



Metal hydride – Graphene composites for hydrogen based energy storage

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ABSTRACT

The paper presents a review of the authors' studies of advanced functional composites of graphene based materials with metals, alloys, intermetallic compounds and their hydrides, and on the creation on their basis of hydrogen-storage materials for a compact and safe hydrogen storage, electrode materials for nickel-metal hydride batteries, highly efficient catalysts for the hydrogenation of metals and organic compounds as well as their integration into the hydrogen energy systems for the backup electric power and for the H-based energy storage.

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1. Introduction

Development of the efficient energy storage and conversion materials is a top priority in the efforts on further advancing the environment-friendly energy technologies. Due to their unique mechanical, thermal, catalytic and other functional properties, graphene and graphene-like materials (GLMs) have been in focus of the related studies [1,2], particularly, the ones considering hydrogen storage [3,4]. According to the recently published results of bibliometric analysis [5], about 5% of the publications on hydrogen storage materials (more than 16,800 in total for the period 2000–2015) were related to graphene.

Graphene and GLMs form layered structures of sp^2 hybridized carbon atoms arranged in a two-dimensional lattice containing regular hexagons [6]. These materials can be synthesized from the commercially available cost-efficient Graphite Oxide (GO) obtained from the natural flake-type graphite by oxidizing it in sulfuric acid, nitric acid, and potassium chlorate. Rapid heating of GO to $\sim 1000^\circ\text{C}$

results in a “thermal explosion” phenomenon – thermal reduction which releases water and carbon-containing (mostly CO_2 and CO) gases because of the evaporation and burning of the oxygen-containing functional groups while forming exfoliated layers of graphene sheets [2,7]. Changing the temperature profile of the heating process and its time allows to control the C/O ratios, from 2 to 3 in the original GO [8] to the values exceeding 20 [9] and even approaching 100 when the reduction is completed. This, in turn, dramatically changes thermal and electrical conductivity, hydrophobic/hydrophilic properties, strength of chemical binding between the surface layers of GLM and substrate materials, and presence or absence of the aggregation in the material. This creates an opportunity to control the functional properties of GLMs in a broad range.

GLMs were shown to significantly improve hydrogenation, dehydrogenation and re-hydrogenation performances and cycle stability of metal hydride materials, particularly, MgH_2 [10–12].

The development of the efficient hydrogen storage materials is frequently related to the studies of the catalysts of the processes, including hydrogenation catalysts, involving molecular hydrogen. Numerous studies have considered graphene and GLMs as promising carriers of nanosized metals and metal oxide catalysts to be used in the development of the functional catalytic composites [13]. A synergy between high specific surface area of a 2D graphene-like component, its high thermal conductivity, and high catalytic activity

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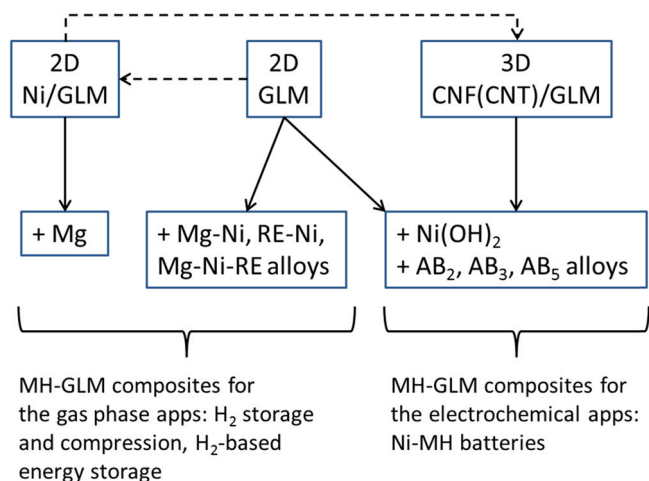


Fig. 1. A scheme illustrating preparation routes of the metal hydride – graphene composites, used by the authors in hydrogen-based energy storage applications.

of the nanosized metal particles supported on GLM allows to prepare metal-graphene composites exhibiting properties of highly active catalysts of the hydrogenation of the various organic compounds [14]. Similar approach can be applied to the hydrogen storage materials.

The most promising techniques for the formation of metal-containing graphene composites include simultaneous reduction of graphite oxide and growth of metal nanoparticles [15].

The aim of this paper is to present an overview of the authors' works focused on the synthesis and studies of new metal hydride-graphene nanocomposites and their various H_2 gas-phase and electrochemical applications in hydrogen-based energy storage technologies, including hydrogen storage and compression, as well as in the chemical power sources (batteries and fuel cells).

2. Synthesis and characterization of GLMs

The main activities in the synthesis and applications of the metal hydride – graphene composites in the H-based energy storage are shown in Fig. 1.

