

Magnesium Hydrogen-generating Materials and a Hydrogen Generation Setup

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Abstract—The reaction of composites consisting of MgH₂ and a graphene-like or nickel–graphene material with water or citric acid solutions of various concentrations was studied. The composites were prepared by mechano-chemical treatment in a hydrogen atmosphere. The reaction of an aqueous citric acid solution with the composites is fast: 98% hydrogen yield is reached at the MgH₂ : citric acid molar ratio of 1 : 1. A setup for preparing compressed hydrogen from the composites was developed. It can be used in autonomous mobile installations for hydrogen generation under high pressure, followed by filling balloons.

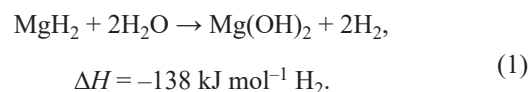
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Efficient, safe, and compact systems for hydrogen storage and transportation are required for the successful development of technologies based on hydrogen energy. Because of low hydrogen density (0.0001 g mL⁻¹ under n.c.), explosiveness, and possibility of diffusion through materials, stringent requirements are imposed upon hydrogen storage systems, especially for mobile and small-size devices. Therefore, along with various hydrogen storage methods based on physical processes (compression, liquefaction) and use of hydrogen storage materials (adsorbents with high specific surface area, metal phases and liquid organic compounds reversibly reacting with hydrogen, etc.), particular attention is paid today to the hydrogen generation by the reaction of various hydrogen-generating materials with water and aqueous solutions [1]. One of the most promising hydrogen-generating materials is MgH₂, which generates large amounts of hydrogen (15.2 wt % H₂ without taking into account the weight of water) and, as compared to other widely used hydrolysis agents such as NaBH₄ [2] or NaSi [3], is cheap and environmentally

safe. In addition, it is stable in anhydrous atmosphere and thus has long shelf life and can be safely transported.

The reaction of MgH₂ with water is an exothermic process yielding H₂ and Mg(OH)₂:



The hydrolysis of MgH₂ starts immediately on contact with water, but the reaction product, Mg(OH)₂, forms a passivating film causing sharp deceleration of the reaction up to its complete cessation, so that the amount of the released hydrogen is as low as 10–20% of the theoretical amount. Various methods are suggested for preventing the formation of the passivating layer. These include, e.g., ultrasonic treatment [4], alloying of Mg with other metals [5], and use of alcoholysis instead of hydrolysis [6].

Another way to accelerate the reaction is the addition of salts, e.g., Na, K, Al, and Mg halides, to the aqueous

solution or their preliminary mixing with MgH_2 [7]. Presumably, the dissolution of the salts is accompanied by hydrolysis and release of hydrogen ions, which favor the destruction of the $\text{Mg}(\text{OH})_2$ base layer and thus accelerate the reaction of MgH_2 with water. The hydrogen release rate strongly depends on the way of introducing the halides. For example, mechanically treated mixtures of MgH_2 with halides (NaCl , MgCl_2 , NH_4Cl , and NH_4Br) react with water faster than MgH_2 reacts with the solutions of the corresponding salts. The hydrogen yield, however, is independent of the way of introducing the salts. In addition, the hydrolysis acceleration is associated with the heat release upon salt dissolution.

The use of Brønsted acids such as aqueous solutions of acids or ammonium salts is suggested for the destabilization or complete removal of the passivating $\text{Mg}(\text{OH})_2$ layer [8]. The following requirements are imposed on the acids used for the hydrogen generation: solubility of the corresponding magnesium salt in water, no aggressiveness toward materials of the hydrogen generation installation, no transfer of the acid vapor with the released hydrogen, and environmental safety of the acid and its magnesium salt. Solid organic acids (glycolic, malonic, citric, succinic), as well as their anhydrides or esters transforming into the corresponding acids in the reaction with water, meet these requirements. The authors of patent [9] suggest using a paste containing MgH_2 and carboxylic acid esters (1,2,3-propanetriol triacetate, pentaerythritol tetrastearate, diisononyl 1,2-cyclohexanedicarboxylate) for hydrogen generation. However, large amounts of the acids are required to overcome the passivation by using Brønsted acids.

