

Use of Magnesium as a Renewable Energy Source

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Abstract—The opportunities of use of metallic magnesium as a generator of hydrogen gas, as well as thermal and electric energy is presented in the paper. Various schemes of magnesium application are discussed and power characteristics of corresponding devices are presented. Economic estimation of hydrogen price obtained by different methods is made, including the use of magnesium as a source of hydrogen for transportation in comparison with gasoline. Details and prospects of our new inexpensive technology of magnesium production from magnesium hydroxide and magnesium bearing rocks (which are available worldwide and in Armenia) are analyzed. It is estimated the threshold cost of Mg production at which application of this metal in power engineering is economically justified.

Keywords—Magnesium, power generation, production, renewable energy.

I. INTRODUCTION

ARMENIA belongs to the countries which hasn't got natural energy resources like oil and gas, that's why it is natural, that the development of renewable energy sources, including both traditional and various new technologies, is an urgent task for the country.

Hydrogen is considered as an environmentally friendly source of thermal and electric energy because the only product of reaction with oxygen is pure water in contrast to fossil fuel. Among many methods of hydrogen generation of particular interest are metals (Na, K, Al, Mg, Zn, Fe, etc.) in reaction with water and water solutions. In the presented work, there are considered opportunities of use of metallic magnesium as a source of hydrogen, as well as thermal and electric energy. There are various methods for hydrogen and energy production based on the physical and chemical properties of magnesium. Due to above mentioned different systems are developed for transportation (fuel cells, internal combustion engines (ICE)) and stationary power units. Besides, some magnesium compounds can be used for hydrogen storage. There are many methods of using metallic magnesium in electrochemical systems as a source of electric energy. Also, burning of magnesium can provide a lot of thermal energy and light.

As a waste of various magnesium reactions is magnesium oxide or hydroxide. They are safe substances which used in medicine and for other purposes. Their inexpensive recycling into metallic magnesium is very urgent and difficult task. This is the reason that Mg is not used widely.

It is considered the use of magnesium as a fuel generating hydrogen for transportation propelled by fuel cells or ICE.

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II. HYDROGEN AS A CLEAN ENERGY SOURCE

Now the molecular hydrogen is considered as a fuel capable to replace fossil fuel (natural gas, oil, coal). For example, BMW and Mazda go on a way of direct burning of hydrogen in ICE. BMW already tests the model «Hydrogen» with the 12-cylinder engine with power of 260 hp operating on hydrogen fuel instead of gasoline. Unlike BMW, engineers of Daimler Chrysler and Ford in cooperation with Ballard, and also Toyota, Honda, General Motors, Nissan have selected another way: they use hydrogen not in ICE but in fuel cells. The engine on fuel cells consists of two parts - hydrogen power unit converting fuel into electric power, and an electric motor driving car in motion.

A. Hydrogen Production and Storage

Hydrogen gas is produced mainly by reforming of natural gas or coal, and water electrolysis. In the near future, there are also considered the technologies of H₂ production from biomass, by high-temperature solar-driven thermochemical conversion and photo-electrochemical water splitting.

The price of gaseous hydrogen is around \$5-10/kg depending on production method and purity. But the price of compressed H₂ in tank suitable for driving the car is around \$50-100/kg. The price of liquefied hydrogen is higher.

The energy content of a gallon of gasoline and a 1 kilogram of hydrogen are approximately equal. This means that now the price of hydrogen is much more than gasoline which price is about \$3 per gallon.

Among barriers interfering large-scale introduction of hydrogen power are: a) absence of a hydrogen infrastructure, i.e. a network of filling stations, b) high cost of hydrogen, c) the problem of storage of enough hydrogen under pressure in tanks or in the form of liquid state because hydrogen represents volatile gas capable to ignite spontaneously. Last problem can be solved by generation of hydrogen on demand, for example, by immersing the tablets or suspensions of hydrogen-containing compounds into the reaction environment (for example water) or heating them at which a gradual generation of hydrogen occurs. An example of such compounds are hydrogen-accumulating and hydrogen-generating materials on the base of MgH₂ or boron hydrides of sodium (NaBH₄), lithium (LiBH₄), etc. containing enough hydrogen in their structure. Effective accumulators-generators of hydrogen [1], [2] have been created on the base of magnesium hydrides. Among hydride-forming metals magnesium deserves special attention as for its hydride is characterized by high mass (7.65 w. %) and volumetric (0.11 g/cm³) contents of hydrogen. Magnesium hydride (MgH₂) can be produced by direct synthesis, at that the reaction of metal with hydrogen is characterized by practically full convertibility. However, kinetic hindrances of reactions