GLMs were synthesized by chemical and thermal reduction of GO which was obtained from the natural graphite GK-1 (its composition is defined by GOST 4404-78; ash content less than 1 wt%) according to the procedure described in [16]. The thermal reduction of GO was

carried out in a tubular furnace. Dried GO (10 mg) was placed in the middle part of a quartz reactor and was kept under the flow of argon gas at a rate of 0.2 l/min, before the reactor was rapidly transferred to a tubular furnace heated to 900 °C. Very rapidly, in 3–5 s, GO explosively decomposed to produce gaseous CO, CO₂, and H₂O. The solid product (its volume considerably increased) was removed from the hot zone flushed with the argon flow. Then the obtained powder was annealed in the atmosphere of argon at 900 °C for 3 h.

Ni/GLM composites were prepared using two different routes: 1) a co-reduction of the mixtures of graphite oxide with nickel salts [17]; and 2) through a preliminary functionalization of graphene oxide with amino groups, during which the growth centers of the metal nanoparticles nucleate to ensure a uniform distribution and small (nano) size of the formed metal clusters [18].

The second route included a simultaneous reduction of GO and nickel(II) from the mixture prepared by freeze drying of GO suspension in Ni(CH₃COO)₂ aqueous solution. For this purpose, the GO aqueous suspension together with the corresponding amount of Ni (CH₃COO)₂·4H₂O were processed in an ultrasonic bath for 60 min. The obtained mixture was placed in a 1 liter pear-shaped flask and frozen by placing the flask into a Dewar vessel filled with liquid nitrogen. Then remaining water vapors were removed at ambient conditions by an operating vacuum pump (~1·10⁻³ atm) equipped with a liquid nitrogen trap until the mixture became completely dry. The reduction of the dried mixture was performed in a tubular reactor, 40 mm in the diameter, at 300–500 °C in the flow of H₂ (rate of 200 ml/min) for 30 min. Depending on the nickel salt / GO initial ratio, the obtained nickel-graphene composites (Fig. 2) contained from 5 to 60 wt% Ni nanoparticles.

Furthermore, Ni/GLM composites were used to prepare three-dimensional (3D) structures of the graphene-nanotube and graphene-nanofiber types with high specific surface areas (more than 700 m²/g), by growing carbon tubular nanostructures through a catalytic decomposition of hydrocarbons over the metal-graphene nanosheets [19]. The catalytic synthesis of 3D-carbon nanostructures such as graphene-supported carbon nanofibers (CNF/GLM) and carbon nanotubes (CNT/GLM) was performed at atmospheric pressure at a temperature of 700 °C in a custom-built laboratory setup [13] containing a horizontal tubular flow reactor. A 50 mg batch of Ni (CH₃COO)₂/GO composite was placed in a quartz boat in the cold zone of the reactor outside the furnace. The reactor was heated in the flow of gas mixture Ar:H₂:C₂H₄ = 1:3:1.6. After reaching the operating temperature, the quartz boat was moved to the hot zone of the reactor. The synthesis time varied from 1 to 60 min. After the synthesis, the boat was moved to the cold zone of the reactor. Then

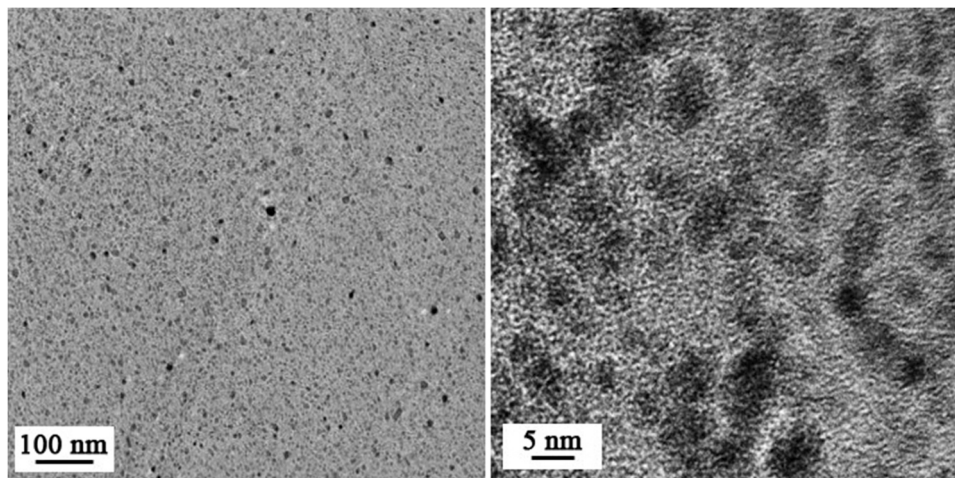


Fig. 2. TEM micrographs of the Ni/GLM composites. Here, the dark spots correspond to the Ni catalyst particles that are attached to the surface of graphene (light areas in the photograph).