Another way to enhance the reactivity of MgH_2 is its preliminary mechanical activation [10]. Treatment of MgH_2 and its mixtures with various additives in a ball mill yields a material with fine particles and accelerates the hydrolysis. The positive effect of the mechanical activation of MgH_2 on the hydrolysis is associated with the break of hydride particle agglomerates in the course of the treatment, to the formation of defects, and to an increase in the specific surface area of the material. Various additives are used to enhance the efficiency of the mechanochemical treatment of MgH_2 . These include metal oxides and halides [11] and carbon materials. Composites of MgH_2 with carbon materials (graphite, carbon nanotubes and nanofibers, graphene materials)

exhibit enhanced activity in thermal decomposition [12] and hydrolysis [13].

This study was aimed at revealing relationships of the hydrogen generation in the reaction of composites consisting of MgH_2 and graphene-like/nickel–graphene material with water or citric acid solution and at developing a procedure for producing compressed hydrogen by the reaction of the hydrogen-generating material with an aqueous solution of citric acid.

EXPERIMENTAL

As starting substances we used magnesium powder of MPF-3 grade (99.95 wt %, KhIMMETPRODUKT, Russia) with the particle size of 100–200 μm , hydrogen (99.999 vol %, NII KM, Russia), graphene-like and nickel–graphene materials, and citric acid (chemically pure grade, KhIMMED, Russia). High-purity hydrogen was generated by heating a metal hydride accumulator based on the intermetallic compound LaNi_5 , fabricated in our laboratory. The design and functioning principle of a similar accumulator and the operation procedure are described elsewhere [14]. Graphite oxide was prepared by oxidation of natural graphite of GK-1 grade (C content no less than 99 wt %, ash residue <1 wt %, volatiles ≤ 0.5 wt %, moisture content $\leq 0.5\%$; Grafit-Garant, Raussia) in a mixture of KMnO_4 (analytically pure grade, KhIMMED) and H_2SO_4 (analytically pure grade, KhIMMED) with NaNO_3 (analytically pure grade, KhIMMED) [15]. The graphene-like material was prepared by thermal reduction of graphite oxide in an Ar atmosphere (99.998 vol %, Tsentrogaz, Russia) at 900°C [15]. The nickel–graphene material is a graphene-like material with nickel nanoparticles (1–5 nm, 5 wt %) immobilized on its surface. Such material was prepared by simultaneous reduction of graphite oxide and nickel(II) with hydrogen at 500°C from their mixture prepared by freeze-drying of a dispersion of graphite oxide in an aqueous solution of $\text{Ni}(\text{CH}_3\text{COO})_2$ (98%, Sisco Research Laboratories) [16]. The hydrogenation of Mg and Mg–graphene composites was performed by the mechanochemical procedure. To this end, 1 g of magnesium powder or a mixture of Mg with graphene-like/nickel–graphene material in a steel beaker with steel balls was treated in a hydrogen atmosphere at a pressure of 25 atm in a Pulverisette 6 planetary ball mill (Fritsch GmbH) at a rotation rate of 500 rpm [12].

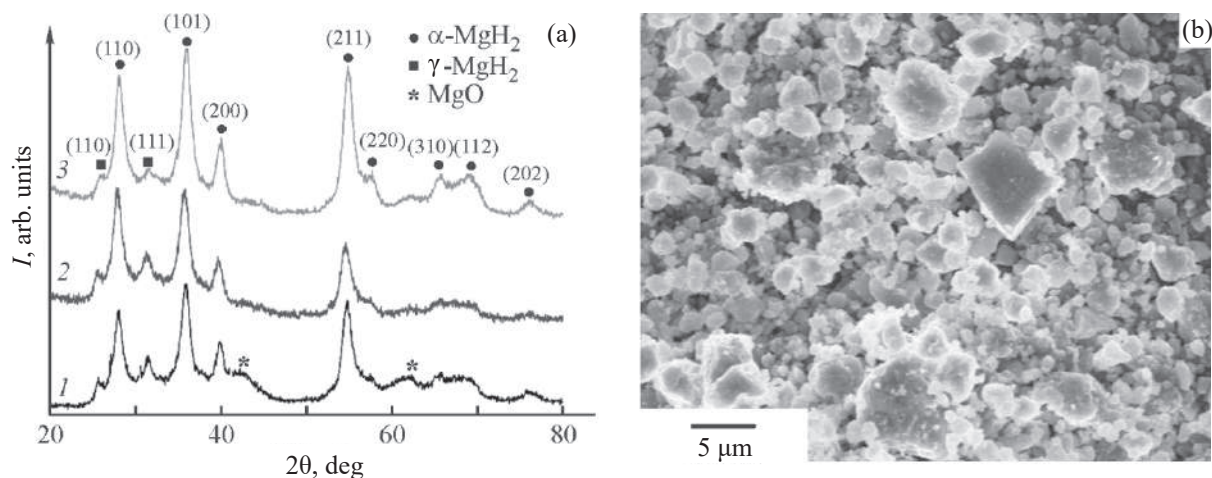


Fig. 1. (a) Diffraction patterns: (1) MgH₂, (2) composite of MgH₂ with the graphene-like material, and (3) composite of MgH₂ with the nickel-graphene material; (b) SEM image of the composite of MgH₂ with the nickel-graphene material.