magnesium and hydrogen especially dehydrogenation and necessity of high temperatures (more than 300°C) is the basic obstacle for its wide practical use as hydrogen-accumulating material. Recently several studies [3], [4] were carried out resulting in new technical decisions for overcoming these disadvantages. They consist in creation of nanocomposite materials.

Advantage of use of these materials is the safe storage, but drawback is their high cost, and also impossibility or complexity of their regeneration. One of the most perspective applications of magnesium hydrides are portable sources of hydrogen based on the interaction of Mg hydride with water in the result of which more than 15 w.% of hydrogen (relative to hydride weight) is evolved according to the reaction



Unlike complex aluminohydrides and boron hydrides of alkaline metals which are applied now in the hydrolytic scheme of hydrogen generation, the magnesium hydride is chemically more stable and the product of its interaction with water is environmentally safe Mg(OH)₂. However formation of poorly soluble magnesium hydroxide on a surface of hydride particles become a barrier of incomplete course of hydrolysis reaction which impedes creation of independent sources of hydrogen on the base of magnesium hydride-water system. One of solution of this problem has been made in work [4] according to which mechanical activation of magnesium hydride increases in 10-15 times the amount of the hydrogen generated in unit time in reaction of interaction with water. Introduction of carbon at mechanical activation led to a change of the mechanism of reaction of hydrolysis. Repeated increase of activity of MgH₂-C composites at interaction with water is caused by suppression of agglomeration process of hydride particles and prevention of formation of a hydroxide layer. For MgH₂-graphite composites an evolution of 1.280 ml of hydrogen from 1g of composite is observed without additional change of water solution acidity. This means that such hydrogen-generating composites on the base of magnesium hydride are perspective materials for creation of disposable chemical sources of hydrogen.

At immersing of metallic magnesium in a water salt solution, for example, NaCl or sea water, at the moderate temperatures (30-60°C) the following exothermic reaction occurs:



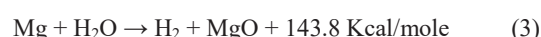
This reaction precedes ionization of magnesium, $\text{Mg} \rightarrow \text{Mg}^{++} + 2\text{e}$, with subsequent decomposition of water, $2\text{e} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{OH}^-$ and formation of hydroxide, $\text{Mg}^{++} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2$. The reaction is slowed down because of formation of a magnesium hydroxide layer on a magnesium surface. For overcoming this factor, the additives to magnesium, such as iron, nickel, cobalt, etc., are used [5], [6]. They form micro galvanic pairs on a surface of magnesium and promote vigorous dissolution of magnesium with

generation of hydrogen with high speed. Another method for effective hydrogen evolution is the increase of magnesium surface, for example, the use of suspension or magnesium powder in any environment [7].

Very efficient method of hydrogen generation is developed by authors of patent [8]. They invented the pellets on the base of micron size Mg with small amount of Fe and Si. This mixture immersed in 11% solution of NaCl resulted in dramatic increase of hydrogen yield and in rate at which the hydrogen was generated (up to 350 cm³ per minute for 1g pellet).

Similar method is described in [9] with other active mixture providing 1013.33 ml/g hydrogen with a maximum hydrogen generation rate of 499.50 ml·min⁻¹·g⁻¹.