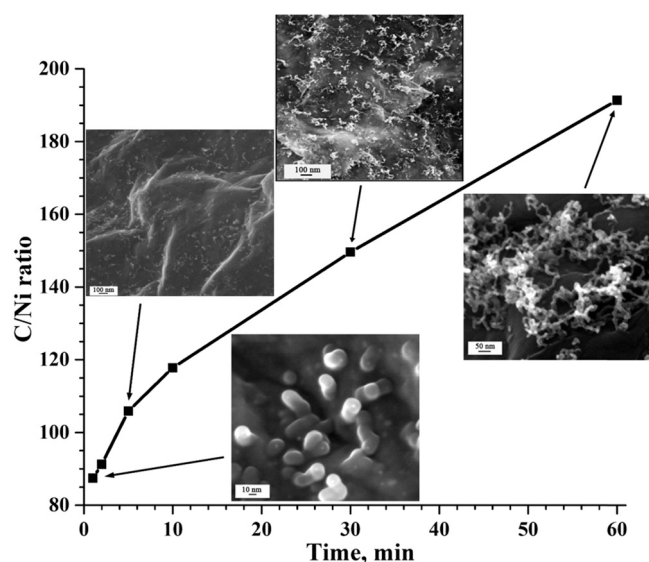


Fig. 3. Increase of C/Ni atomic ratio during the synthesis duration and SEM micrographs of the Ni/CNF/GLM composites.

the sample was cooled to the room temperature in a flow of argon gas. It was found that the catalytic decomposition of ethylene on Ni/GLM at temperatures of 500–700 °C results in the formation of CNFs formed on the surface of GLM [20], while the decomposition of methane at 900 °C yields CNTs [21]. The resulting CNFs have diameters ranging from 5 to 20 nm, while their length increases from 5 to 300 nm when the synthesis time increases from 1 to 60 min (Fig. 3).

The proposed mechanism of the formation of the metal-carbon-graphene composites during their preparation is presented in Fig. 4. The process consists of four stages: 1) Reduction of graphite oxide and metal ions; 2) Formation and growth of metal clusters on reduced graphite oxide; 3) Catalytic pyrolysis of CH_4 or C_2H_4 on the single crystal metal particles supported on a graphene-like support; and 4) Formation and growth of carbon nanostructures on the surface of the graphene-like material. Such three-dimensional structures having a high specific surface area (more than $700 \text{ m}^2/\text{g}$) serve as supports of the metal catalysts, components of electrically conductive composites [19], and promising gas sorbents. In theoretical studies [22,23], it was shown that three-dimensional structures are capable of absorbing more than 7 wt% of molecular hydrogen at temperature of 77 K and hydrogen pressure of 100 bar H_2 .

3. GLM-containing hydrogen storage composites

The obtained nickel-graphene catalysts were used for the fabrication of hydrogen storage composite materials based on hydride forming individual metals (Mg), alloys (Mg-Ni, Mg-La(Mm)-Ni), and intermetallic alloys [24,25]. Highly dispersed metal powders were

prepared by hydrogen and ammonia assisted decrepitation proceeding after the mechanochemical treatment in hydrogen [26].

Nickel-graphene catalysts were utilized to prepare highly efficient MgH_2 -based hydrogen storage composite materials with a reversible hydrogen storage capacity of more than 6.5 wt% H. The composites were fabricated by using a mechanochemical method: the required amounts of graphene material, 1 g of 0.5–1 mm in size magnesium particles, and 10 mm steel balls (sample-to-balls mass ratio was 1/40) were placed in an 80 ml steel grinding vial in a dry argon box. The vial was then sealed with a lid equipped with a valve for gas inlet was filled with 99.9999% pure hydrogen to the setpoint pressure of 25 atm H_2 . The hydrogenation was carried out in a Pulverisette 6 planetary ball mill, at the rotational speed of 500 rpm. The hydrogenation rate was determined by monitoring the changes of hydrogen pressure (accuracy ± 0.2 atm) measured in one-hour intervals during the mechanochemical processing. Similarly, were obtained MgH_2 -based hydrogen storage materials with nickel-carbon-graphene composite (Ni/CNF/GLM).

The additions of Ni/GLM and Ni/CNF/GLM were found to cause increase in the rates of Mg hydrogenation [24,27], due to a catalytic influence of the nanosized Ni causing increased rates of the dissociation of H_2 molecules, while the GLM coating of highly dispersed MgH_2 retains preserved the submicron sizes of the Mg particles formed during the hydrogenation, milling and dehydrogenation while achieving a high thermal conductivity of the $\text{Mg}/\text{MgH}_2 + \text{Ni}/\text{GLM}$ (Ni/CNF/GLM) composites (Fig. 5).

The preparation methods of heat-conductive intermetallic-graphene composites were optimized for the studied materials, including the $\text{Mg}_2\text{Ni}/\text{Mg} + \text{GLM}$ composite [25,28]. An increase in the thermal conductivity of the powdered intermetallic hydrides was facilitated by the addition of up to 5 wt. % of GLM to the mixture subjected to the mechanochemical treatment by its ball milling is hydrogen gas. The occurring coating of the metal particles with graphene ensured a good thermal conductivity and reduced the sintering of the metal particles during the processing at high temperatures. Topological features of the microstructures of the composites containing magnesium, intermetallic compounds, and the GLM particles with characteristic sizes less than $1 \mu\text{m}$, show their close contacts while this morphology remained unchanged during the cycling of hydrogenation / dehydrogenation thus contributing to the improvement of the reversible hydrogen storage performance of the materials. The composites reversibly absorbed 5 wt. % H with a high rate (90% absorption in 5 min at 300 °C). The resulting composites are easy to compact, that is very valuable for their accommodation into the portable metal hydride stores and hydrogen generators.

