deposited elemental germanium with the cathode hydrogen, we carried out experiments on the reduction of metallic germanium in an H-shaped electrolyzer with the electrode compartments separated by a cation-exchange membrane. As can be seen from Table 4, the current efficiency for germane was within 1%. This indicates that germane formation via the hydrogen reduction of the elemental germanium deposited on the cathode during the electrolysis of the germanate anion is unlikely.

Thus, with a nickel cathode in alkaline solutions, the germane yield is within 35%.

The reduction of the germanate anion is known to significantly depend on the nature of the cathode material. In view of this, we examined different cathode materials under comparable conditions.

It can be seen from Table 5 that a higher (above 40%) germane yield is reached with cathodes from metals that possess a higher hydrogen overvoltage, though the difference is not so great as might be expected.

It is of interest to follow the dynamics of germane, hydrogen, and germanium formation in a series of successive experiments. Figure 1 illustrates the variation in germane yield for various cathode materials. In all cases, the germane yield in the first experiment is lower than that in subsequent experiments. Occasionally, a slight decrease in GeH_4 yield occurs in the fourth experiment. Note also interesting data on the balance of the current responsible for the germane and hydrogen release. In the first two experiments, a well-defined unbalance takes place, which is obviously due to the formation of a germanium coating on the cathode surface. In subsequent experiments, no current is consumed for germanium deposition, which means that electrolysis yields only two products: germane and hydrogen. The relatively weak effect of the cathode material seems to be due to the fact that germane is formed on the surface of the metallic germanium deposited on the cathode. At the same time, in the surface areas free of germanium (where the germanium particles were washed off by the solution), we observed hydrogen evolution, and the rate of that process was determined by its overvoltage. Thus, we are led to conclude that the optimal cathode materials are cadmium and copper, because Pb and Sn can be reduced to volatile hydrides, contaminating the forming germane. In our opinion, this effect calls for further investigation.

One way to enhance the current efficiency for germane is to tune the adsorption of the germanate anion by introducing substances capable of changing the surface tension at the cathode–electrolyte interface. To this end, we tested quaternary ammonium salts, *p*-toluenesulfonic acid, and zinc and mercury salts. The results were surprising (Table 6). In particular, the introduction of tetraethylammonium fluoroborate significantly suppresses germane formation. *p*-Toluenesulfonic acid, an anionic surfactant, has little or no effect on the reduction of the germanate anion. In the presence of the zinc salt, the major product is elemental germanium, which accumulates in the electrolyte in the form of a highly dispersed suspension. The mercury salt was tested with a graphite electrode for the possible reduction of the germanate on the highly active mercurated graphite. We

Table 3. Effect of GeO_2 content and KOH concentration on the germane yield

KOH, mol/l	GeO_2, g/l	η_{GeH_4}, %*
3.0	150	24.2
4.0	165	33.8
5.0	180	33.5
6.0	250	31.1

Note: Nickel cathode, $j = 0.6$ A/cm^2, $Q = 3.6$ A h.
* Average over four experiments.

Table 4. Reduction of metallic germanium in aqueous electrolyte solutions

Catholyte	j, A/cm^2	η_{GeH_4}, %
10% NaOH	0.05	0.96
	0.1	0.5
	0.5	0.2
10% H_2SO_4	0.05	0.3
	0.1	0.3
	0.5	0.2

Note: Germanium cathode.

Table 5. Effect of cathode material on the germane yield

Cathode material	η_{GeH_4}, %	
	max	min
Pt	22.9	19.9
Zn	23.7	19.2
Ti	27.7	21.5
Graphite	26.7	24.1
Cu	32.4	27.2
Ni	34.3	24.9
Cd	34.3	29.6
Pb	41.7	35.1
Sn	44.2	35.8

Note: 3 M KOH, $j = 0.3$ A/cm^2, GeO_2 concentration of 150 g/l.

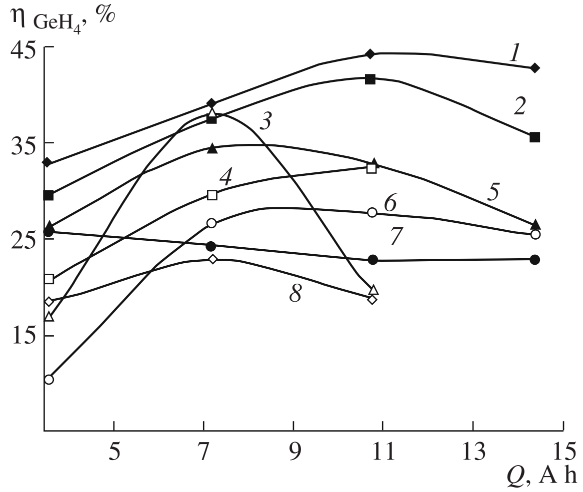

Fig. 1. Current efficiency for germane as a function of the quantity of electricity for various electrode materials in a series of successive experiments without cathode pretreatment: (*1*) tin, (*2*) lead, (*3*) titanium, (*4*) copper, (*5*) cadmium, (*6*) nickel, (*7*) graphite, (*8*) platinum.