Another way of hydrogen generation by magnesium is the use of high-temperature reaction



In Russian Federal State Unitary Central Scientific-Research Institute "SHIP's ELECTRICAL ENGINEERING AND TECHNOLOGIES" the magnesium-steam irreversible process of hydrogen production is elaborated on the base of this reaction with mass hydrogen content of 8.3 % [10]. On the other hand, the heat of magnesium oxidation can be transformed to electric power not only step by step by using steam, but also directly by means of thermoelectric transformation. Two ways of direct transformation of heat into electricity are known: a) by means of thermo-generators from thermo-cells; b) by means of thermo-emission converters (TEC) which are especially perspective. Their efficiency can be comparable to the efficiency of solar cells. Thus, the magnesium-thermoelectric power generation is a perspective direction.

III. MAGNESIUM IN ELECTROCHEMICAL POWER SOURCES

A. Electrochemical Properties of Magnesium

Magnesium has negative standard electrode potential of -2.37 V (vs SHE) [11], which is more negative than those of aluminum (-2.31 V (vs SHE)) and zinc (-1.25 V (vs SHE)) [11], [12]. Thus, magnesium anode could theoretically exhibit high discharge activity and possess strong ability to deliver electrons for power generation. At the same time, the magnesium has high Faradic capacity of 2.205 A·h/g which is lower than those of lithium (3.862 A·h/g) and aluminum (2.980 A·h/g) [11], but significantly higher than that of zinc (0.820 A·h/g) [12]. The low specific weight of magnesium provides its high volumetric and weight power and energy density in electrochemical devices.

If any another metal having more positive electrochemical potential is placed in a solution together with magnesium, then along with hydrogen generation, the electric potential difference is formed between electrodes and the current is generated.

First magnesium based batteries were developed in the 1940s to meet the demands of the defense industry. There are

the following active systems: Mg/AgCl, Mg/CuCl, Mg/Cu₂I₂, Mg/PbCl₂, Mg/AgCl.

In Fig. 1, the variant of an electrochemical cell-generator of hydrogen under the patent of Bolivian inventor Pacheco [12] is presented.

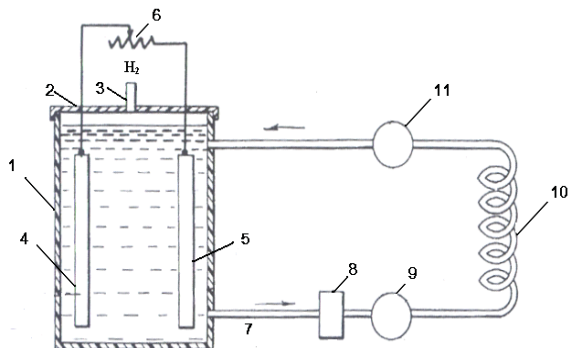


Fig. 1 Pacheco generator, adopted from [13]

Here in the tank 1 filled by a salt solution, the magnesium anode 4 and the inert cathode 5 (for example, from carbon, steel, etc.) are located. The tank is closed by a tight cover 2 in which there is an aperture for release of hydrogen 3. Electrodes 4 and 5 are connected through a variable resistor 6. As loading other electro-devices, such as the motor or a lamp can serve also. That is why Pacheco generator generates both hydrogen and an electric current. Speed of hydrogen generation is inversely proportional to resistance of load and can be controlled. Electrochemical process is accompanied by formation and sedimentation of magnesium hydroxide at the bottom of tank. The magnesium hydroxide is removed by electrolyte cycling, which is provided by a tube 7 in which filter 8, pump 9, heat-exchanger 10 and adjustable valve 11 are installed. The pump 9 can work by means of electric power produced by electrodes. Heat-exchanger serves for removal of heat and maintenance of optimum temperature.

Secondary (rechargeable) magnesium based batteries are in the initial stage of development. Such systems have an anode from magnesium or magnesium alloys, and sulfides, oxides or organic compounds of other metals as a cathode. Magnesium recovery is also linked to the instability in aqueous solutions, therefore as electrolyte the organic complexes or ionic liquids are used [13]. The use of these organic solvents enables the proceeding of anodic redox reactions with low overpotential and increases their operating performance.

B. Magnesium-Air Fuel Cells

The special types of electrochemical generators represent metal-air systems. Table I shows characteristics of some such systems in comparison with other known batteries [14]. Fig. 2 shows the structure of the typical Mg-air battery.