4. Composite materials for metal hydride power sources

Nickel-metal hydride (Ni-MH) batteries are broadly used in portable electronic devices due to their high energy density, cyclic stability, resistance to overcharging and good environmental compatibility. The efficiency of a Ni-MH battery depends on both electrode materials – cathode and anode – particularly on the method of

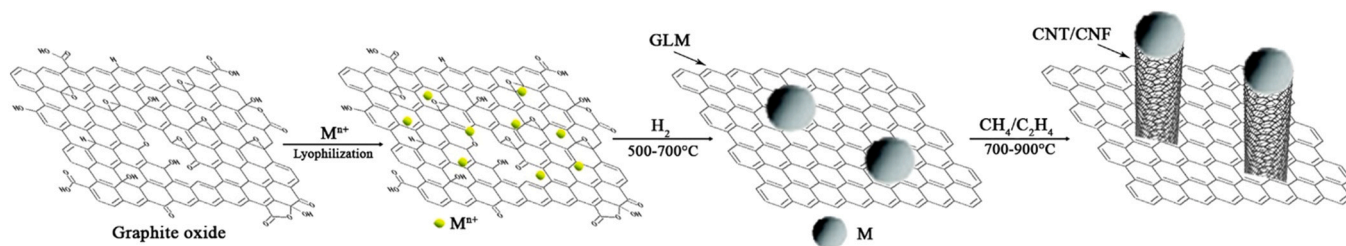


Fig. 4. Preparation of metal-carbon-graphene composites.

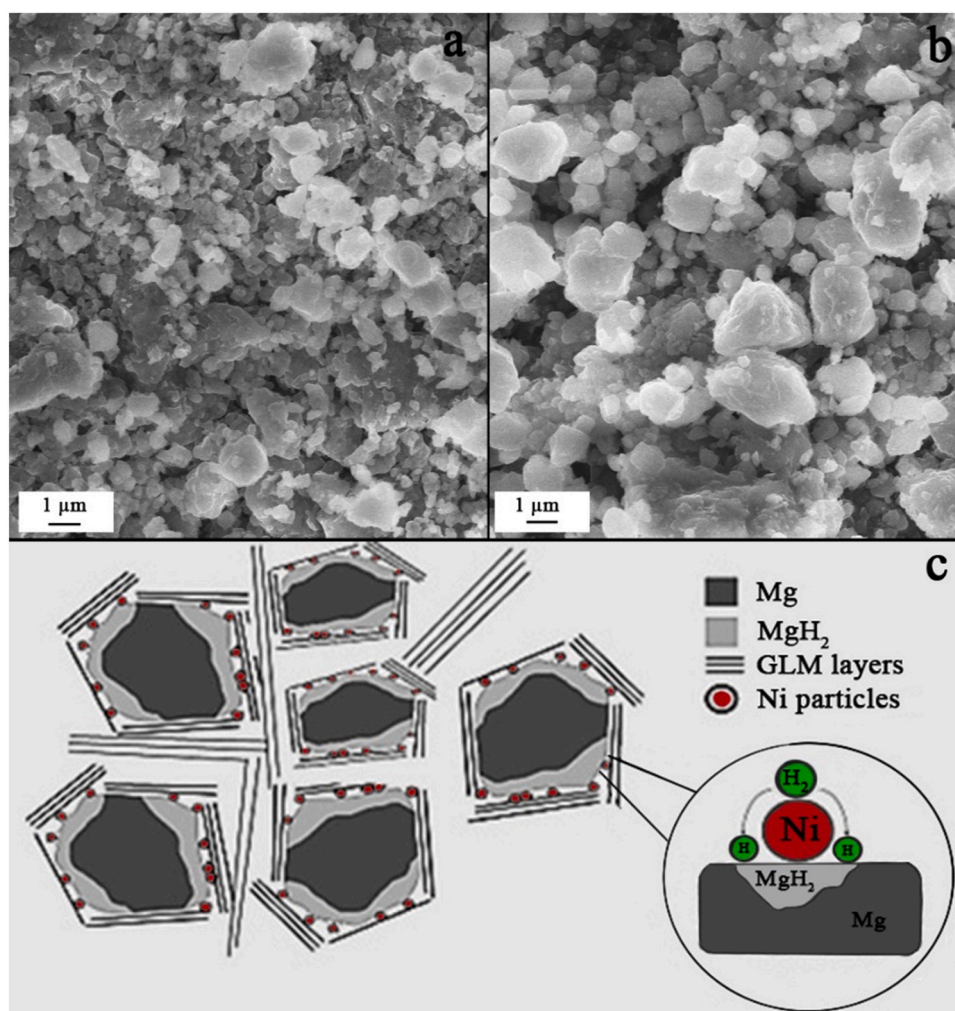


Fig. 5. SEM micrographs of $\text{MgH}_2 + \text{Ni/GLM}$ composite before (a) and after (b) dehydrogenation, and its schematic representation (c).

Table 1
Characteristics of the various anode electrode materials.