The materials obtained were analyzed using a set of physicochemical methods. The elemental composition was determined with a Vario MICRO Cube universal elemental CHNOS analyzer (Elementar). X-ray diffraction analysis was performed with DRON-UM2 (Burevestnik, Russia) and Siemens D500 diffractometers. The SEM images of the materials were taken with a Zeiss LEO SUPRA 25 scanning electron microscope (Carl Zeiss Industrielle Messtechnik GmbH). The pH values of the solutions were determined with a Hanna HI 8314 portable pH meter (Hanna Instruments). The completeness and rate of the reaction of MgH₂ and its composites with water or citric acid solutions of various concentrations were evaluated volumetrically at room temperature. To this end, a 30-mg portion of the composite was placed in a three-necked flask equipped with tubes for purging with argon, feeding water (or citric acid solution), and connecting with a measuring burette.

RESULTS AND DISCUSSION

It is known [17] that the addition of graphene-like and nickel-graphene materials to Mg allows the rate of the MgH₂ mechanochemical synthesis in a hydrogen atmosphere to be increased by a factor of 1.5–2. The nickel-graphene material has at least three functions: (1) it acts as a hydrogenation catalyst, ensuring the dissociation of hydrogen molecules into atoms; (2) it increases the thermal conductivity of the composite material; (3) it prevents sintering of highly

dispersed particles in the course of high-temperature decomposition of the hydride phases. All the samples prepared by the mechanochemical synthesis contained, along with the α-MgH₂ phase, also the metastable γ-phase (Fig. 1a). The MgH₂ sample prepared by mechanochemical treatment of pure Mg contained impurities of nanocrystalline MgO formed presumably by oxidation of highly active finely dispersed MgH₂ in the course of handling the samples and performing the experiments. However, in the X-ray diffraction patterns of the composites with graphene-like/nickel-graphene material, the MgO reflections are considerably weaker or are not observed, which can be attributed to coverage of the MgH₂ particles, preventing oxidation of the composite samples. The unit cell parameters of α-MgH₂ (tetragonal system, $a = 0.4515$ nm, $c = 0.3019$ nm) and γ-MgH₂ (orthorhombic system, $a = 0.4526$ nm, $b = 0.5448$ nm, $c = 0.4936$ nm) were determined. The MgH₂ particle size in all the materials prepared by the mechanochemical synthesis ranges from 0.5 to 5 μm (Fig. 1b).

In the reaction of mechanochemically prepared MgH₂ with water, the conversion in 1 min is $\alpha = 0.08$, and by the 13th minute α reaches 0.12 (Fig. 2a, curve 1). The highest reaction rate is observed in the initial period (up to 30 s), after which it sharply decreases owing with the formation of a Mg(OH)₂ film, and at 2 min from the start of the reaction the rate becomes virtually independent of time. The time dependences of the conversion in the hydrolysis of the composites are similar (Fig. 2a,