As can be seen from Table I, the Mg-air system has a good performance and although Li-air battery has better properties it is unstable in aqueous solutions while Mg is abundant on the earth, has a high reaction activity, is light

weight and inexpensive, has low toxicity and has relatively high safety.

TABLE I
Theoretical Voltage and Specific Capacity of Some Batteries

Selected batteries	Voltage (V vs. SHE)	Specific energy density (kW·h/kg)
Li-ion	3.8	0.387
Li-air	2.91	13.0
Li-sulfur	2.2	2.6
Zn-air	1.65	1.3
Mg-air	3.1	6.8

Magnesium-air (oxygen) system is primary battery and in the same time is a semi-fuel cell in which instead of hydrogen the metallic magnesium [14]-[17] is used as a source of electrons. Such anodes have unlimited lifetime and give practically 100% of the internal capacity after tens years of storage. On the base of this system a water-activated (reserve) types of current sources are developed. As an electrolyte the water solution of table salt or water with dry NaCl component preliminary absorbed in cellulose matrix are used. Advantage of such electrolyte is availability and chemical inaggressivity. Here the current generating anode reaction is the ionization (oxidation) of magnesium:



The role of a positive electrode consists in creation of necessary conditions for reaction

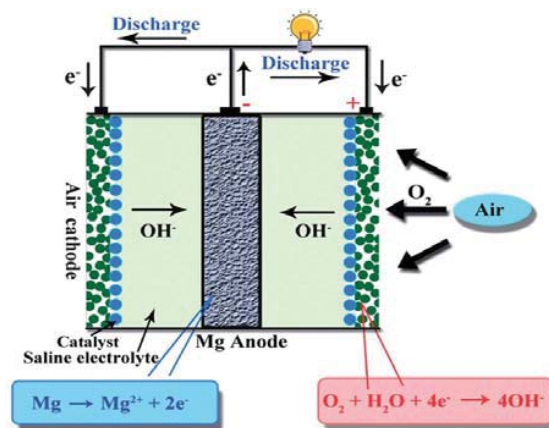
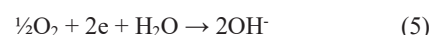


Fig. 2 Structure and working principle of Mg-air battery, adopted from [13]

The cathode usually represents a layer of active carbon-containing the catalyst and hydrophobic additives (TEFLON suspension in a quantity of 10 - 25%) contacting with free electrolyte. The waterproof layer of the cathode (an external layer) is fabricated from hydrophobic acetylene carbon black, permeable for air and impermeable for electrolyte. For imparting mechanical strength the electrode is reinforced by metal grid which also serves as current collector.

After discharge of the cell the magnesium hydroxide is poured out and the spent anode is replaced by the new one. The cathode can serve in many cycles [18].

Though Mg-air batteries have a relative high theoretical voltage and energy density, there is much must be improved in battery work principles, in order to have a battery with sufficient parameters. The drawback of Mg-air batteries is the high polarization and low coulombic efficiency. Besides, characteristics of system are deteriorated due to corrosion of magnesium anode by the reaction (2).

To overcome the existing problems of Mg-air batteries, it is necessary to study and improve characteristics of anode, cathode and electrolyte. According to the recent efforts on Mg anode materials, it is concluded that for developing Mg anodes with high performance, the alloying with some metals, as well as a small size of Mg particles, especially with nanostructures, promotes the reaction activity.

As for electrolytes, there are some successes by the use of some hydrogen evolution inhibitors such as stannates, quaternary ammonium salts, dithiobiuret and their mixtures that can be added into the electrolyte to suppress the HER [14].

For solving the problems related to the cathode it is necessary to enhance the oxygen reduction reaction (5) activity. The ways in this field are directed on the use of efficient and inexpensive catalysts, such as transition metal oxides, N-containing metal macrocyclic compounds, cobalt and iron tetra methoxyphenyl porphyrin (CoTMPP and FeTMPP) catalysts loaded on carbons, N-doped graphenes, etc. [14].