Anode	E_{eq} (V)	C (mAh/g)		S_{100} (%)	Ref.
		(100 mA/g)	(300 mA/g)		
AB₅-type					
MmNi _{3.6} Mn _{0.35} Co _{0.6} Al _{0.25} B _{0.1}	-0.90	320	310	88.60	[30]
MmNi _{4.15} Mn _{0.35} Co _{0.45} Al _{0.3}	-0.91	317	310	95.60	[31]
La _{0.7} Ce _{0.3} Ni _{4.2} Mn _{0.9} Cu _{0.37}	-0.90	320	310	76.60	[32]
MmNi _{3.8} Co _{0.7} Mn _{0.3} Al _{0.2}	-0.90	356	332	79.50	[33]
La _{0.78} Ce _{0.22} Ni _{4.4} Co _{0.6}	-0.92	230	228	69.05	[34]
MmNi _{3.7} Co _{0.7} Mn _{0.3} Al _{0.3}	-0.90	318	286	82.43	[35]
La _{0.8} Ce _{0.2} Ni ₄ Co _{0.4} Mn _{0.3} Al _{0.3}	-0.89	322	318	63.90	[36]
A₂B₇-type					
La _{0.4} Nd _{0.4} Mg _{0.2} Ni _{3.2} Co _{0.2} Al _{0.2}	-0.89	372	328	82.30	[37]
La _{0.72} Nd _{0.08} Mg _{0.2} Ni _{3.4} Al _{0.1}	-1.28	390	353	87.20	[38]
La _{0.75} Mg _{0.25} Ni _{3.3}	-0.86	365	293	81.10	[39]
La _{0.6} Nd _{0.15} Mg _{0.25} Ni _{3.3}	-0.88	376	365	76.70	[39]
La _{0.8} Ce _{0.2} MgNi _{3.4} Co _{0.4} Al _{0.1}	-0.85	363	298	70.22	[43]
AB₃-type					
La _{1.25} Ce _{0.25} Pr _{0.25} Nd _{0.25} MgNi ₉	-0.88	343	337	75.36	[40]
La ₂ MgNi ₉	-0.88	390	337	85.45	[41]
La _{1.5} Nd _{0.5} MgNi ₉	-0.88	400	365	90.32	[41]
La _{1.9} Mg _{1.1} Ni ₉	-0.87	380	344	87.38	[42]
AB₂-type					
Ti _{0.15} Zr _{0.85} La _{0.03} Ni _{1.2} Mn _{0.7} V _{0.12} Fe _{0.12}	-0.88	370	323	90.20	[44]
Ti _{0.15} Zr _{0.85} La _{0.03} Ni _{1.155} Mn _{0.674} V _{0.116} Fe _{0.116}	-0.87	375	270	89.28	[45]

electrode preparation. AB_5 , layered Mg-containing intermetallics AB_3 and A_2B_7 and Laves type AB_2 alloys are broadly used as working materials for the anodes of the Ni-MH batteries [29–45]. Table 1 shows some characteristics of the anode materials for the high-power Ni-MH batteries. As it can be seen from the Table 1, the AB_3 , A_2B_7 and AB_2 alloys show the highest capacity, while the AB_5 type alloys have the best cyclic stability. At present, AB_5 -type alloys still are the most used anode materials. The hydrogen storage capacity of the $LaNi_5H_{6.6}$ hydride is ~1.4 wt% [46], and the power sources based on Co-doped $LaNi_5$ reach ~350 mAh/g in capacity [31]. In order to increase the capacity, the alloys are usually alloyed with lighter elements, such as Mg. It is impossible to directly introduce Mg into the composition of $LaNi_5$ therefore AB_3 - and A_2B_7 -type layered structures alloys are used [47]. In their case it is possible to improve the electrochemical performance by combining two or more rare-earth metals (La, Ce, Nd, Pr). As an example, the introduction of Nd can increase the exchange rate of the hydrogen oxidation/reduction reactions, as well as the rate of diffusion of hydrogen atoms in the hydride [41].

$Ni(OH)_2$ is used as a cathode material in alkaline Nickel-Metal Hydride power sources due to its low cost, satisfactory performance and wide operating temperature range. The specific energy capacity of the cathode part (~290 mAh/g) is provided by a conventionally used β - $Ni(OH)_2$. The performance of a polymorphic modification of α - $Ni(OH)_2$ is better, but this phase is unfortunately unstable. To stabilize α - $Ni(OH)_2$, a partial substitution of nickel ions in the hydroxide lattice by cobalt [48] or aluminum ions [49] is utilized. In the last reference work it was shown that the addition of 7 mol.% Al to $Ni(OH)_2$ leads to an improvement in the reversibility of the charge/discharge process, a decrease in the electrode resistance, together with an increase in the specific capacity and cyclic stability.

As in the case of anode materials, the improved efficiency of the charge transfer process is the major challenge and the most important goal. β - $Ni(OH)_2$ has a very low electronic conductivity (10^{-14} ... 10^{-8} S/cm) due to a large distance between the neighboring Ni atoms ($d_{Ni-Ni} = 3.12$ Å). Shorter Ni–Ni bonds (2.86 Å) as in $NiOOH$ favor a better overlap of the orbitals causing a higher electrical conductivity (0.01–0.05 S/cm), but this value unfortunately does not allow achieving the desired performance of the battery in total.