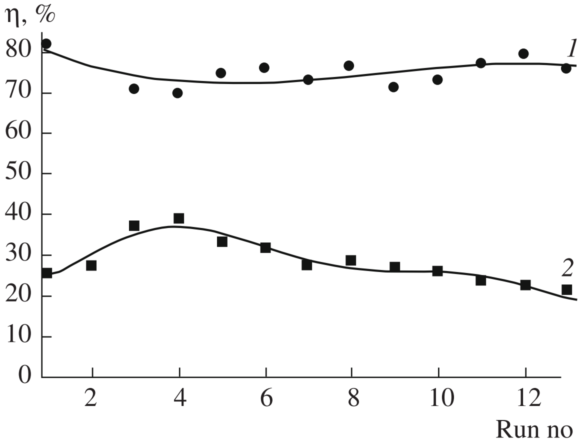

Fig. 2. Variation in the current efficiency for (*1*) hydrogen and (*2*) germane at a copper cathode in a series of successive experiments with no cathode pretreatment: 3 M KOH, current density of 0.3 A/cm^2, GeO_2 concentration of 150 g/l.

observed a substantial decrease in both the germane and hydrogen yields, and the catholyte remained absolutely transparent. Metallic germanium deposited on the cathode in the form of a dense coating.

A copper cathode was subjected to long-term testing under the optimal conditions (3 M KOH, 150 g/l GeO_2, current density of 0.2 A/cm^2). As seen in Fig. 2, the germane yield gradually decreases with time, and a 0.5- to 1-mm-thick layer of elemental germanium forms on the cathode. It is reasonable to assume that the fine-particle germanium deposit reduces the true current density, leading to a drop in the current efficiency for germane.

Note that the purity of the germanium obtained through the thermal decomposition of electrochemically synthesized germane corresponds to extrapure grade. According to spectrochemical analysis data, the total content of metallic impurities in the germanium is at a level of several ppmw, which is 1.5–2 orders of magnitude lower than their concentration in the starting reagents. These results attest to a selective character of the electrochemical germane synthesis and agree with earlier data [7, 8]. Elemental germanium prepared through the thermal decomposition of germane is an attractive material for the preparation of a high-purity product.

Table 6. Effects of surfactant additions and metal ions on the germane yield

Cathode material	Surfactant	η, %			Note
		GeH_4	Ge	H_2	
Nickel	–	15.5	<1.0	79.0	
	$(C_2H_5)_4NCl$	10.6	<1.0	88.3	
	$(C_2H_5)_4NCl$	11.4	<1.0	87.1	
	–	26.1	<1.0	65.4	
	p-PTSA*	22.1	<1.0	60.0	
	$Zn(CH_3CO_2)_2$	8.5	30.0	60.3	Ge suspension in the catholyte
Graphite	–	24.1	–	74.6	
	$(C_2H_5)_4NBr$	4.0	–	93.1	
	$Hg(NO_3)_2$	25.3	15.0	66.4	Ge coating on the cathode

Note: 3 M KOH, $j = 0.3$ A/cm^2, $Q = 3.6$ A h, GeO_2 concentration of 150 g/l.

* *p*-Toluenesulfonic acid.

CONCLUSIONS

We developed physicochemical principles of the electrochemical synthesis of germane through the reduction of germanium dioxide in alkaline solutions and optimized the process conditions: cadmium or copper cathode; germanium dioxide concentration in solution, 150 g/l; alkali (KOH) concentration, 3 M; current density, 0.3 A/cm^2.

The current efficiency for germane is 35–40%. A byproduct of the reduction process is elemental germanium, with a current efficiency within 1%.

Cationic surfactants added to the catholyte suppress germane formation; anionic surfactants have no effect on the reduction of the germanate anion. In the presence of zinc ions, the process ends in the formation of elemental germanium, which passes into the solution in the form of a highly dispersed suspension.

The energy consumption in the preparation of germane with yields up to 40% at a voltage applied to the electrolyzer from 5 to 6 V is within 6.5 kW h/kg GeH_4.

The purity of the elemental germanium obtained through the thermal decomposition of electrochemically synthesized germane corresponds to extrapure grade, and the total content of metallic impurities in it is at a level of several ppmw.

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