Original approach is presented in [19] for additionally using hydrogen generated in Mg-air battery in attached traditional hydrogen-air fuel cell. This combined system increases the overall electricity production. A practical specific energy density of the alloy anodes above 1200 W·h/kg and 3000 W·h/l is achieved, when feeding the produced hydrogen into an ambient air fuel cell.

IV. MAGNESIUM AS THERMAL ENERGY SOURCE

Finally, it is necessary to know reaction of magnesium burning in air, in the result of which a great quantity of thermal energy (25.000 KJ/kg or 6000 Kcal/kg), light and pressure is generated. Owing to this magnesium is used as a component of explosives and solid rocket fuels.

Besides in reaction of Mg with water or steam the heat is generated which can be utilized for various secondary processes. In paper [20] it is described the use of magnesium hydride for thermal energy storage in a small-scale solar-thermal power station.

It should be noted, that flameless heat generation in reaction of magnesium with water salt solutions is used in so-called chemical heaters. They are applied for warming up food, water, medical supplies, heating hands or legs in emergency situations and in field conditions for soldiers, tourists [20], [21]. In these cases, by means of additives such as CuCl_2 , it is possible to suppress undesirable formation of hydrogen [21].

The method of thermal energy storage by conversion of

$\text{Mg}(\text{OH})_2$ into MgO , based on reversible magnesium oxide/water reaction system is developed by authors of paper [22].

V. NEW MAGNESIUM PRODUCTION METHODS

All above-mentioned methods of magnesium application are accompanied by formation of magnesium hydroxide or oxide. For their conversion into metallic magnesium it is necessary to dissolve Mg in hydrochloric acid with production of MgCl_2 water solution. Then, according to traditional method, MgCl_2 should be dehydrated for obtaining the melt with subsequent high-temperature electrolysis. This is very energy consumable process (18 - 20kW per 1kg of magnesium). Another method is a carbothermic reduction of MgO which also involve significant power expenses. For covering these expenses it is proposed to use alternative energy sources (hydro, solar, wind). Now the price of metallic magnesium is around 2.2 - 2.5 USD/kg therefore the price of hydrogen obtained from magnesium according to the reaction (1) makes \$30/kg. Therefore, it is needed to reduce the cost of metallic magnesium significantly by searching new technologies of its production.

Recently Japanese scientists [23], [24] reported on recycling of Mg from $\text{Mg}(\text{OH})_2$ or MgO by solar energy pumped laser. The calculated price of produced magnesium is about \$1/kg. In this case the hydrogen price will be \$12/kg.

Another technology of magnesium recycling is invented in our company [25]. It is based on efficiently extracting and producing large volumes of metals from aqueous electrolyte solutions and allows to obtain active metals having greater negative electrochemical potential than the potential of hydrogen evolution due to splitting of water. Among such metals are alkaline metals (Li, Na, K, Rb), alkaline-earth metals (Mg, Ca, Ba), and some other metals such as Al, Mo, Ti, W, and etc.

This low-temperature method and airtight apparatus is based on electro dialysis. Here is provided a substantially inert environment within which a metallic element M is generated (reduced) from a metal ion M^{z+} , with the inert environment being the result of a conductive, but a chemically neutral solution that circulates within a neutral cathode chamber. The metal extractor comprises an ion exchange processor separated into one or more cation ion exchange processing cells and an anion ion exchange processing unit. The inert environment is a result of skin effect on a conductive medium.

This method is illustrated on an example of MgCl_2 solution.

Beside the use of electro dialysis chambers, the know-how of method is the utilization of metals (which are liquid at room temperature, e.g. Hg, Ga and their alloys) as a conductive medium in metal extractor, as well as the use for washing of the produced metal from cathode by organic compounds (silicon oil, carbon tetrachloride, kerosene, benzene, etc.) which do not react with metal. The chlorine gas is generated in the process which can be removed or utilized as a hydrochloric acid.