Acetylene carbon black (CB) or graphite (G) are usually added to improve the conductivity of the electrode materials. It is necessary to introduce these additives in large quantities that reduces the capacity of the electrodes, since a small amount of the carbon additive does not result in the desired effect. The use of extended carbon nanostructures such as GLM, CNT and CNF, as alternatives to acetylene soot and graphite are of a particular interest. Composites of anodic and cathodic materials have been obtained earlier by mixing the active components with graphene-like materials [50]. In [51], multi-walled nanotubes were grown on the surface of electrode materials from a nickel foam. The resulting increased electrode capacity reached 360 mAh/g, which is 18 % higher than the electrode capacity without nanotubes. The authors of [52] grew $Ni(OH)_2$ crystals on the surface of a GLM. Such composite materials not only show an improved charge transfer, but also demonstrate a reduced internal resistance. However, studies of this type are rather sporadic and they need to be performed systematically in order to achieve an optimal result.

We studied Carbon/Metal hydride and Carbon/Hydroxide composites as promising materials for the development of the advanced Ni-MH power sources. Electroconductive composites of $Ni(OH)_2$ and metal hydrides with various carbon materials – graphite, carbon nanotubes, carbon nanofibers, and GLM were prepared by a mechanochemical treatment of the corresponding mixtures in a ball mill (Fig. 6). It has been shown that the conductivity of $Ni(OH)_2$ with carbon nanostructures (3 wt. %) is much higher than that of the hydroxide with graphite. The addition of carbon nanomaterials to Ni

$(OH)_2$ increases the electrical conductivity by seven orders of magnitude (Table 2). On the basis of the developed electro-conductive metal hydride-graphene and nickel hydroxide-graphene composites, the electrodes for the nickel-metal hydride batteries were fabricated [53]. The capacity of the electrodes was shown to be 20 % higher than that of the commonly used ones.

5. Hydrogen-based energy storage

The use of hydrogen as an energy carrier makes it possible to create power systems with a specific energy density much superior to that of any types of the available rechargeable batteries. Furthermore, much simpler and less demanding maintenance and higher efficiencies of the systems significantly reduce the cost, increase the operating periods and improve the reliability of the power supply. Power plants using hydrogen as an energy carrier can supplement or even replace a whole range of the equipment based on diesel electric generators and electrochemical batteries.

Uninterruptible power supply, for example, in health infrastructure or transport infrastructure is crucial to ensure the safety, quality of life and healthcare of the people. Uninterruptible power supply of information and computing complexes and processing centers is necessary to prevent the data loss and failures of the operation in the banking sector. Autonomous systems for stable power supply are necessary for telemetry equipment designed to monitor the status of the gas and oil pipelines, operate cathodic protection stations, to provide power to the telemetry radio relay systems located along the gas pipelines in remote and hard-to-reach areas.

Installation and connection of hydrogen power supply systems does not require large capital expenditures, as the units can be supplied in a modular design, and consequently being installed in unequipped sites near the consumers, while they are convenient in operation, reliable and efficient. The absence of self-discharge problems and the need for recharging, guarantees the stability of energy parameters, simplifies the operation, thereby increasing the reliability of the equipment for the end users.

The use of hydrogen energy storage plants is most expedient in combination with renewable energy sources in remote and sparsely populated areas with an abundance of renewable energy sources. Examples of such locations are the sea and ocean coasts of Russia's Arctic and Far East. In these areas, for photovoltaics it is possible to use excess insolation during a polar day, as well as consistently intense sea breezes and other winds occurring at the border of land and sea for wind generation. In addition, the presence of hydrogen reservoirs of sufficient volume will make it possible to level the stochastic nature of energy production from renewable energy sources.

An integrated power plant includes a primary source of electricity (including renewable energy sources), an electrolyzer, a metal hydride hydrogen storage unit, a fuel cell, a control and monitoring system, and auxiliary components (housing, safety automation, voltage converters).

In general, hydrogen power supply systems do not require strict storage, transportation and operation conditions in order to preserve the service life, and also, unlike all types of batteries, do not require compliance with measures of "preventive" replacement before the expiration of the service life. In addition, the modular system allows the formation of a wide range of power systems, having various power and energy consumption, without changing their production technology.