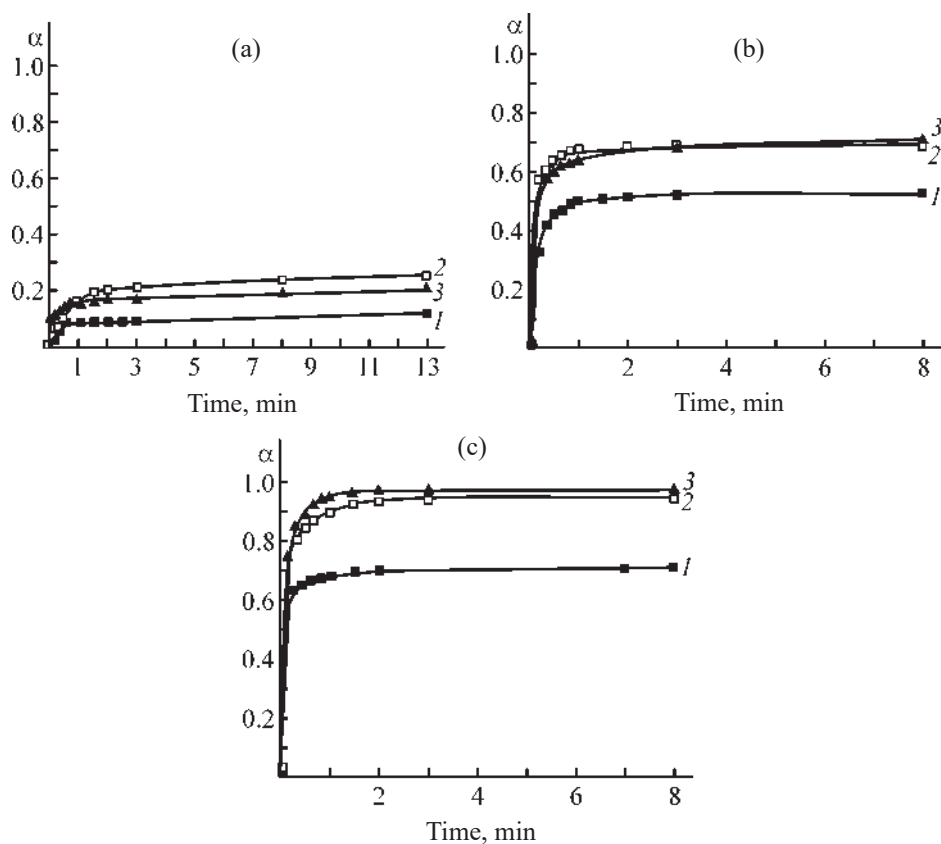


Fig. 2. Conversion in the reaction of (1) MgH_2 and composites consisting of MgH_2 and the (2) graphene-like and (3) nickel-graphene materials (a) with water and with (b) 0.1 and (c) 0.3 M citric acid solutions as a function of time.

curves 2 and 3). The conversion in the reaction of composites consisting of MgH_2 and the graphene-like/nickel-graphene material with water is 0.16 in 1 min after the start of the reaction and reaches 0.25 and 0.21, respectively, in 13 min. The addition of the graphene-like/nickel-graphene material in the course of the mechanochemical synthesis of MgH_2 favors an increase in the degree of conversion in hydrolysis by a factor of 1.8–2 (Fig. 2a). According to [16], the reactivity of α - and γ - MgH_2 toward water is similar; therefore, high content of γ - MgH_2 in the composites with the graphene-like/nickel-graphene material is not a decisive factor in the enhancement of their reactivity. The observed effect is probably associated with an increase in the number of defects and with a decrease in the particle size in the course of mechanochemical synthesis due to additions of the graphene-like/nickel-graphene material, which can stabilize submicrometer MgH_2 particles and prevent their agglomeration.

Citric acid [$HOOC-CH_2-C(OH)(COOH)-CH_2COOH$] is a tribasic organic acid readily soluble

in water (133 g per 100 g of water). Its dissociation constants for the first, second, and third steps at 25°C are 7.4×10^{-4} , 1.8×10^{-5} , and 4.0×10^{-7} , respectively [18]. To study specific features of the reaction of MgH_2 with citric acid, we determined the pH values of the solutions after performing the reaction at different reactant ratios. For example, at the MgH_2 : citric acid molar ratio of 3 : 2, after the reaction completion we observed the formation of the $Mg(OH)_2$ precipitate, and pH of the solution was 8.7 (pH of the initial citric acid solution was 1.2). After the reaction of MgH_2 with an aqueous citric acid solution at molar ratios of 1 : 1 and 1 : 2, the $Mg(OH)_2$ precipitate was not formed, and pH of the final solution was 3.5 and 2.6, respectively.

In the reaction of MgH_2 with a 0.1 M citric acid solution, the maximal reaction rate is reached in the first 10 s, and α reaches 0.33. In 2 min, α increases to 0.52, after which it becomes independent of time. The dependences of α on the time of the reaction of the citric acid solution with MgH_2 /graphene-like material and MgH_2 /nickel-graphene material composites are similar, but the