Our calculations based on performed experiments show that the electricity expenses are around 6.5 kW/kg and the price of

produced magnesium can reach 0.5USD per kg. Except for significant reduction of the cost of magnesium, this technology will allow to close the cycle of “Magnesium Energy” (Fig. 3), i.e. to obtain metallic magnesium again from waste (its oxides) formed in the result of various chemical and electrochemical processes described above.

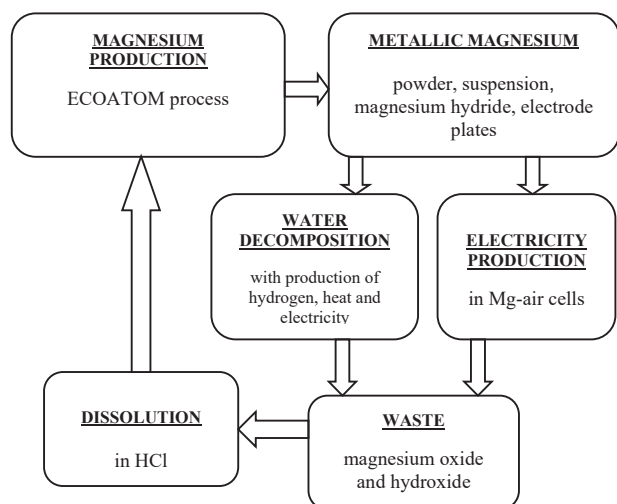


Fig. 3 Scheme of “Magnesium Energy” cycle

Instead of storing hydrogen in heavy tanks or in refrigerators, magnesium may be safely stored on board and fed into the salt solution in the form of a powder, briquettes or suspension which will allow generating desirable and necessary amount of hydrogen. Let us to make calculations and compare the using of magnesium and gasoline. Gasoline price is \$3/gallon (\$1.1/kg) and 4 kg is needed for 100 km mileage. The total price for 100 km is around \$4.4.

1 kg of H₂ is enough for 100 km mileage if fuel cells are used, and 1.5 kg H₂ for running the same distance with ICE car [27]. 12 kg of metallic magnesium generate 1 kg of H₂ and driving 100 km, and the price of magnesium produced by new ECOATOM technology will be \$6. So, application of magnesium as a fuel for propulsion can be competitive with gasoline, not to mention the other advantages associated with safety and environmental friendliness.

It is worth to note that recently the Korea Institute of Science and Technology (KIST) has developed an electric car with magnesium-air fuel cell to travel a distance of 800 kilometers on a full battery [26]. Magnesium has other essential advantages in comparison with other substances, namely:

1. The use of magnesium in automobile and aerospace industry, as one of the lightest metals, is essentially reflected in energy economy because weight reduction of vehicles leads to direct economy of fuel.
2. Waste from use of magnesium, magnesium oxide and hydroxide, are not only ecologically harmless, but also present useful substances from the point of view of medicine. They in itself are valuable products, for example, magnesium oxide is the basic feedstock for

refractory materials (which increase energy efficiency due to reduction in heat losses in furnaces), for special cements, fillers for polymers, paints, etc.

3. Magnesium resources in the Earth's crust are practically inexhaustible (much more than carbon). The basic solid sources of magnesium are dolomite and ultrabasic rocks such as olivine and serpentine which great reserves are available also in Armenia. Only oceans, seas and salty lakes contain about 10¹⁷ tons of magnesium (4 kg of magnesium in one cubic meter of sea water) [24].

The version of technology for producing the magnesium oxide from ultrabasic rocks is developed by ECOATOM scientists and presented in [27]. It is based on the leaching of rocks by hydrochloric acid with obtaining of magnesium and silicon oxides.

Finally, it should be noted the importance of use of magnesium which is perfectly revealed in the book “Magnesium Civilization” [28]. This book covers how magnesium can be used for metal-air fuel cells for automobiles and power plants. The automobile with zinc-air-fuel cell achieved 600km mileage in 2003 and magnesium-air fuel cell can give 3 times more energy which is 7.5 times more effective than lithium-ion battery. Solar-pumped laser regenerates metallic magnesium from combusted magnesium oxide. The book also describes how low-cost desalination with solar-power will be a promising solution to the global water shortage.

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