Industrial production of various types of hydrogen energy supply systems is actively being achieved in many countries (EU countries, USA, Japan, etc.). There have been developed electrolyzers with specific power characteristics that exceed the specific characteristics of traditional generators on internal combustion engines (Nedstack, Hydrogenics, Protonex, Plug Power, Ballard, Intelligent Energy,

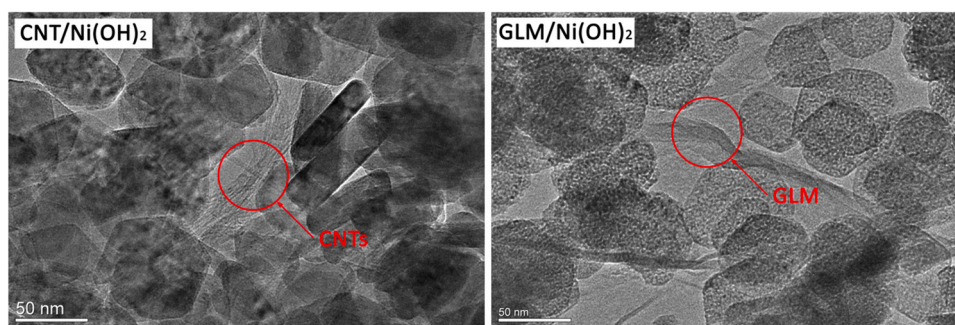


Fig. 6. TEM micrographs of the CNS/Ni(OH)₂ composites.

Table 2

Characteristics of the carbon (3 wt%)/nickel hydroxide composite electrodes.

Component	ρ (g/cm ³)	d (nm)	SSA (m ² /g)	Composite	σ (S/cm)	C (mAh/g)
Ni(OH) ₂	3.45	50	35	Ni(OH) ₂	3.7×10^{-9}	100
G	2.24	200	15	Ni(OH) ₂ /G	1.3×10^{-7}	145
CNT	1.61	1–5	700	Ni(OH) ₂ /CNT	3.9×10^{-3}	265
CNF	1.39	20–30	300	Ni(OH) ₂ /CNF	6.8×10^{-3}	220
GLM	1.48	1–10	900	Ni(OH) ₂ /GLM	8.9×10^{-2}	195

PowerCell). Among many solutions for the conversion, storage and further use of energy, those offered by Hydrogenics, Heliocentris and HYFLEXPOWER are notable.

5.1. Hydrogenics Power-to-Gas solutions

Canadian company Hydrogenics (presently co-owned by Cummins Inc. and Air Liquide [54]) is one of the leaders in the hydrogen energy technology. It is one of the oldest manufacturers of hydrogen fuel cells.

Hydrogenics offers Power-to-Gas hybrid systems that convert surplus renewable generated energy to hydrogen using electrolysis and then use for hydrogen the existing natural gas infrastructure. Natural gas pipelines and underground facilities provide high capacity energy storage tanks. Then the hydrogen can be used on demand.

5.2. Heliocentris hydrogen cycle solar power system

This Renewable Energy Trainer is intended for the simulation of the renewable energy systems which include storage of electricity generated by a solar panel using hydrogen [55]. The direct current from the solar modules charges the batteries in the system under the control of the load regulator. The power electronics, consisting of an inverter and an AC/DC converter, provides the user with 12 V DC and 230 V AC.

The control system ensures optimum performance of the hydrogen generator. It does not start working until the battery reaches the minimum charge. This ensures uninterrupted operation of the system in the event of unstable sunlight radiation. The hydrogen is stored in the metal hydride tanks.

5.3. HYFLEXPOWER Power-to-X-to-Power demonstration model with an innovative hydrogen turbine

A consortium of ENGIE Solutions, Siemens Neftegaz & Energetika, Centrax, Arttic, the German Aerospace Center (DLR) and four European universities have launched a project under the support of the European Commission within the Horizon 2020 research development program [56].

The goal of the project is to prove that hydrogen can be produced using renewable energy sources, stored and then added up to 100 % to natural gas that is currently used in thermal power plants. For these purposes, an existing Siemens industrial gas turbine SGT-400 is being modernized.

The hydrogen-based energy storage is beneficial in energy intensive systems (≥ 10 kWh) operating in broad ranges of units power (1–200 kW), particularly when the footprint of the system has to be limited. There are still remaining challenges hindering implementation of the hydrogen energy storage systems. The first challenge is a safe and efficient hydrogen storage and supply [57,58]. To respond to the challenge, hydrogen storage in metal hydrides can be used as a promising option for small-to-medium-scale applications (0.01–30 Nm³ H₂) [59–62]. Another key component of the hydrogen energy storage method is hydrogen compression, which allows an increase in energy storage density. Here metal hydride thermal sorption hydrogen compression also has several advantages over the other commonly used methods such as mechanical compression [62].

Development of integrated systems containing metal hydride-based energy storage components is well supported by international funding agencies. One recent example is **EU Horizon 2020 project HyCARE** where a number of the collaborating research groups from Italy, France, Germany and Norway aimed at the development of a large-scale prototype hydrogen storage tank utilizing solid-state hydrogen carrier. As the tank combines hydrogen and heat storage, this improves energy efficiency of the whole system [63] while it uses an optimized hydrogen storage alloy based on Mn-modified Ti_{1+x}Fe intermetallic [64].

Our studies on practical application of the GLM-based composites have also been focused on the development of metal hydride hydrogen storage tanks and hydrogen compressors, the performances of which were found to be significantly improved with the use of the composites of metal hydrides with various carbon species, making them suitable to fabricate prototypes of hydrogen energy backup and storage systems (Fig. 7) [65].