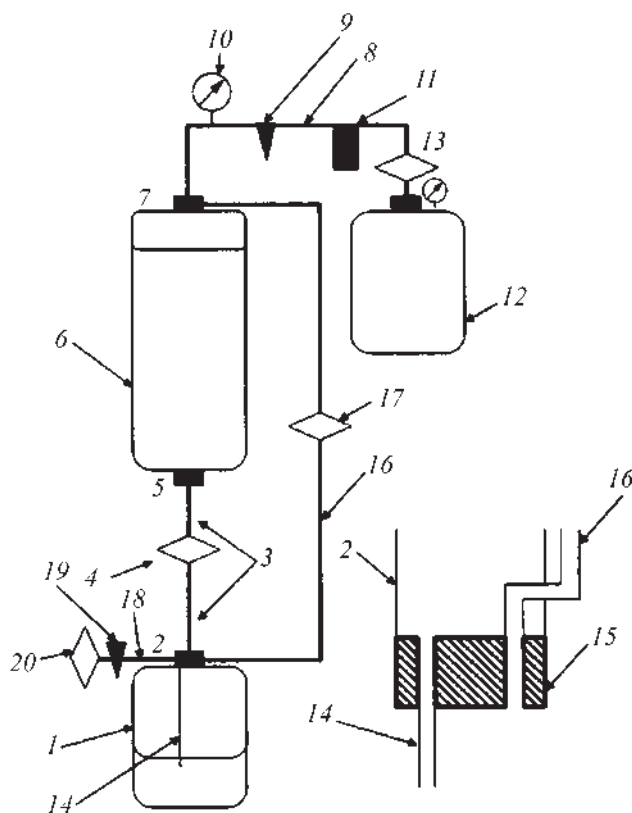


Fig. 3. Setup for producing compressed hydrogen: (1) reactor, (2) dosing fitting, (3) tube for connecting the reactor with the vessel for the liquid reagent, (4) stopcock for separating the vessel from the reactor, (5) fitting for connecting the vessel with the stopcock, (6) vessel for the liquid reagent, (7) fitting for connecting the vessel and gas tube with the hydrogen treatment system, (8) tube for connecting the elements of the hydrogen treatment system, (9) safety valve of the hydrogen treatment system, (10) pressure gage, (11) filtering elements, (12) balloon being filled, (13) stopcock of the cylinder being filled, (14) tube for feeding the liquid reagent, (15) dosing fitting gasket, (16) gas tube, (17) gas tube stopcock, (18) tube of the overpressure release system, (19) safety valve of the overpressure release system, and (20) stopcock of the overpressure release system.

reactions are characterized by the higher rate in the initial period of the reaction and by the higher hydrogen yield compared to MgH_2 . In 10 s, α reaches 0.52, and in 2 min after the start of the reaction it reaches 0.68. An increase in the citric acid concentration to 0.3 M (corresponds to the MgH_2 : citric acid molar ratio of 1 : 1) leads to an increase in the hydrogen yield and in the rate of the reaction with the mechanochemically prepared MgH_2 and composites of MgH_2 with the graphene-like and nickel-graphene materials. For example, in the reaction with c MgH_2 , α reaches 0.59 in 10 s and 0.70

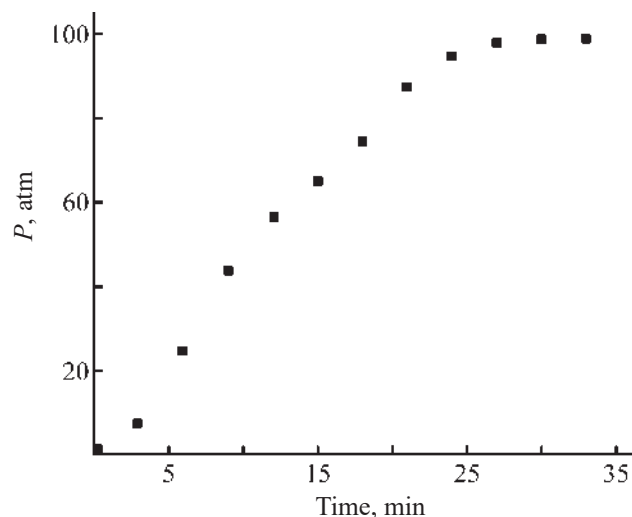


Fig. 4. An example of reaching a pressure of 100 atm in the course of filling a balloon with hydrogen using the suggested setup.

in 2 min. In the reactions of a 0.3 M citric acid solution with the MgH_2 /graphene-like material and MgH_2 /nickel-graphene material composites, the conversion is similar: 0.75 and 0.76 in 10 s, 0.95 and 0.98 in 2 min, respectively. An increase in the reaction rate and hydrogen yield on compounding Mg with the graphene-like/nickel-graphene material may be due not only to an increase in the number of defects and to stabilization of submicrometer MgH_2 particles, but also to the formation of a magnesium citrate/citric acid buffer solution maintaining the pH value required for the reaction completion and preventing the formation of the passivating $\text{Mg}(\text{OH})_2$ layer on the surface of MgH_2 particles.

Kushch et al. [19] reported that, in the reaction of MgH_2 with a citric acid solution, the conversion close to 1 was reached at the MgH_2 : citric acid molar ratio of 1 : 2. This fact leads to significant limitations in the practical use, because the production of 1 m³ of hydrogen (n.c.) requires 0.587 kg of MgH_2 and 8.574 kg of citric acid. The use of composites of MgH_2 with the graphene-like/nickel-graphene material allows the hydrogen yield of 95–98% to be reached at the MgH_2 : citric acid molar ratio of 1 : 1. Thus, 2 times smaller amount of citric acid is required for hydrogen generation in a high yield when using the composites described in this paper. This considerably expands the prospects for the practical use, e.g., in the development of mobile autonomous systems for hydrogen generation and compression.

Hydrogen can be produced and compressed using standard apparatus: an electrolyzer and a compressor.

However, such scheme is unsuitable for devices operating under field conditions and requiring mobile sources for hydrogen production and compression. Therefore, for solving this problem there are numerous procedures and devices based on using hydrogen-generating materials. The requirements are cheapness, safe storage, and availability [20, 21]. In the course of this study, we developed a process for producing compressed hydrogen, suitable for use in autonomous mobile installations for hydrogen generation at high pressure, followed by filling balloon and using in fuel cells to ensure operation of unmanned aerial vehicles, telecommunications equipment, computers, and other autonomous objects consuming electric power. The production of compressed hydrogen consists in performing a chemical reaction of a hydrogen-generating material such as Mg, MgH₂, or above-described composites consisting of MgH₂ and the graphene-like/nickel-graphene material with a liquid reagent such as a citric acid solution in a closed volume. The setup that we developed includes a device for producing compressed hydrogen (Fig. 3), in which the reactants are stored separately: the hydrogen-generating material, in reactor 1, and the acid solution, in vessel 6. After opening stopcock 4, the acid solution starts to flow into reactor 1 first through tube 3 connecting the reactor and the vessel and then through tube 14 for feeding the liquid reagent, fixed in dosing fitting 2 using gasket 15. The released hydrogen flows through tube 16 equipped with stopcock 17 into vessel 6. To stop filling balloon 12, stopcock 4 separating the vessel from the reactor is closed. A pressure-releasing system consisting of pressure release valve 18, safety valve 19, and/or pressure release stopcock 20 is provided for preventing the reactor failure under the action of high pressure of hydrogen formed by the reaction of the hydrogen-generating material with citric acid fed into the reactor before closing stopcock 4. Composite or any other balloons, the material of which is inert to the reactants and reaction products, can be used as the reactor and vessel.

To demonstrate the setup operation, we performed tests on filling a composite balloon of 1 L volume with hydrogen to a pressure of 100 atm (Fig. 4). Reactor 1 of 1 L capacity was charged with 148 g of Mg, and vessel 6 for storage of the liquid reagent, with 1.6 L of a 4 M citric acid solution. After the start of the reaction of Mg with citric acid, the balloon connected to the setup was gradually filled with hydrogen to a pressure of 100 atm.

The rate and completeness of filling were controlled with a stopcock connecting reactor 1 and vessel 6.

Complete filling of the 1-L balloon to a pressure of 100 atm is reached in 30 min. Low filling rate is caused by controlled feeding of citric acid into the reactor, limited by rapid self-heating of the reaction mixture, and by the use of Mg as a hydrogen-generating material. To accelerate filling with hydrogen, it is necessary to ensure more efficient heat exchange and use composites described in the paper. The use of composites of MgH₂ with the graphene-like/nickel-graphene material also allows the required amount of citric acid to be reduced, which will increase the mobility of the device.

CONCLUSIONS

Composites of MgH₂ with the graphene-like/nickel-graphene material can be used as hydrogen-generating materials ensuring high rate of hydrogen release and high hydrogen yield.

The procedure and setup developed can be used for filling balloon with compressed hydrogen. Such setup has simple design, can be readily disassembled functions without the use of additional energy sources, and allows producing hydrogen and filling one or several (in succession) cylinders with hydrogen to the required pressure.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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