Recently, we showed that the use of composites on the basis of AB₅- and AB₂-type alloys with minor amounts (≥ 1 wt%) of carbon additives, particularly with Expanded Natural Graphite (ENG), results in noticeable performance improvements of medium-scale (up to 1 kg H₂) containers for hydrogen storage and compression including augmentation of heat transfer in the MH bed and reducing stresses on the container's wall associated with the increase of the volume of the MH particles during the hydrogenation [66,67]. We expect that the improvements will be more pronounced when using GLMs instead of ENG. The corresponding experimental studies are presently on-going; the results will be published in a due course.

Our estimations show that manufacturing of 1 kg of MH-based hydrogen storage composite containing 10 wt% GLM results in the formation of by-products, 21 g CO and 5 g CO₂. Taking into account a

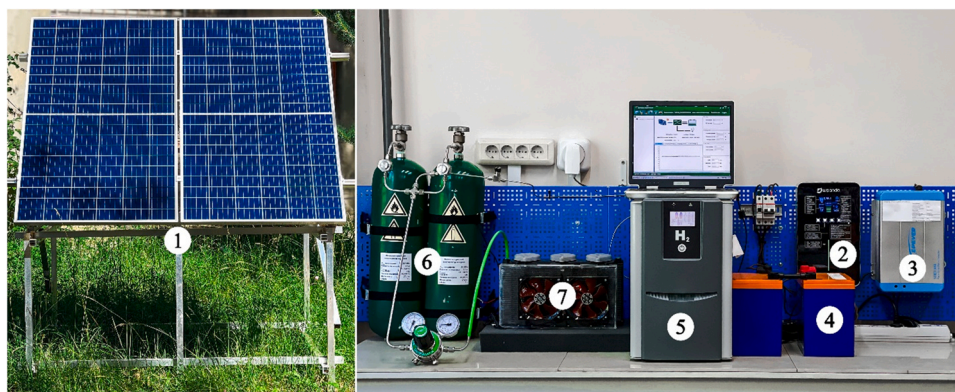


Fig. 7. A hydrogen-based energy storage system developed in the Co-authors' institution (IPCP RAS; Russia). The system includes: 1 – Seraphim Blade SRP-280-BPB 48 V solar panels; 2 – I-Panda RUNNER charge controller (max 60 A 48 V); 3 – EPsolar Epever SHI1000 inverter (~220 V, 50 Hz); 4 – Delta HRL 24 V lead-acid batteries; 5 – HG Pro 1500 electrolyzer (640 W, 13 bar H₂ output pressure, max 90 NI/h H₂ output flow rate); 6 – in-house made metal hydride hydrogen storage units (2 × 3.2 Nm³, 1.15 bar H₂ pressure and 13 NI/min H₂ flow rate in the output pipeline); 7 – Ballard FCGen 1020ACS max. 1.2 kW hydrogen-air fuel cell supplying electricity to a load (not shown). The laptop having an installed automatic control system software is powered from the lead-acid batteries through the charge controller.

long-service lifetime of the MH materials in hydrogen storage and compression systems ($\geq 10,000$ H₂ absorption / desorption cycles [68]), the carbon footprint of their optimization reached by adding GLMs is considered as insignificant. A detailed techno-economic assessment is planned to be carried out in a separate study.

6. Conclusions

Use of Graphene-Like-Materials opens new avenues in the development of hydrogen-based energy storage technologies. 2D (Ni/GLM) and 3D (CNT/GLM, CNF/GLM and Ni/CNF(CNT)/GLM) graphene structures benefit from use of fairly simple and easily scalable synthesis technologies of their preparation allowing large scale applications. The inclusion of such structures into the composition of metal hydride composites contributes to a significant increase in the rate of hydrogen sorption-desorption, achieved because of the high thermal conductivity of the composites. Furthermore, these metal hydride composites can be easily compacted and used in the portable hydrogen storage devices and generators. Composites prepared using metal hydrides and hydroxide materials and carbon nanostructures show a successful performance in the Ni-MH power sources. The specific electrical conductivity of composites of nickel hydroxide with carbon nanostructures (3 wt. %) exceeds the electrical conductivity of pure hydroxide by more than seven orders of magnitude and by five orders of magnitude as compared to the composite containing graphite at the same weight ratio. The use of carbon – metal hydride composites increases the specific capacity of the electrodes by 10–20 %, particularly at high current densities. Finally, metal hydride – graphene composites can also significantly improve the efficiency of the metal hydride hydrogen storage tanks used in hydrogen storage and compression units, as well as in hydrogen-based energy systems for energy supply backup and storage.

CRedit authorship contribution statement

Boris P. Tarasov: Conceptualization, Methodology, Supervision, Writing – original draft. **Artem A. Arbutov:** Investigation, Data curation, Writing – original draft. **Alexey A. Volodin:** Investigation, Data curation, Writing – original draft. **Pavel V. Fursikov:** Investigation, Data curation, Writing – original draft. **Sergey A. Mozhzhuhin:** Investigation, Data curation. **Mykhaylo V. Lototsky:** Formal analysis, Writing – original draft. **Volodymyr A. Yartys:** Formal analysis, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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